MULTIPHASE THERMOMECHANICS WITH INTERFACIAL STRUCTURE. 1. HEAT CONDUCTION AND THE CAPILLARY BALANCE LAW

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Research Report No. 88-13 2

April 1988

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1. Introduction.

In [1986g,1988g] I began the development of a nonequilibrium thermomechanics of two-phase continua, a development based on dynamical statements of the thermomechanical laws in conjunction with Gibbs' notion of a sharp phase-interface endowed with energy and entropy. I have since come to realize that there is an additional balance law appropriate to the interface $\mathcal{S}$. This law, which represents **balance of capillary forces**, has the form[1]

$$\int_{\partial\mathcal{C}} \mathbf{C}\boldsymbol{\nu} + \int_{\mathcal{C}} \boldsymbol{\pi} = \mathbf{0}, \tag{1.1}$$

with $\mathcal{C}$ an arbitrary subsurface of $\mathcal{S}$ and $\boldsymbol{\nu}$ the outward unit normal to the boundary curve $\partial\mathcal{C}$ of $\mathcal{C}$. Here $\mathbf{C}(\mathbf{x},t)$, the **capillary stress**, is a linear transformation of tangent vectors into (not necessarily tangent) vectors, while $\boldsymbol{\pi}(\mathbf{x},t)$, the **interaction**, is a vector field; $\mathbf{C}(\mathbf{x},t)$ represents microforces exerted across $\partial\mathcal{C}$ in response to the creation of new surface; $\boldsymbol{\pi}(\mathbf{x},t)$ characterizes the interaction between the interface and the bulk material. I view (1.1) as a balance law which is supplementary to the usual laws for forces and moments.

Balance of capillary forces has the local form

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[1] In the absence of external supplies.

$$\mathrm{div}_{\mathcal{S}}\,\mathbf{C} + \boldsymbol{\pi} = \mathbf{0}, \tag{1.2}$$

with $\mathrm{div}_{\mathcal{S}}$ the surface divergence on $\mathcal{S}$. The normal component of (1.2) arises in previous theories, emerging as an Euler-Lagrange equation corresponding to the requirement that a global Gibbs function be stationary.[2] This is not surprising: balance laws often follow as Euler-Lagrange equations, an example being balance of forces and moments in elastostatics. Such variational derivations underline the consistency between theories and, what is more important, often point the way toward a correct statement of the relevant law. On the other hand, such derivations tend to obscure the fundamental nature of balance laws as basic axioms in any general dynamical framework which includes dissipation.

In [1986g,1988g] I derived the normal component of (1.2) as a consequence of the second law. While this approach might seem advantageous, the more general framework necessitates a more complicated constitutive theory: in the present study, capillary balance furnishes a relation between the interfacial temperature and the curvature, orientation, and normal velocity of the interface; this relation is a constitutive postulate in [1986g,1988g].

It is the purpose of this paper to develop a fairly complete thermomechanics based on capillary balance as an independent axiom. To avoid inessential complications that might obscure an understanding of this law, attention is limited to nondeformable bodies in the absence of diffusion. The

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[2]Herring [1951], Cahn and Hoffman [1972,1974]; the notion of capillary forces is implied by these authors. Another special case of (1.1), the requirement that $\mathbf{C}\boldsymbol{\nu}$ be continuous across a corner, was derived variationally by Herring [1951] and used by Herring and others to discuss the formation of facets.

addition of diffusion is elementary; the extension to deformable bodies will be the subject of [1988s].

The theory is based on three physical laws: balance of capillary forces, balance of energy, growth of entropy. A fundamental assumption underlying balance of energy is that interfacial forces supply power to the interface through the velocity $V\mathbf{m}$, where $\mathbf{m}$ is a unit-normal field for the interface and V is the corresponding normal velocity; in particular, the power expended on the interface by the capillary stress has the form

$$\int_{\partial c} (V\mathbf{m}) \cdot \mathbb{C}\nu, \qquad (1.3)^3$$

indicating a sharp departure from classical ideas. Power is generally a force acting on a material point (particle) times the velocity of the point. Here material points do not move, but there is expended power, and this power is reckoned by the motion of the phase boundary.[4]

A fairly general constitutive theory is considered for the interface. The free energy f and entropy s are allowed to depend on the temperature θ, and - to have a theory of sufficient generality to model crystal growth - also on the orientation $\mathbf{m}$ and the normal velocity V; in addition, constitutive equations are given for the symmetric and normal components,[5] $\mathbb{C}_{sym}$ and c, of the capillary stress and for

[3] Cf. Remark 4.4.

[4] Conceptually, it is useful to identify the interface with a collection of particles transported with velocity $V\mathbf{m}$. This view is emphasized by Angenant and Gurtin [1988].

[5] At each point the capillary stress $\mathbb{C}$ maps tangent vectors into vectors in $\mathbb{R}^3$; we write $\mathbb{C} = \mathbb{T} + \mathbf{m} \otimes \mathbf{c}$, where $\mathbb{T}$ maps tangent vectors into tangent vectors; $\mathbb{C}_{sym}$ is then the symmetric part of $\mathbb{T}$.

the normal component π of the interaction:

$$f = \hat{f}(\theta,\mathbf{m},V), \qquad s = \hat{s}(\theta,\mathbf{m},V),$$
$$\mathbf{C}_{sym} = \hat{\mathbf{C}}_{sym}(\theta,\mathbf{m},V), \qquad c = \hat{c}(\theta,\mathbf{m},V), \tag{1.4}$$
$$\pi = \hat{\pi}(\theta,\mathbf{m},V).$$

Use of the second law[6] then leads to the following list of constitutive restrictions:
(i) the free energy, the entropy, and the normal and symmetric components of the capillary stress are independent of the normal velocity V and

$$\hat{s}(\theta,\mathbf{m}) = -\partial_\theta \hat{f}(\theta,\mathbf{m}), \qquad \hat{c}(\theta,\mathbf{m}) = -\partial_{\mathbf{m}} \hat{f}(\theta,\mathbf{m}), \tag{1.5}$$
$\hat{\mathbf{C}}_{sym}(\theta,\mathbf{m})$ is a surface tension of amount $\hat{f}(\theta,\mathbf{m})$;

(ii) the interaction $\hat{\pi}(\theta,V,\mathbf{m})$ equals the jump in bulk free energy across the interface minus a drag force of the form $\beta(\theta,\mathbf{m},V)V$, $\beta \geq 0$.

In classical theories of melting - in which the interface is devoid of structure - changes of phase occur at the transition temperature θ_M, which is the temperature at which the bulk free energies of the two phases coincide. Within our theory a flat and stationary interface has temperature θ_M, but a curved and moving interface need not; in fact, the relation

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[6] In the manner of Coleman and Noll [1963]. This procedure is applied in [1988g], but the absence of capillary balance severely complicates the analysis. See also Murdoch [1976], who obtains restrictions for a materially-stationary interface in a deforming continua.

[7] $\partial_z g$ denotes the derivative (usually partial) of g with respect to z. In particular, $\partial_{\mathbf{m}} g$ is the surface gradient with respect to $\mathbf{m}$ on the surface of the unit ball in $\mathbb{R}^3$.

$$u = f(\mathbf{m})H + \partial_{\mathbf{m}}\partial_{\mathbf{m}} f(\mathbf{m}) \cdot \mathbb{L} - \beta(\mathbf{m})V, \qquad (1.6)$$

for the (dimensionless) temperature difference

$$u = \frac{\theta - \theta_M}{\theta_M}$$

as a function of V, the curvature tensor $\mathbb{L}$, and the corresponding mean curvature H, follows from capillary balance as an approximation appropriate to a weak interface; that is, to an interface for which the interfacial densities are small and the dependence on V weak. Here $f(\mathbf{m}) = f\hat{}(\theta_M, \mathbf{m})$, $\beta(\mathbf{m}) = \beta(\theta_M, \mathbf{m}, 0)$, and we have chosen a scaling in which the latent heat ℓ satisfies $\ell = 1$.

The usual heat equation in bulk combined with (1.6) and a similar approximation for balance of energy lead to the partial differential equations and free-boundary conditions:

$$\begin{aligned} &C_i u^\bullet = -\operatorname{div} \mathbf{q}, \quad \mathbf{q} = -K_i \nabla u && \text{in bulk,} \\ &u = \mathbb{B}(\mathbf{m}) \cdot \mathbb{L} - \beta(\mathbf{m})V \\ &V = [\mathbf{q}] \cdot \mathbf{m} && \text{on the interface,} \end{aligned} \qquad (1.7)$$

Here C_i and K_i, respectively, denote the bulk specific heat and bulk conductivity (tensor) for phase i $(i = 1,2)$; $\mathbf{q}$ is the heat flux; $[\mathbf{q}]$ is the jump in $\mathbf{q}$ across the interface; $\mathbb{B}(\mathbf{m}) \cdot \mathbb{L}$ represents the first two terms on the right side of (1.6).

Global growth conditions are found for the system (1.7) in a bounded domain under various boundary conditions. In particular, for a bounded solid $S(t)$ in a liquid melt, enclosed

by a container B whose boundary ∂B is held at the spatially-constant temperature $U = U(t)$,

$$F(\varsigma)^{\bullet} + U\mathrm{vol}(S)^{\bullet} + (C/2)\Big\{\int_B (u-U)^2\Big\}^{\bullet} \leq 0, \qquad (1.8)$$

where

$$F(\varsigma) = \int_{\varsigma} f(m)$$

is the total interfacial free-energy at the transition temperature.

We also consider perfect conductors, which are materials with infinite thermal conductivity. We give a plausibility argument, based on our general theory, leading to the conclusion that, for a boundary held at the temperature $U = U(t)$, the motion of the interface is governed by the relation[8]

$$\beta(m)V - \mathbf{B}(m)\cdot\mathbf{L} = -U(t) \qquad (1.9)$$

in conjunction with various kinematical equations relating V and $\mathbf{L}$ to the motion of the interface. It is shown that, for an interface consistent with (1.9),

$$F(\varsigma)^{\bullet} + U\mathrm{vol}(S)^{\bullet} \leq 0. \qquad (1.10)$$

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[8]Generalizing "flow by mean curvature" in which $V = H$ (cf. Brakke [1978], Allen and Cahn [1979], Gage and Hamilton [1986], Grayson [1987]). Consequences of (1.9), for the motion of an interfacial curve in $\mathbb{R}^2$, will be discussed by Angenent and Gurtin [1988].

2. Primitive quantities.

We consider a body consisting of two phases separated, at each time t, by an **interface** $\varsigma(t)$, and write $B_i(t)$ for the subregion of the body occupied by phase i. We assume that the body occupies all of $\mathbb{R}^3$; that the $B_i(t)$ are closed regions with $\mathbb{R}^3$ as their union and $\varsigma(t)$ as their intersection; and that $\varsigma(t)$ is a smoothly propagating surface.[9] We orient $\varsigma(t)$ by a choice of unit normal field $\mathbf{m}(x,t)$, called the **orientation** of $\varsigma(t)$, chosen so that

$\mathbf{m}(x,t)$ coincides with the outward unit normal to $\partial B_1(t)$.

We write $V(x,t)$ for the **normal velocity** of $\varsigma(t)$ in the direction $\mathbf{m}(x,t)$, $\mathbb{L}(x,t)$ for the **curvature tensor** on $\varsigma(t)$, and $H = \mathrm{tr}\mathbb{L}$ for (twice) the **mean curvature**.

The thermodynamics of the body is described by three types of fields: bulk fields that describe the bulk behavior of the individual phases; superficial fields that describe the behavior of the interface; external supplies that describe the interaction between the body and the external world. In particular, we have the following primitive quantities:[10]

bulk fields

$\varepsilon(x,t)$, **bulk internal energy** (volume),
$\eta(x,t)$, **bulk entropy** (volume),
$\theta(x,t)$, **absolute temperature**,
$\mathbf{q}(x,t)$, **heat flux** (area),

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[9]Concerning surfaces, we use the notation and many of the results of Gurtin and Murdoch [1974], Murdoch [1976,1978], and Gurtin [1986g,1988g]; these are discussed in the Appendix. To agree with standard terminology, we take $\mathbb{L} = -\nabla_\varsigma \mathbf{m}$, rather than $\mathbb{L} = \nabla_\varsigma \mathbf{m}$ as was done in [1986g,1988g].

[10](volume) is shorthand for "per unit volume", and so forth.

interfacial fields

$e(x,t)$, **interfacial internal energy** (area),

$s(x,t)$, **interfacial entropy** (area),

$\mathbb{C}(x,t)$, **capillary stress** (length),

$\pi(x,t)$, **interaction** (area),

external supplies

$q(x,t)$, **bulk heat supply** (volume),

$r(x,t)$, **interfacial heat supply** (area),

$b(x,t)$, **capillary supply** (area).

Here ε, η, θ, and q are bulk scalar fields; $\mathbf{q}$ is a bulk vector field; e, s, and r are superficial scalar fields; $\mathbb{C}$ is a superficial tensor field; π and $\mathbf{b}$ are superficial vector fields. (Superficial and bulk fields are defined in the Appendix.)

We assume that the

temperature is continuous across the interface; (2.1)

generally, we will not specify regularity hypotheses other than to note that the remaining bulk fields are allowed to suffer jump discontinuities across the interface.

3. Basic laws.

3.1. Balance of capillary forces.

Let $c(t)$ be a sufficiently regular subsurface of $\varsigma(t)$, and let $\nu(x,t)$, a vector field tangential to $\varsigma(t)$, be the outward unit normal to the boundary curve $\partial c(t)$. The integrals

$$\int_{\partial c} \mathbf{C}\nu, \qquad \int_{c} \pi, \qquad \int_{c} \mathbf{b} \tag{3.1}$$

represent forces involved with the creation of new surface: the first gives the force exerted across ∂c by the interface; the second and third give forces exerted on c by the bulk material and by the external world.

We write $\mathbf{C}_{sym}$, $\mathbf{C}_{skw}$, and $\mathbf{c}$ for the **symmetric**, **skew**, and **normal** components of the capillary stress $\mathbf{C}$ (cf. the paragraph containing (A8)). The interfacial force $\mathbf{C}\nu$ in (3.1) is then the sum of a tangential force $(\mathbf{C}_{sym} + \mathbf{C}_{skw})\nu$ and a normal force $(\mathbf{c}\cdot\nu)\mathbf{m}$.

We postulate that each subsurface $c(t)$ be consistent with **balance of capillary forces**

$$\int_{\partial c} \mathbf{C}\nu + \int_{c} \mathbf{b} + \int_{c} \pi = 0. \tag{3.2}$$

This law has an equivalent local form, which is easily derived using the surface divergence theorem (A16):

$$\mathrm{div}_{\varsigma}\,\mathbf{C} + \mathbf{b} + \pi = 0 \tag{3.3}$$

with div_{ς} the surface divergence on ς (cf. (A13)).

We regard the normal velocity V as <u>intrinsic</u> in the sense that superficial forces supply power to the interface through the velocity $V\mathbf{m}$. The next result characterizes this power.

Theorem of expended power.

$$\int_{\partial c}(V\mathbf{m})\cdot\mathbf{C}\boldsymbol{\nu} + \int_{c}V\mathbf{m}\cdot(\mathbf{b}+\boldsymbol{\pi}) = -\int_{c}(V\mathbf{C}_{sym}\cdot\mathbf{L} + \mathbf{c}\cdot\mathbf{m}^{\bullet}). \qquad (3.4)$$

Proof. By (A7), (A8), (A11), (A12), (A14), and (B1),

$$\begin{aligned} &\mathrm{div}_{\zeta}(V\mathbf{C}^{T}\mathbf{m}) = V\mathbf{m}\cdot\mathrm{div}_{\zeta}\mathbf{C} + \mathbf{C}\cdot\nabla_{\zeta}(V\mathbf{m}), \qquad (3.5)\\ &\mathbf{C}\cdot\nabla_{\zeta}(V\mathbf{m}) = -V\mathbf{C}_{sym}\cdot\mathbf{L} - \mathbf{c}\cdot\mathbf{m}^{\bullet}; \end{aligned}$$

(3.3) and (3.5) imply (3.4). ■

The left side of (3.4) gives the total power expended on c, while the right side catalogs the manner in which this power is used: $-V\mathbf{C}_{sym}\cdot\mathbf{L}$ represents power expended in creating new surface; $-\mathbf{c}\cdot\mathbf{m}^{\bullet}$ represents power expended in changing the orientation of the interface. Note that the skew part of $\mathbf{C}$ does not expend power. Note also that for $\mathbf{C}_{sym}$ a surface tension σ, $V\mathbf{C}_{sym}\cdot\mathbf{L} = V\sigma H$.

If we introduce the normal components

$$\pi = \boldsymbol{\pi}\cdot\mathbf{m}, \qquad b = \mathbf{b}\cdot\mathbf{m} \qquad (3.6)$$

of the interaction and capillary supply, then, by $(A14)_{2-4}$ and (3.6), the normal component of (3.3) has the form

$$\mathbf{C}_{sym}\cdot\mathbf{L} + \mathrm{div}_{\zeta}\mathbf{c} + b + \pi = 0; \qquad (3.7)$$

this relation is central to what follows.

Remark 3.1. The balance law (3.2) should be viewed as a conservation law over and above the usual balance laws for

forces and moments. When the current theory is extended to include deformations of the body, balance of forces across the interface yields the equation

$$\operatorname{div}_{\mathcal{S}} \mathbb{T} + \mathbf{f} = -[\mathbf{T}]\mathbf{m} \tag{3.8}$$

for the bulk and interfacial Cauchy stress tensors $\mathbf{T}$ and $\mathbb{T}$ and the interfacial body force $\mathbf{f}$ (cf. Gurtin and Murdoch [1974], Alexander and Johnson [1985,1986], and Leo [1987]); in this extended theory (3.2) and (3.8) are separate balance laws (Gurtin and Struthers [1988]), and for that reason one should not attempt to here identify $\mathbb{C}$, $\mathbf{b}$, and $\boldsymbol{\pi}$ with $\mathbb{T}$, $\mathbf{f}$, and $[\mathbf{T}]\mathbf{m}$, as tempting as this might seem. Introducing conservation laws which bear formal resemblance to the usual balance laws for forces and moments, but are, in fact, supplementary to such laws, has been fruitful in other theories, especially those which model internal structure; an example is Ericksen's [1961] theory of liquid crystals (cf. Truesdell and Noll [1965], Section 127). ■

Remark 3.2. Let $\mathbf{r}(\mathbf{x}) = \mathbf{x} - \mathbf{x}_0$. Then given any sufficiently regular subsurface $\mathcal{C}$ of $\mathcal{S}$,

$$\mathbf{M}(\mathcal{C}) = \int_{\partial\mathcal{C}} \mathbf{r} \wedge \mathbb{C}\boldsymbol{\nu} + \int_{\mathcal{C}} \mathbf{r} \wedge \boldsymbol{\pi} + \int_{\mathcal{C}} \mathbf{r} \wedge \mathbf{b}$$

is the **total moment** (about $\mathbf{x}_0$) exerted on $\mathcal{C}$ by the capillary stress, the interaction, and the capillary supply. By (A17) and (3.3),

$$\mathbf{M}(\mathcal{C}) = -\int_{\partial\mathcal{C}} (\mathbf{m} \wedge \mathbf{c} + 2\mathbb{C}_{\mathrm{skw}}\mathbb{P}).$$

Thus <u>the existing forces, by themselves, do not satisfy balance of moments</u>: $-\mathbf{m} \wedge \mathbf{c} - 2\mathbb{C}_{\mathrm{skw}}\mathbb{P}$ represents a distributed couple,

per unit length of ς, that must be balanced by surface couples in the interaction between the interface and the bulk material. Such couples are regarded as indeterminate in the present theory ■

3.2. Balance of energy. Growth of entropy.

Consider an arbitrary fixed subbody Ω with $\mathbf{n}$ the outward unit normal on $\partial\Omega$, and let c be the portion of ς that lies in Ω:

$$c(t) = \Omega \cap \varsigma(t).$$

The internal energy and internal entropy of Ω are given by

$$\int_\Omega \varepsilon + \int_c e, \qquad \int_\Omega \eta + \int_c s.$$

Ω can loose energy and entropy because of the possible motion of the interface relative to $\partial\Omega$; these flows are represented by the quantities $\mathrm{outflow}(e,\Omega)$ and $\mathrm{outflow}(s,\Omega)$ defined by (B2) (cf. [1986g], p. 218). The integrals

$$-\int_{\partial\Omega} \mathbf{q}\cdot\mathbf{n}, \qquad -\int_{\partial\Omega} (\mathbf{q}/\theta)\cdot\mathbf{n}, \qquad \int_\Omega q, \qquad \int_\Omega q/\theta,$$

respectively, measure bulk heat and entropy flow into Ω by conduction, and heat and entropy supplied directly to Ω by the external world. We also allow the external world to supply heat and entropy to the interface; these supplies are represented by the terms

$$\int_c r, \qquad \int_c r/\theta.$$

Finally, the power expended on Ω is given by the left side of (3.4), but without the term involving π (since π represents

interactions <u>within</u> Ω).

In view of this discussion, the <u>first two laws</u> for Ω have the form:

balance of energy

$$\{\int_\Omega \varepsilon + \int_c e\}^\bullet + \text{outflow}(e,\Omega) = -\int_{\partial\Omega} \mathbf{q}\cdot\mathbf{n} + \int_\Omega q + \int_{\partial c} (\mathbf{V}\mathbf{m})\cdot\mathbb{C}\boldsymbol{\nu} + \int_c \mathbf{V}\mathbf{m}\cdot\mathbf{b} + \int_c r, \tag{3.9}$$

[11]

growth of entropy

$$\{\int_\Omega \eta + \int_c s\}^\bullet + \text{outflow}(s,\Omega) \geq -\int_{\partial\Omega} (q/\theta)\cdot\mathbf{n} + \int_\Omega q/\theta + \int_c r/\theta. \tag{3.10}$$

[12]

In view of the general balance theorem (Appendix B), we are led to the classical local **bulk relations**

$$\begin{aligned} \varepsilon^\bullet &= -\operatorname{div}\mathbf{q} + q, \\ \eta^\bullet &\geq -\operatorname{div}(q/\theta) + q/\theta, \end{aligned} \tag{3.11}$$

in conjunction with the **interface conditions**

$$\begin{aligned} -[\varepsilon]V + e^\bullet - eHV &= -[\mathbf{q}]\cdot\mathbf{m} + r + \operatorname{div}_\zeta(V\mathbf{c}) + V\mathbf{b}, \\ -[\eta]V + s^\bullet - sHV &\geq (-[\mathbf{q}]\cdot\mathbf{m} + r)/\theta. \end{aligned} \tag{3.12}$$

Crucial to the derivation of (3.12) is the assumption that θ be continuous across the interface.

Remark 3.3. We have taken the normal velocity of the interface as the kinematic variable that characterizes the

[11] Cf. [1988g]. Similar versions of the first law, but <u>without</u> the capillary stress, are contained in the work of Moeckel [1975], Fernandez-Diaz and Williams [1979], and Gurtin [1986g].

[12] Cf. [1986g,1988g].

manner in which capillary forces expend power; tangential motion does not induce power. As is consistent with a "constraint" of this form, we leave as indeterminate the tangential component of the interaction π, and therefore concern ourselves only with π, b, and the normal component (3.7) of balance of forces (3.3). Moreover, the skew component $\mathbb{C}_{skw}$ of the capillary force enters neither (3.7) nor the interface conditions (3.12), and hence will not appear in any of the subsequent results. However, while irrelevant to our further discussions, $\mathbb{C}_{skw}$ does appear when discussing interfaces with corners (facets). ■

Remark 3.4. Heat flow within the interface is easily accounted for by the addition of an energy flow

$$-\int_{\partial c} \mathbf{h} \cdot \boldsymbol{\nu}$$

to the right side of (3.9), and by the addition of an entropy flow

$$-\int_{\partial c} (\mathbf{h}/\theta) \cdot \boldsymbol{\nu}$$

to the right side of (3.10), where $\mathbf{h}(\mathbf{x},t)$, a tangential vector field, is the interfacial heat flux. ■

3.3. Free-energy inequalities.

The subsequent analysis is simplified if we introduce the **bulk** and **interfacial free energies**

$$\psi = \varepsilon - \theta\eta, \qquad f = e - \theta s. \tag{3.13}$$

The local relations (3.11) may then be combined to give the **bulk free-energy inequality**

$$\Gamma := \psi^\circ + \eta\theta^\bullet + \theta^{-1}\mathbf{q}\cdot\mathbf{g} \leq 0, \tag{3.14}$$

where

$$\mathbf{g} = \nabla\theta \tag{3.15}$$

is the **temperature gradient**. Further, in view of (3.7) and (B1), (3.12) imply the **interfacial free-energy inequality**:

$$\gamma := f^\bullet + s\theta^\bullet + \mathbf{c}\cdot\mathbf{m}^\bullet + V\{-fH + \mathbb{C}_{sym}\cdot\mathbb{L} - [\psi] + \pi\} \leq 0. \tag{3.16}$$

Remark 3.5. The global axioms (3.2) and (3.9) for force and energy balance are together equivalent to the corresponding local relations (3.3), $(3.11)_1$, and $(3.12)_1$. Further, granted force and energy balance, the global axiom (3.10) expressing growth of entropy is equivalent to the free-energy inequalities (3.14) and (3.16).

Remark 3.6. The difference between the left and right sides of (3.10) is

$$-\int_\Omega (\Gamma/\theta) - \int_c (\gamma/\theta);$$

thus $-\Gamma/\theta$ is the <u>bulk entropy-production</u> per unit volume, $-\gamma/\theta$ is the <u>interfacial entropy-production</u> per unit area. ■

4. Constitutive equations. Thermodynamic restrictions.

4.1. Bulk and interfacial constitutive equations.

We consider, for the two phases ($i=1,2$), **bulk constitutive equations** of the form

$$\psi = \psi_i(\theta,\mathbf{g}), \qquad \eta = \eta_i(\theta,\mathbf{g}), \qquad \mathbf{q} = \mathbf{q}_i(\theta,\mathbf{g}) \tag{4.1}$$

with $\mathbf{g} = \nabla\theta$ the temperature gradient. These are supplemented by **interfacial constitutive equations**:

$$\begin{aligned} &f = \hat{f}(\theta,\mathbf{m},V), && s = \hat{s}(\theta,\mathbf{m},V),\\ &\mathbb{C}_{sym} = \hat{\mathbb{C}}_{sym}(\theta,\mathbf{m},V), && \mathbf{c} = \hat{\mathbf{c}}(\theta,\mathbf{m},V), \qquad (4.2)\\ &&& \pi = \hat{\pi}(\theta,\mathbf{m},V). \end{aligned}$$

In view of Remark 3.3, we leave as <u>indeterminate</u> the tangential component of the interaction $\boldsymbol{\pi}$, and, since the skew component $\mathbb{C}_{skw}$ of the capillary stress is irrelevant to all subsequent discussions, we do not discuss its corresponding constitutive behavior.

Note that, by (3.13), the constitutive equations (4.1) and (4.2) induce auxiliary relations for the internal energies:

$$\varepsilon = \varepsilon_i(\theta,\mathbf{g}), \qquad e = \hat{e}(\theta,\mathbf{m},V). \tag{4.3}$$

4.2. Thermodynamic restrictions.

Given any time interval T, any temperature field $\theta(\mathbf{x},t)$, $(\mathbf{x},t)\in\mathbb{R}^3\times T$, and any motion of the interface $\mathcal{S}(t)$, $t\in T$, the constitutive equations (4.1) and (4.2) may be used to compute a corresponding **process** $(\psi,\eta,\mathbf{q},f,s,\mathbb{C}_{sym},\mathbf{c},\pi)$. The local capillary-balance (3.7) and the local energy balances $(3.11)_2$ and $(3.12)_2$ then determine the capillary supply b and the heat supplies q and r needed to support the process.[13] Granted

[13]One might object to the premise of the availibility of arbitrary

this, Remark 3.5 implies that the global law of entropy growth (3.10) will be satisfied if and only if the free-energy inequalities (3.14) and (3.16) are satisfied.

Definition. The **constitutive equations are compatible with thermodynamics** if given any temperature field and any motion of the interface, the corresponding process satisfies (3.14) and (3.16).

The inequality (3.14), when required to hold for all temperature fields, is equivalent to the requirement that $\psi_i(\theta,\mathbf{g})$ and $\eta_i(\theta,\mathbf{g})$ be independent of $\mathbf{g}$ and satisfy

$$\eta_i(\theta) = -\partial_\theta \psi_i(\theta), \qquad \mathbf{q}_i(\theta,\mathbf{g})\cdot\mathbf{g} \leq 0 \tag{4.4}$$

(Coleman and Noll [1963], Coleman and Mizel [1963]). The next theorem, our main result, gives corresponding restrictions for the interfacial constitutive equations.

Compatibility theorem. The constitutive equations are compatible with thermodynamics if and only if, in addition to (4.4), the following restrictions are satisfied:
(i) $f\hat{}(\theta,\mathbf{m},V)$, $\mathbf{C}_{sym}(\theta,\mathbf{m},V)$, $\mathbf{c}\hat{}(\theta,\mathbf{m},V)$, and $s\hat{}(\theta,\mathbf{m},V)$ are independent of the normal velocity V and satisfy

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supplies, especially the capillary supply b. Allowing a supply for each balance law is an assumption now standard in continuum mechanics. Assumptions of this form are generally tacit throughout physics. Indeed, statical equations are often derived from the requirement that a functional, for example a global free energy, be stationary. The corresponding analyses generally require arbitrary variation of the underlying state, with the assumption left tacit that suitable supplies are available to support such variations.

$$\hat{s}(\theta,\mathbf{m}) = -\partial_\theta \hat{f}(\theta,\mathbf{m}), \qquad \hat{\mathbf{c}}(\theta,\mathbf{m}) = -\partial_{\mathbf{m}} \hat{f}(\theta,\mathbf{m}), \tag{4.5}$$
$$\hat{\mathbf{C}}_{sym}(\theta,\mathbf{m}) = \hat{f}(\theta,\mathbf{m})\mathbf{I}(\mathbf{m}),$$

so that the free energy determines entropy and the normal and symmetric components of the capillary stress, and the symmetric component is a surface tension of amount $\hat{f}(\theta,\mathbf{m})$; (ii) the interaction $\hat{\pi}(\theta,V,\mathbf{m})$ has the form

$$\hat{\pi}(\theta,\mathbf{m},V) = \psi_2(\theta) - \psi_1(\theta) - \hat{\beta}(\theta,\mathbf{m},V)V, \tag{4.6}$$

where the **kinetic coefficient** $\hat{\beta}(\theta,\mathbf{m},V)$ is consistent with

$$\hat{\beta}(\theta,\mathbf{m},V) \geq 0. \tag{4.7}$$

Proof. We must show that (i) and (ii) are equivalent to the requirement that the interfacial inequality (3.16) hold in all processes. In view of the constitutive equations (4.1) and (4.2), (3.16) is equivalent to the inequality

$$(\partial_\theta \hat{f} + \hat{s})\cdot\theta^\bullet + (\partial_{\mathbf{m}} \hat{f} + \hat{\mathbf{c}})\cdot\mathbf{m}^\bullet + (\partial_V \hat{f})\cdot V^\bullet \tag{4.8}$$
$$+ V\{-\hat{f}H + \hat{\mathbf{C}}_{sym}\cdot\mathbf{L} + (\psi_1 - \psi_2) + \hat{\pi}\} \leq 0,$$

where, for convenience, we have omitted all arguments.

Assume that (4.8) holds for all temperature fields and motions of the interface. In view of the Variation Lemma ([1988g]), the rates $\theta^\bullet$, $\mathbf{m}^\bullet$, and $V^\bullet$ in (4.8) may be specified independently of the other quantities; this leads to all of the assertions of (i) except those concerning $\hat{\mathbf{C}}_{sym}$, and also to the inequality

$$V\{-\hat{f}(\theta,\mathbf{m})H + \hat{\mathbf{C}}_{sym}(\theta,\mathbf{m},V)\cdot\mathbf{L} + (\psi_1 - \psi_2)(\theta) + \hat{\pi}(\theta,\mathbf{m},V)\} \leq 0.$$

Since the dependence on $\mathbf{L}$ is linear, $\mathbf{C}_{sym}\hat{}$ must be consistent with (i), and the remaining inequality implies (4.6). Conversely, the assertions (i) and (ii) trivially yield (4.8) in all processes. ■

Remark 4.1. By definition, π and V are components with respect to the same direction, so that, for V positive, π may be regarded as a force in the direction of motion exerted on the interface by the bulk material. Equation (4.6) gives this force as the sum of two terms. The first term is a force $[\psi]$ which is positive if the phase into which the interface is moving has higher free energy (and is thus less stable) than the other phase. The second term $-\beta\hat{}V$ is, by (4.7), negative, and represents a drag force, a force on the interface which opposes its motion. ■

Remark 4.2. The paper [1988g] begins with an arbitrary energy flux $\mathbf{j}\cdot\boldsymbol{\nu}$ in place of $(V\mathbf{m})\cdot\mathbf{C}\boldsymbol{\nu} = V\mathbf{c}\cdot\boldsymbol{\nu}$ in (3.9) and shows, as a consequence of the second law, that $\mathbf{j}$ necessarily has the form $V\mathbf{c}$. However, the more general framework necessitates a more complicated constitutive theory: in the present study, capillary balance furnishes a relation between interfacial temperature, curvature, orientation, and normal velocity; such a relation is a constitutive postulate in [1986g,1988g]. Moreover, the structure of the constitutive theory in [1988g] leads to the (somewhat strange) requirement that the entropy be independent of orientation. ■

To avoid repeated hypotheses, we now make the following:

Assumption. We assume, for the remainder of the paper, that the constitutive equations are compatible with thermodynamics, and

that the capillary supply and the bulk and interfacial heat supplies vanish:

$$b = 0, \qquad q = 0, \qquad r = 0. \tag{4.9}$$

Note that (3.13) and (4.5) yield the **Gibbs relations**

$$f^{\bullet} = -s\theta^{\bullet} - \mathbf{c}\cdot\mathbf{m}^{\bullet}, \qquad e^{\bullet} = \theta s^{\bullet} - \mathbf{c}\cdot\mathbf{m}^{\bullet}, \tag{4.10}$$

while (3.14), (3.16), (4.4), $(4.5)_3$, (4.6), (4.10), and Remark 3.6 imply that

$$\theta\Gamma = \mathbf{q}\cdot\mathbf{g}, \qquad \gamma = -\beta V^2. \tag{4.11}$$

5. The general free-boundary problem.

5.1. Bulk equations. Interface conditions.

The equations derived thus far combine to form an important free-boundary problem for the temperature. The differential equation, to be satisfied in bulk, is balance of energy $(3.11)_2$. If we let

$$C_i(\theta) = \partial_\theta \varepsilon_i(\theta) \tag{5.1}$$

denote the **bulk specific heats**, and assume that the heat flux is given by Fourier's law

$$\mathbf{q}_i(\theta, \nabla\theta) = -K_i(\theta)\nabla\theta \tag{5.2}$$

with $K_i(\theta) \in \mathrm{lin}(\mathbb{R}^3, \mathbb{R}^3)$ the **conductivity tensor** for phase i, then balance of energy has the form

$$C_i(\theta)\dot{\theta} = \mathrm{div}\{K_i(\theta)\nabla\theta\}. \tag{5.3}$$

Equally important are the conditions expressing force and energy balance for the interface. The latter is given by $(3.12)_1$. By $(4.5)_3$, the equation (3.7) expressing normal force-balance has the form

$$\pi = -fH - \mathrm{div}_s \mathbf{c}, \tag{5.4}$$

or equivalently, using (4.6) and writing $\beta = \hat{\beta}(\theta, \mathbf{m}, V)$,

$$[\psi] = \beta V - fH - \mathrm{div}_s \mathbf{c}. \tag{5.5}$$[14]

---

[14] Within a statical theory ($V = 0$) Herring [1951] and Cahn and Hoffman [1974] derive an equation of this form as a necessary condition for the free energy to be a minimum. With $\mathbf{c}$ and V zero, (5.5) is usually referred to as the Gibbs-Thomson relation

The basic equations which govern the evolution of the interface consist of the bulk equations (5.3), the interface conditions $(3.12)_1$ and (5.5), and the appropriate interfacial constitutive equations:

bulk equations

$$C_i(\theta)\dot{\theta} = \operatorname{div}\{K_i(\theta)\nabla\theta\}, \tag{5.6}$$

interface conditions

$$\begin{aligned}
&[\psi_i(\theta)] = \beta V - fH - \operatorname{div}_s \mathbf{c},\\
&[\varepsilon_i(\theta)]V = -[K_i(\theta)\nabla\theta]\cdot\mathbf{m} + e^{\bullet} - eHV - \operatorname{div}_s(V\mathbf{c}),\\
&f = \hat{f}(\theta,\mathbf{m}), \quad e = \hat{e}(\theta,\mathbf{m}), \quad \beta = \hat{\beta}(\theta,\mathbf{m},V), \quad \mathbf{c} = -\partial_{\mathbf{m}}\hat{f}(\theta,\mathbf{m}).
\end{aligned} \tag{5.7}$$

Here we have used the obvious notation for the jump in a bulk constitutive function; for example,

$$[\psi_i(\theta)] = \psi_2(\theta) - \psi_1(\theta), \qquad [K_i(\theta)\nabla\theta] = K_2(\theta)\nabla\theta - K_1(\theta)\nabla\theta.$$

5.2. Initial conditions. Boundary conditions.

Appropriate **initial conditions** are:

$$\begin{aligned}
&\theta(\mathbf{x},0) = \theta_0(\mathbf{x}) \quad \text{for all } \mathbf{x}\in\mathbb{R}^3,\\
&B_i(0) = B_{0i}
\end{aligned} \tag{5.8}$$

with $\theta_0(\mathbf{x})$ the prescribed initial temperature and B_{0i} the

(cf., e.g., Mullins and Sekerka [1964], eq. (3b)). In [1986g,1988g] the relation (5.5) (with $\beta=0$) follows as a consequence of the second law, but the derivation requires a constitutive equation (for the interfacial temperature) which in a sense replaces the law of capillary balance.

prescribed initial phase regions.

Since the body (the region of space occupied by the two phases) is all of $\mathbb{R}^3$, conditions at infinity are required. Such conditions are standard if the interface is finite.

Thus far we have limited our discussion to unbounded bodies. If the **body** $\mathcal{B}$ is a <u>bounded region</u> (fixed in time), then boundary conditions are required. When the interface $\mathcal{S}(t)$ touches the boundary, conditions expressing balance of capillary forces are needed at the juncture of the interface and the boundary; these require a detailed description of the <u>boundary interface</u> between the individual phases and $\partial\mathcal{B}$, a description beyond the scope of this paper. Here we shall restrict our attention to situations in which the interface does not touch the boundary; in the same spirit, when discussing boundary conditions away from $\mathcal{S}(t)$, we will ignore the effects of a boundary interface. Appropriate boundary conditions are then a prescription of

$$\begin{aligned} &\theta(x,t) \quad \text{on a portion of } \partial\mathcal{B} \quad \text{and} \\ &\mathbf{q}(x,t)\cdot\mathbf{n}(x) \quad \text{on the remainder, with} \\ &\mathbf{n} \quad \text{the outward unit normal to } \partial\mathcal{B}. \end{aligned} \tag{5.9}$$

The free-boundary problem described by (5.6)-(5.9) is extremely difficult, chiefly because of the nonlinearities inherent in the free-boundary conditions (5.7). For that reason we shall develop, in the next section, an approximate theory for weak interfaces.

6. Weak interfaces.

6.1. Behavior near the transition temperature.

We assume that there is a unique temperature θ_M, called the **transition temperature**, at which the bulk free energies coincide:

$$\psi_1(\theta_M) = \psi_2(\theta_M). \tag{6.1}$$

Remark 6.1. In the absence of interfacial structure (i.e., for f, $\mathbf{c}$, and β identically zero) $(5.7)_1$ yields $[\psi]=0$, so that $\theta=\theta_M$. This is a free-boundary condition of the classical (Stefan) theory of melting. As we shall see, within the current framework the interfacial temperature will generally not equal the transition temperature. ■

The difference

$$\ell = \varepsilon_2(\theta_M) - \varepsilon_1(\theta_M) \tag{6.2}$$

in energy between phases at the transition temperature is the **latent heat**, which we assume to be nonzero:

$$\ell \neq 0. \tag{6.3}$$

By (3.13), $(4.4)_1$, and (6.2),

$$\partial_\theta\{\psi_2(\theta) - \psi_1(\theta)\}\big|_{\theta=\theta_M} = -\ell/\theta_M\,. \tag{6.4}$$

We are interested in behavior near the transition temperature and therefore introduce the (dimensionless) **temperature difference**

$$u = \frac{\theta - \theta_M}{\theta_M}. \tag{6.5}$$

Then, by (6.1), (6.2), and (6.4), for u small,

$$\psi_2(\theta) - \psi_1(\theta) = -\ell u + O(u^2), \qquad \varepsilon_2(\theta) - \varepsilon_1(\theta) = \ell + O(u). \tag{6.6}$$

6.2. Approximate conditions for weak interfaces.

We now derive approximate interface conditions appropriate to a **weak interface**; that is, an interface whose free energy, internal energy, and kinetic coefficient are small, and whose kinetic coefficient depends only weakly on V:

$$f\hat{}(\theta,m) = \delta f^*(\theta,m), \qquad e\hat{}(\theta,m) = \delta e^*(\theta,m), \qquad \beta\hat{}(\theta,m,V) = \delta\beta^*(\theta,m,\delta V). \tag{6.7}$$

Here $\delta > 0$ is small and the starred quantities are $O(1)$ in magnitude. By $(4.5)_2$,

$$c\hat{}(\theta,m) = \delta c^*(\theta,m).$$

For convenience, let

$$f_0(m) = f\hat{}(\theta_M,m), \qquad c_0(m) = c\hat{}(\theta_M,m), \qquad \beta_0(m) = \beta\hat{}(\theta_M,m,0). \tag{6.8}$$

Then, arguing formally, it is clear from $(6.6)_1$ and $(5.7)_1$ that $u = O(\delta)$, so that, by (6.6) and (6.7), the interface conditions (5.7) have the asymptotic forms

$$\ell u = -\beta_0(m)V + f_0(m)H + \operatorname{div}_\xi c_0(m) + O(\delta^2),$$

$$\ell V = -[K_i(\theta)\nabla\theta]\cdot m + O(\delta).$$

Neglecting higher-order terms and, for convenience, dropping the subscript zero, we are led to the **approximate interface conditions**:

$$\begin{aligned} \ell u &= -\beta(m)V + f(m)H + \mathrm{div}_{\zeta} c(m), \\ \ell V &= -[K_1(\theta)\nabla\theta]\cdot m. \end{aligned} \tag{6.9}$$[15]

By $(4.5)_2$,

$$c(m) = -\partial_m f(m),$$

and we may use (A11) to write $(6.9)_1$ in the form

$$\ell u = -\beta(m)V + f(m)H + \partial_m\partial_m f(m)\cdot\mathbb{L},$$

showing that the interfacial temperature generally depends on the entire curvature tensor, rather than simply on the mean curvature. If we let $\mathbb{B}(m)$ denote the linear transformation from $m^{\perp}$ into $\mathbb{R}^3$ defined by

$$\mathbb{B}(m)w = f(m)w + [\partial_m\partial_m f(m)]w \quad \text{for} \quad w\in m^{\perp}, \tag{6.10}$$

---

[15]Cf. [1988g], eq. (6.5). The boundary condition $(6.9)_2$ is a classical Stefan condition. Free-boundary conditions of the form $\ell u = -\beta(m)V$ were introduced by Frank [1958] and used by Chernov [1963a,b]; $\ell u = fH$ was introduced by Mullins and Sekerka [1963,1964]; $\ell u = -\beta V + fH$ was used by Voronkov [1964]. See also Seidensticker [1966], Tarshis and Tiller [1966], and the review articles by Sekerka [1968,1973,1984], Chernov [1971,1974], Delves [1974], and Langer [1980].

then $(6.9)_1$ has the succint form

$$\ell u = -\beta(m)V + \mathbb{B}(m)\cdot\mathbb{L}. \qquad (6.11)$$

7. Free-boundary problems for weak interfaces.

7.1. The quasi-linear and quasi-static problems.

We now consider free-boundary problems based on the approximate interface conditions $(6.9)_2$ and (6.11) in conjunction with (5.6) linearized about the transition temperature θ_M:

$$C_i u^\circ = \operatorname{div}(K_i \nabla u), \qquad C_i = C_i(\theta_M), \qquad K_i = K_i(\theta_M).$$

We label phases so that phase 2 has the higher internal energy at the transition temperature. Then

$$\ell > 0, \tag{7.1}$$

and to avoid an unnecessary constant, we rescale by defining $C^*_i = C_i/(\theta_M \ell)$, $K^*_i = K_i/(\theta_M \ell)$, $f^* = f/\ell$, and $\beta^* = \beta/\ell$, and then dropping the star superscript. We are then led to the **quasi-linear system**:

$$\begin{aligned} &C_i u^\circ = \operatorname{div}(K_i \nabla u) && \text{in bulk,} \\ &u = -\beta(\mathbf{m})V + \mathcal{B}(\mathbf{m})\cdot\mathbf{L} && \text{on the interface,} \\ &V = -[K_i \nabla u]\cdot\mathbf{m} \end{aligned} \tag{7.2}$$

with $\mathcal{B}(\mathbf{m})$ given by (6.10). Note that, by $(4.4)_2$ and (4.7),

$$\beta(\mathbf{m}) \geq 0, \qquad K_i \text{ is positive semi-definite.}$$

The quasi-linear problem consists of (7.2) supplemented by the initial conditions (5.8) and the boundary conditions (5.9) (with θ replaced by u and $\mathbf{q} = -K_i \nabla u$).

Generally, one expects the interface to move slowly in comparison to the time scale for heat conduction. With this in mind, we consider the **quasi-static system** which neglects the

terms $C_i u^\bullet$ in the bulk equations:

$$\begin{aligned} &\operatorname{div}(K_i \nabla u) = 0 && \text{in bulk,} \\ &u = -\beta(m)V + \mathbb{B}(m)\cdot L && \text{on the interface.} \\ &V = -[K_i \nabla u]\cdot m \end{aligned} \tag{7.3}$$

The quasi-static problem consists of (7.3) suplemented by $(5.8)_2$ and (5.9). (The condition $(5.8)_1$, involving the prescription of $u(x,0)$, is dropped.) If the body is infinite, the boundary conditions (5.9) are replaced by conditions at infinity.

In discussing the above problems, it is tacit that the interface does not touch ∂B; in particular, the initial data must be consistent with this assumption.

7.2. Growth theorems.

We now establish Lyapunov functions for solutions of the quasi-linear and quasi-static systems. We restrict our attention to a bounded body and to the following two types of boundary conditions:

(i) **isolated boundary**:

$$n\cdot K_i \nabla u = 0 \quad \text{on} \quad \partial B \quad \text{for all time;} \tag{7.4}$$

(ii) **thermally-uniform boundary**:

$$u = U \quad \text{on} \quad \partial B \quad \text{for all time.} \tag{7.5}$$

In (ii), $U = U(t)$, a function of time alone, is the prescribed **boundary temperature**.

By (6.8),

$$F(\zeta) = \int_{\zeta} f(m) \tag{7.6}$$

is the **total interfacial free energy** at the transition temperature, and, by (4.11) and Remark 3.6,

$$\mathfrak{D}(u) = \sum_{B_i} \int \nabla u \cdot K_i \nabla u + \int_{\zeta} \beta(m) V^2 \geq 0 \tag{7.7}$$

is, within the approximation of a weak interface, proportional to the **total production of entropy**.

Growth theorem.[16] Let u be a solution of the quasi-linear system with $C_1 = C_2 = C$.

(i) If the boundary is isolated,

$$\begin{aligned} &\{\mathrm{vol}(B_1) - C\int_B u\}^{\cdot} = 0, \\ &\{F(\zeta) + (C/2)\int_B u^2\}^{\cdot} = -\mathfrak{D}(u) \leq 0. \end{aligned} \tag{7.8}$$

(ii) If the boundary is thermally uniform,

$$F(\zeta)^{\cdot} + U\mathrm{vol}(B_1)^{\cdot} + (C/2)\{\int_B (u-U)^2\}^{\cdot} = -\mathfrak{D}(u) \leq 0. \tag{7.9}$$

Let u be a solution of the quasi-static system.

(iii) If the boundary is isolated,

$$\mathrm{vol}(B_1)^{\cdot} = 0, \qquad F(\zeta)^{\cdot} = -\mathfrak{D}(u) \leq 0. \tag{7.10}$$

(iv) If the boundary is thermally uniform,

$$F(\zeta)^{\cdot} + U\mathrm{vol}(B_1)^{\cdot} = -\mathfrak{D}(u) \leq 0. \tag{7.11}$$

---

[16] Cf. [1986g], Sections 10,11; [1988g], eqs. (7.9), (7.10). We write vol(D) for the volume of regions D in $\mathbb{R}^3$.

Proof. The proof is based on three identities. The first, a direct consequence of the divergence theorem, asserts that

$$\sum_{i=1,2} \int_{B_i} \mathrm{div}\,\mathbf{h} = \int_{\partial B} \mathbf{h}\cdot\mathbf{n} - \int_{\varsigma} [\mathbf{h}]\cdot\mathbf{m} \qquad (7.12)$$

for any bulk vector field $\mathbf{h}$. The other two identities are:

$$\int_{\varsigma} V = \mathrm{vol}(B_1)^{\circ}, \qquad \int_{\varsigma} uV = -F(\varsigma)^{\circ} - \int_{\varsigma} \beta(\mathbf{m})V^2. \qquad (7.13)^{17}$$

The first of (7.13) follows from $(B3)_1$. We now sketch a proof of $(7.13)_2$; this proof uses only interface condition

$$u = -\beta(\mathbf{m})V + \mathbf{f}(\mathbf{m})\cdot\mathbf{H} + \partial_{\mathbf{m}}\partial_{\mathbf{m}}\mathbf{f}(\mathbf{m})\cdot\mathbb{L} \qquad (7.14)$$

and the fact that ς is a closed surface. In view of $(B3)_2$ with $\Omega = B$, (7.6), (A11), (B1), and the surface divergence theorem (A15) with $c = \varsigma$,

$$\begin{aligned} F(\varsigma)^{\circ} &= \int_{\varsigma} \mathbf{f}(\mathbf{m})^{\bullet} - \int_{\varsigma} \mathbf{f}(\mathbf{m})\mathbf{H}V, \\ &= \int_{\varsigma} \partial_{\mathbf{m}}\mathbf{f}(\mathbf{m})\cdot\mathbf{m}^{\bullet} - \int_{\varsigma} \mathbf{f}(\mathbf{m})\mathbf{H}V, \\ &= -\int_{\varsigma} \{\partial_{\mathbf{m}}\partial_{\mathbf{m}}\mathbf{f}(\mathbf{m})\cdot\mathbb{L} + \mathbf{f}(\mathbf{m})\mathbf{H}\}V; \end{aligned}$$

and $(7.13)_2$ follows from (7.14).

Let u be a solution of the quasi-linear system with $C_1 = C_2$. Since u is continuous across the interface

$$\{\int_B u^p\}^{\circ} = \int_B (u^p)^{\circ}, \qquad (7.15)$$

$p = 1,2$. Let $\mathbf{q}$ be the bulk field defined by $\mathbf{q} = K_i\nabla u$ in B_i.

[17] [1988g], eq. (6.6).

Assume that the boundary is isolated in the sense of (7.4). Then $(7.8)_1$ follows from (7.12) with $\mathbf{h}=\mathbf{q}$, $(7.2)_{1,3}$, $(7.13)_1$, and (7.15); while $(7.8)_2$ is a consequence of (7.12) with $\mathbf{h}=u\mathbf{q}$, $(7.2)_{1,2}$, (7.7), $(7.13)_2$, and (7.15). On the other hand, assume that the boundary is thermally uniform. Then, since $U(t)$ is independent of $\mathbf{x}$,

$$\int_{\partial B} u\mathbf{q}\cdot\mathbf{n} = U\int_{\partial B}\mathbf{q}\cdot\mathbf{n}; \tag{7.16}$$

(7.9) follows from (7.12) with $\mathbf{h}=\mathbf{q}$ and with $\mathbf{h}=u\mathbf{q}$, (7.2), (7.7), (7.13), (7.15), and (7.16).

Finally, (7.10) and (7.11) follow from (7.8) and (7.9) with $C=0$. ■

Remark 7.1. In view of the agreement (7.1), phase 2 has higher internal energy at the transition temperature; thus for a solid-liquid system $B_1(t)$ would be the region occupied by the solid phase. If the boundary is supercooled, then $U<0$, and the fact that $U\mathrm{vol}(B_1)$ is negative in (7.9) and (7.11) at least indicates the tendency of the solid phase to grow. ■

For an isotropic material the quasi-static system reduces to the Mullins-Sekerka system:[18]

$$\Delta u = 0 \qquad \text{in bulk,}$$

$$u = -\beta V + fH, \quad V = -[k_i\nabla u]\cdot\mathbf{m} \qquad \text{on the interface,}$$

with β, f, and k_i scalar constants and Δ the laplacian. In this case (7.10) becomes

$$\mathrm{vol}(B_1)^\bullet = 0, \qquad \mathrm{farea}(\varsigma)^\bullet = -\mathfrak{D}(u) \le 0,$$

---

[18] [1963,1964], although Mullins and Sekerka take $\beta=0$.

while (7.11) takes the form

$$\text{farea}(\zeta)^\circ + U\text{vol}(B_1)^\circ = -\mathfrak{D}(u) \leq 0.$$

An analogous simplification holds for the quasi-linear problem.

8. Perfect conductors.

Consider the quasi-linear system (7.2) for a bounded region with boundary held at the spatially-constant temperature $U(t)$ (cf. (7.5)). We now discuss the asymptotic form this system takes when the conductivity of each phase is large. Precisely, we consider (7.2) and (7.5) with

$$K_i \text{ replaced by } \delta^{-1}K_i \tag{8.1}$$

under the assumption that δ is small. Writing a formal perturbation for u in powers of δ, it is clear that the lowest-order term, also written u, should be consistent with

$$\operatorname{div}(K_i\nabla u) = 0 \text{ in bulk}, \quad [K_i\nabla u]\cdot m = 0 \text{ on the interface},$$
$$u = U \text{ on } \partial B \tag{8.2}$$

as well as the interface condition $u = -\beta(m)V + \mathbb{B}(m)\cdot\mathbb{L}$. Under reasonable assumptions, the problem (8.2) has the unique solution $u(x,t) \equiv U(t)$; the only equation then left to solve is then the free-boundary condition for u:

$$\beta(m)V - \mathbb{B}(m)\cdot\mathbb{L} = -U(t) \text{ on the interface.} \tag{8.3}$$

This equation, together with kinematical conditions for $\zeta(t)$, forms a boundary-value problem for the evolution of the interface.

Let $F(\zeta)$ be defined by (7.6) and $\mathfrak{D}(\zeta)$ by

$$\mathfrak{D}(\zeta) = \int_{\zeta} \beta(m)V^2.$$

Then $(7.13)_2$ with $u = U$ and $(7.13)_1$ yield the

Growth theorem for perfect conductors. For an

interface consistent with (8.3),

$$F(\varsigma)^{\bullet} + U\,\mathrm{vol}(B_1)^{\bullet} = -\mathfrak{D}(\varsigma) \leq 0. \tag{8.4}$$

Remark 8.1. If, instead of a thermally-uniform boundary, we consider an isolated boundary, then the condition $u = U$ in (8.2) is replaced by $(K_1 \nabla u)\cdot \mathbf{n} = 0$ on ∂B; (8.2) thus modified still has the solution $u(x,t) \equiv U(t)$, but now $U(t)$ is indeterminate. On the other hand, for δ in (8.1) small but nonzero, (7.8) is satisfied (granted $C_1 = C_2 = C$); we therefore expect that an isolated perfect conductor is described by the interface equations

$$\beta(\mathbf{m})V - \mathbf{B}(\mathbf{m})\cdot\mathbf{L} = -U(t), \qquad \mathrm{vol}(B_1)^{\bullet} = C_0 U^{\bullet}, \tag{8.5}$$

where $C_0 = C\,\mathrm{vol}(B)$. Within the approximations underlying the linear heat equation, $(8.5)_2$ is the requirement that the internal energy be constant. Moreover, (8.4) remains valid; thus, using (8.5),

$$\left\{F(\varsigma) + \tfrac{1}{2} C_0 U^2\right\}^{\bullet} = -\mathfrak{D}(\varsigma) \leq 0. \tag{8.6}$$

Remark 8.2. For materials which have both large conductivity and small specific heat, one might consider the previous analysis with (8.1) supplemented by the replacement of C_i by δC_i. In this instance, the arguments leading to (8.3) and (8.4) remain unchanged, but (8.5) is replaced by the system

$$\beta(\mathbf{m})V - \mathbf{B}(\mathbf{m})\cdot\mathbf{L} = -U(t), \qquad \mathrm{vol}(B_1)^{\bullet} = 0, \tag{8.7}$$

while (8.6) reduces to

$$F(\varsigma)^{\bullet} = -\mathfrak{D}(\varsigma) \leq 0. \qquad (8.8)$$

Acknowledgment. I greatly acknowledge valuable discussions with S. Angenant, N. Milic, and A. Struthers. This work was supported by the Army Research Office and by the National Science Foundation.

Appendix on surfaces.

A. Surfaces.

We use the notation and many of the results of Gurtin and Murdoch [1975], Murdoch [1976,1978], and Gurtin [1986g,1988g]. Given inner product spaces $\mathbb{U}$ and $\mathbb{W}$, $\mathrm{lin}(\mathbb{U},\mathbb{W})$ is the space of linear transformations from $\mathbb{U}$ into $\mathbb{W}$; $\mathrm{lin}(\mathbb{U},\mathbb{W})$ is equipped with inner product $A\cdot B=\mathrm{tr}(AB^T)$. Here tr denotes the **trace**, B^T is the **transpose** of B, and we write $u\cdot v$ for the **inner product** of u and v, regardless of the space in question. Further, $A\in\mathrm{lin}(\mathbb{U},\mathbb{U})$ is **symmetric** if $A=A^T$, **skew** if $A=-A^T$; more generally, each $A\in\mathrm{lin}(\mathbb{U},\mathbb{U})$ admits a unique additive decomposition into **symmetric** and **skew parts**

$$\tfrac{1}{2}(A+A^T) \quad \underline{\text{and}} \quad \tfrac{1}{2}(A-A^T). \tag{A1}$$

The **tensor product** of $v\in\mathbb{U}$ and $w\in\mathbb{W}$ is the transformation $v\otimes w\in\mathrm{lin}(\mathbb{W},\mathbb{U})$ defined by $(v\otimes w)z=(w\cdot z)v$ for all $z\in\mathbb{W}$.

Let m be a <u>unit vector</u>. $\mathbf{I}(m)\in\mathrm{lin}(m^\perp,\mathbb{R}^3)$ is the **inclusion** of $m^\perp$ into $\mathbb{R}^3$: $\mathbf{I}(m)$ maps $a\in m^\perp$ into a considered as a vector in $\mathbb{R}^3$. $\mathbf{P}(m)$ is the **perpendicular projection** from $\mathbb{R}^3$ onto the plane $m^\perp$: for each $a\in\mathbb{R}^3$, $\mathbf{P}(m)a\in m^\perp$ is defined by

$$\mathbf{P}(m)a = a - (a\cdot m)m. \tag{A2}$$

We consider $\mathbf{P}(m)$ as an element of $\mathrm{lin}(\mathbb{R}^3,m^\perp)$. Thus the codomain[19] of $\mathbf{P}(m)$ is $m^\perp$ and not $\mathbb{R}^3$; with this agreement,

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[19]We very carefully identify the domain $\mathbb{U}$ and codomain $\mathbb{W}$ of transformations in $\mathrm{lin}(\mathbb{U},\mathbb{W})$; identification of the codomain is crucial, since the domain of the transpose is the codomain of the original map.

$$\mathbf{I}(\mathbf{m})^T = \mathbf{P}(\mathbf{m}). \qquad \text{(A3)}$$

Let ς denote a smooth, oriented **surface** in $\mathbb{R}^3$ with unit normal field $\mathbf{m}(\mathbf{x})$, the **orientation** of ς. Then $\mathbf{m}(\mathbf{x})^\perp$ is the **tangent plane** to ς at $\mathbf{x}\in\varsigma$. We use the shorthand

$$\mathbf{I}(\mathbf{x}) = \mathbf{I}(\mathbf{m}(\mathbf{x})), \qquad \mathbf{P}(\mathbf{x}) = \mathbf{P}(\mathbf{m}(\mathbf{x})), \qquad \text{(A4)}$$

so that $\mathbf{P}(\mathbf{x})$ is the projection onto the tangent plane at $\mathbf{x}$, while $\mathbf{I}(\mathbf{x})$ is the inclusion of the tangent plane into $\mathbb{R}^3$.

We will consistently use the following terminology:

superficial scalar or vector field: a scalar or vector field on ς;

tangential vector field: a superficial vector field whose values are tangential to ς;

superficial tensor field: a field $\mathbf{C}$ on ς with values $\mathbf{C}(\mathbf{x})\in\mathrm{lin}(\mathbf{m}(\mathbf{x})^\perp,\mathbb{R}^3)$;

tangential tensor field: a superficial tensor field $\mathbf{C}$ whose values satisfy $\mathbf{C}(\mathbf{x})\mathbf{a}\in\mathbf{m}(\mathbf{x})^\perp$ for each $\mathbf{a}\in\mathbf{m}(\mathbf{x})^\perp$.

For $\mathbf{C}$ a superficial tensor field:

$$\mathbf{C} \ \underline{\text{tangential}} \iff \mathbf{C} = \mathbf{IPC} \iff \mathbf{C}^T\mathbf{m} = \mathbf{0}. \qquad \text{(A5)}$$

The first implication in (A5) is immediate. To derive the second, note that $\mathbf{m}\cdot\mathbf{C}\mathbf{a} = \mathbf{a}\cdot\mathbf{C}^T\mathbf{m}$ for $\mathbf{a}\in\mathbf{m}^\perp$, and $\mathbf{m}\cdot\mathbf{C}\mathbf{a} = 0$ for all such $\mathbf{a}$ if and only if $\mathbf{C}$ is tangential.

Let $\mathbf{T}$ be a tangential tensor field. Although $\mathbf{T}(\mathbf{x})$ maps tangent vectors into tangent vectors, we consider the codomain of $\mathbf{T}(\mathbf{x})$ to be $\mathbb{R}^3$. Postmultiplying by $\mathbf{P}(\mathbf{x})$ transforms $\mathbf{T}(\mathbf{x})$ to an element of $\mathrm{lin}(\mathbf{m}(\mathbf{x})^\perp,\mathbf{m}(\mathbf{x})^\perp)$, premultiplying by $\mathbf{P}(\mathbf{x})$

extends $\mathbf{T}(x)$ to an element of $\mathrm{lin}(\mathbb{R}^3,\mathbb{R}^3)$, and neither of these adjustments changes its essential character:

$$\mathbf{T}(x)a = \mathbf{P}(x)\mathbf{T}(x)a = \mathbf{T}(x)\mathbf{P}(x)a \ \underline{\text{for every}}\ a\in m(x)^{\perp},\ \underline{\text{but}}$$
$$\mathbf{T}(x)\in \mathrm{lin}\,(m(x)^{\perp},\mathbb{R}^3),\ \ \mathbf{P}(x)\mathbf{T}(x)\in \mathrm{lin}(m(x)^{\perp},m(x)^{\perp}),\ \ \mathbf{T}(x)\mathbf{P}(x)\in \mathrm{lin}(\mathbb{R}^3,\mathbb{R}^3).$$

Moreover,

$$\begin{aligned} \mathbf{PT}\ \underline{\text{symmetric}} &\iff \mathbf{TP}\ \underline{\text{symmetric}}, \\ \mathbf{PT}\ \underline{\text{skew}} &\iff \mathbf{TP}\ \underline{\text{skew}}. \end{aligned} \qquad \text{(A6)}$$

Indeed, let $\mathbf{PT}$ be symmetric. Then $\mathbf{PT}=\mathbf{T}^{\mathsf{T}}\mathbf{I}$. Also, by (A5), $\mathbf{T}=\mathbf{IPT}$ and $\mathbf{T}^{\mathsf{T}}=\mathbf{T}^{\mathsf{T}}\mathbf{IP}$. Thus $\mathbf{TP}=\mathbf{IPTP}=\mathbf{IT}^{\mathsf{T}}\mathbf{IP}=\mathbf{IT}^{\mathsf{T}}$, and $\mathbf{TP}$ is symmetric. The remaining assertions of (A6) are proved analogously.

Guided by (A6), we refer to a tangential tensor field $\mathbf{T}$ as **symmetric** or **skew** according as $\mathbf{P}(x)\mathbf{T}(x)$ (or equivalently $\mathbf{T}(x)\mathbf{P}(x)$) is symmetric or skew at each $x\in\mathcal{S}$. With this terminology, <u>the inclusion $\mathbf{I}$ is a symmetric tangential tensor field</u>. A further consequence of this definition is that

$$\mathbf{T}\cdot\mathbf{F} = 0 \ \underline{\text{for}}\ \mathbf{T}\ \underline{\text{symmetric and}}\ \mathbf{F}\ \underline{\text{skew}}. \qquad \text{(A7)}$$

Similarly, we define the **trace**, $\mathrm{tr}\mathbf{T}$, of a tangential field $\mathbf{T}$ by $\mathrm{tr}\mathbf{T}=\mathrm{tr}(\mathbf{PT})=\mathrm{tr}(\mathbf{TP})$.

Let $\mathbf{T}$ be a <u>tangential</u> tensor field. Then $\mathbf{T}$ admits the unique decomposition

$$\mathbf{T} = \mathbf{T}_{\mathrm{sym}} + \mathbf{T}_{\mathrm{skw}},$$

where $\mathbf{T}_{\mathrm{sym}}$ and $\mathbf{T}_{\mathrm{skw}}$, respectively, are <u>symmetric</u> and <u>skew</u> tangential tensor fields called the symmetric and skew parts of

$\mathbf{T}$. In fact,

$$\mathbf{T}_{sym} = \tfrac{1}{2}\mathbf{I}(\mathbf{P}\mathbf{T} + \mathbf{T}^T\mathbf{I}), \qquad \mathbf{T}_{skw} = \tfrac{1}{2}\mathbf{I}(\mathbf{P}\mathbf{T} - \mathbf{T}^T\mathbf{I});$$

i.e., e.g., the symmetric part of $\mathbf{T}$ is the symmetric part of $\mathbf{P}(x)\mathbf{T}(x)\in lin(\mathbf{m}(x)^\perp,\mathbf{m}(x)^\perp)$ postmultiplied by $\mathbf{I}(x)$ to convert to $lin(\mathbf{m}(x)^\perp,\mathbb{R}^3)$.

Each superficial tensor $\mathbf{C}$ admits the unique decomposition

$$\mathbf{C} = \mathbf{C}_{sym} + \mathbf{C}_{skw} + \mathbf{m}\otimes\mathbf{c}, \tag{A8}$$

where $\mathbf{C}_{sym}$ is a <u>symmetric tangential</u> tensor field, $\mathbf{C}_{skw}$ is a <u>skew tangential</u> tensor field, and $\mathbf{c}$ is a <u>tangential vector field</u>. Indeed,

$$\mathbf{c} = \mathbf{C}^T\mathbf{m}, \tag{A9}$$

while $\mathbf{C}_{sym}$ and $\mathbf{C}_{skw}$ are the symmetric and skew parts of the <u>tangential</u> tensor field $\mathbf{C}-\mathbf{m}\otimes\mathbf{C}^T\mathbf{m}$. We will refer to $\mathbf{C}_{sym}$, $\mathbf{C}_{skw}$, and $\mathbf{c}$, respectively, as the **symmetric**, **skew**, and **normal components** of $\mathbf{C}$. If for some scalar field σ,

$$\mathbf{C} = \mathbf{C}_{sym} = \sigma\mathbf{I}, \tag{A10}$$

then $\mathbf{C}$ is a **surface tension** σ.

We write ∇_s for the **surface gradient**.[20] For ϕ a superficial scalar field, $\nabla_s\phi$ is a tangential vector field; for

[20] For $z = z(t)$ a curve on s, $\phi(z)^\circ = \nabla_s\phi(z)\cdot z^\circ$, $v(z)^\circ = [\nabla_s v(z)]z^\circ$; for $\mathbf{v}$ tangential, $\mathbf{P}\nabla_s\mathbf{v}$ is the covariant derivative of $\mathbf{v}$.

$\mathbf{v}$ a superficial vector field, $\nabla_s \mathbf{v}$ is a superficial tensor field. The trace of $\mathbf{P}\nabla_s \mathbf{v}$ is the **surface divergence** of $\mathbf{v}$:

$$\mathrm{div}_s \mathbf{v} = \mathrm{tr}(\mathbf{P}\nabla_s \mathbf{v}).$$

The superficial tensor field

$$\mathbf{L} = -\nabla_s \mathbf{m} \tag{A11}$$

is the **curvature tensor**. A classical result is that

$$\mathbf{L} \text{ is tangential and symmetric.} \tag{A12}$$

We write

$$H = \mathrm{tr}\mathbf{L}$$

for (twice) the **mean curvature**.

Let $\mathbf{C}$ be a superficial tensor field. Then $\mathrm{div}_s \mathbf{C}$ is the unique vector field on s with the property

$$\mathbf{a} \cdot \mathrm{div}_s \mathbf{C} = \mathrm{div}_s(\mathbf{C}^T \mathbf{a}) \tag{A13}$$

for all vectors $\mathbf{a}$.

The surface gradient and surface divergence obey the usual laws for the differentiation of scalar products and inner products (cf. Gurtin and Murdoch [1975], eq. (2.17)). Less standard are the **identities**:

$$\begin{aligned}
&\mathrm{div}_{\varsigma}(\mathbf{C}^{T}\mathbf{v}) = \mathbf{v}\cdot\mathrm{div}_{\varsigma}\mathbf{C} + \mathbf{C}\cdot\nabla_{\varsigma}\mathbf{v},\\
&\mathrm{div}_{\varsigma}\mathbf{C} = \mathrm{div}_{\varsigma}(\mathbf{C}_{\mathrm{sym}} + \mathbf{C}_{\mathrm{skw}}) + (\mathrm{div}_{\varsigma}\mathbf{c})\mathbf{m} - \mathbf{L}\mathbf{c},\\
&\mathbf{m}\cdot\mathrm{div}_{\varsigma}\mathbf{C}_{\mathrm{skw}} = 0,\\
&\mathbf{m}\cdot\mathrm{div}_{\varsigma}\mathbf{C}_{\mathrm{sym}} = \mathbf{C}_{\mathrm{sym}}\cdot\mathbf{L}.
\end{aligned} \tag{A14}$$

Here $\mathbf{v}$ is a superficial vector field, while $\mathbf{C}$ is a superficial tensor field with $\mathbf{C}_{\mathrm{sym}}$, $\mathbf{C}_{\mathrm{skw}}$, and $\mathbf{c}$ the corresponding symmetric, skew, and normal components.

The identities $(A14)_{1,2}$ are easily derived using (A13) and (A8), while $(A14)_{3,4}$ are consequences of $(A14)_1$ with $\mathbf{v}=\mathbf{m}$ in conjunction with (A5), (A7), and (A11).

If c is a sufficiently regular subsurface of ς whose boundary curve ∂c is sufficiently smooth, and $\mathbf{v}$ is a <u>tangential</u> vector field, then the **surface divergence theorem** asserts that

$$\int_{\partial c}\mathbf{v}\cdot\boldsymbol{\nu} = \int_{c}\mathrm{div}_{\varsigma}\mathbf{v}, \tag{A15}$$

where $\boldsymbol{\nu}$, a vector field tangential to ς, is the outward unit normal to ∂c. For $\mathbf{C}$ a superficial tensor field and $\mathbf{a}$ a constant vector, $\mathbf{C}^{T}\mathbf{a}$ is tangential, and (A13) and (A15) yield

$$\int_{\partial c}\mathbf{C}\boldsymbol{\nu} = \int_{c}\mathrm{div}_{\varsigma}\mathbf{C}. \tag{A16}$$

Given vectors $\mathbf{a},\mathbf{b}\in\mathbb{R}^{3}$, we define

$$\mathbf{a}\wedge\mathbf{b} = \mathbf{a}\otimes\mathbf{b} - \mathbf{b}\otimes\mathbf{a}.$$

Further, we write

$$\mathbf{r}(\mathbf{x}) = \mathbf{x} - \mathbf{x}_0$$

for the position vector from a fixed point $\mathbf{x}_0 \in \mathbb{R}^3$. We then have the following identity (cf. Gurtin and Murdoch [1975], p. 305), valid for $\mathbf{C}$ a sufficiently smooth superficial tensor field:

$$\int_{\partial c} \mathbf{r} \wedge \mathbf{C}\boldsymbol{\nu} = \int_{c} (\mathbf{r} \wedge \operatorname{div}_{\varsigma} \mathbf{C} + \mathbf{I}\mathbf{C}^{T} - \mathbf{C}\mathbf{P}),$$

or equivalently, by (A8) and the definitions given in the paragraph containing (A7),

$$\int_{\partial c} \mathbf{r} \wedge \mathbf{C}\boldsymbol{\nu} = \int_{c} \{\mathbf{r} \wedge \operatorname{div}_{\varsigma} \mathbf{C} - \mathbf{m} \wedge \mathbf{c} - 2\mathbf{C}_{\mathrm{skw}}\mathbf{P}\}, \qquad \text{(A17)}$$

with the tangential field $\mathbf{c}$ here viewed as having values in $\mathbb{R}^3$.

B. Smoothly propagating surfaces.

Suppose now that $\varsigma(t)$ is a smoothly propagating surface ([1988g], Appendix D), so that, for each time t, $\varsigma(t)$ divides $\mathbb{R}^3$ into closed regions $B_1(t)$ and $B_2(t)$ with $\mathbb{R}^3$ as their union and $\varsigma(t)$ as their intersection. We orient $\varsigma(t)$ by choosing, as unit normal field $\mathbf{m}(\mathbf{x},t)$, the outward unit normal to $\partial B_1(t)$. We write $V(\mathbf{x},t)$ for the **normal velocity** of $\varsigma(t)$ in the direction $\mathbf{m}(\mathbf{x},t)$.

We use the following notation regarding time derivatives: for $\phi = \phi(t)$, $\phi^{\bullet} = d\phi/dt$; for ϕ a bulk field, $\phi^{\bullet}(\mathbf{x},t) = \partial_t \phi(\mathbf{x},t)$; for ϕ a superficial scalar or vector field, $\phi^{\bullet}$ is the **normal**

time derivative, the time derivative following the interface (cf. [1986g], eqt. (4.4); [1988g], eq. (D5)). Then (cf. [1988g], eq. (D15))

$$\mathbf{m}^{\bullet} = -\nabla_{\zeta} V. \qquad \text{(B1)}$$

Superficial fields and **tangential fields** are as specified in Appendix A, but here they are defined for all $x \in \zeta(t)$ and all t; in the same spirit, **bulk fields** are fields on $\mathbb{R}^3$ for all time. The assertion that a relation or inequality is satisfied "**in bulk**" signifies that it holds "in the interiors of $B_1(t)$ and $B_2(t)$ for all t"; similarly, the quantifier "**on the interface**" is shorthand for "on $\zeta(t)$ for all t".

For $\mathbf{v}$ a bulk vector or tensor field, $\mathrm{div}\mathbf{v}$ is the corresponding divergence. For ϕ a bulk field we write $[\phi]$ for the **jump** in ϕ across the interface (the limit from phase 2 minus that from phase 1).

Let Ω be a (sufficiently regular) closed region of space with outward unit normal $\mathbf{n}$, and let

$$c(t) = \Omega \cap \zeta(t), \qquad \Omega_i(t) = \Omega \cap B_i(t).$$

For g a superficial scalar field,

$$\mathrm{outflow}(g,\Omega) = \int_{\partial c} g V p/(1-p^2)^{1/2}, \qquad p = \mathbf{m} \cdot \mathbf{n}; \qquad \text{(B2)}$$

this integral represents the rate at which g is carried out of Ω across $\partial\Omega$ due to the motion of the interface. We then have the identities:

$$\{\int_{\Omega} g\}^{\circ} = \int_{\Omega_1} g^{\circ} + \int_{\Omega_2} g^{\circ} - \int_{c} [g]V$$
$$\{\int_{c} g\}^{\circ} + \text{outflow}(g,\Omega) = \int_{c} (g^{\bullet} - gHV). \qquad (B3)^{21}$$

The next result, which we state without proof,[22] allows the reduction of global balance laws to differential equations and jump conditions. In the statement of this theorem Ω and c are as specified above, while ν, a vector field tangential to ς, is the outward unit normal to ∂c.

General balance theorem. Let α and β be bulk scalar fields, $\mathbf{u}$ a bulk vector field, $\mathbf{v}$ a tangential vector field, g and b superficial scalar fields, all sufficiently smooth. Then:

(i) the balance law

$$\{\int_{\Omega} \alpha + \int_{c} g\}^{\circ} + \text{outflow}(g,\Omega) = \int_{\partial\Omega} \mathbf{u}\cdot\mathbf{n} + \int_{\Omega} \beta + \int_{\partial c} \mathbf{v}\cdot\nu + \int_{c} b \qquad (B4)$$

holds for all Ω if and only if

$$\alpha^{\circ} = \operatorname{div}\mathbf{u} + \beta \quad \text{in bulk},$$
$$-[\alpha]V + g^{\bullet} - gHV = [\mathbf{u}]\cdot\mathbf{m} + \operatorname{div}_{\varsigma}\mathbf{v} + b \quad \text{on the interface}. \qquad (B5)$$

(ii) (B4) holds with "=" replaced by "≥" if and only if (B5) holds with the same replacement.

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[21] $(B3)_1$ is standard; I am not aware of a rigorous proof of $(B3)_2$ (cf. Scriven [1960], Moeckel [1975]), although a proof is given by Angenant and Gurtin [1988g] for ς a curve in $\mathbb{R}^2$.

[22] Essential ingredients of the proof are the identities (B3); cf. the proof of (6.4) and (6.5) of [1986g] and (2.5) of [1988g].

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