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ORIGINAL ARTICLE

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Thermomechanics of the interface between a body and its environment

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Abstract We formulate integral statements of force balance, energy balance, and entropy imbalance for an interface between a body and its environment. These statements account for interfacial energy, entropy, and stress but neglect the inertia of the interface. Our final results consist of boundary conditions describing thermomechanical interactions between the body and its environment. In their most general forms, these results are partial differential equations that account for dissipation and encompass as special cases Navier's slip law, Newton's law of cooling, and Kirchhoff's law of radiation. When dissipation is neglected, our results reduce to the well-known zero-slip, free-surface, zero-shear, prescribed temperature, and flux-free conditions.

Keywords Interfaces · Boundary conditions · Surface interactions

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1 Introduction

The framework of modern continuum physics is based on three principal ingredients: (i) *balance laws* (for mass, momenta, energy, etc.), (ii) *an imbalance that represents the second law of thermodynamics*, (iii) *constitutive equations*. A careful distinction is maintained between the basic laws expressed within (i) and (ii), which apply broadly, and the relations (iii) that define particular materials.

To date the process of formulating boundary conditions that account for interactions between a body and its surroundings remains largely disjoint from this framework; for example, boundary conditions are often improvised on a problem-by-problem basis using:[1]

(a) Ad hoc methods based on physical considerations
(b) Variational methods based on energy minimization or on principles such as virtual power (work).

Here our goal is a fairly complete theory of body–environment interactions based on statements of the basic laws appropriate to such interactions. Specifically: we confine our attention to an interface separating a body

Dedicated to James K. Knowles: teacher, colleague, friend

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[1] Cf. the discussion of Capriz and Podio-Guidugli [1].

and its environment; we allow for slip at the interface, but ignore the possibility of cavitation; we endow the interface with energy and entropy while allowing also for interfacial surface stress and heat flux. On the other hand, we neglect mass transport within and the inertia of the interface. Our discussion begins from integral statements of force and moment balance, energy balance, and entropy imbalance for the interface formulated for pillboxes which include infinitesimal portions of the body and the environment. Our final results consist of boundary conditions describing thermomechanical interactions between the body and the environment. In their most general forms, these results are partial differential equations that account for dissipation and encompass as special cases Navier's slip law, Newton's law of cooling, and Kirchhoff's law of radiation. When dissipation is neglected, our results reduce to the well-known zero-slip, free-surface, zero-shear, prescribed temperature, and flux-free conditions.[2]

In an addendum, we describe an alternative formulation of the first and second laws of thermodynamics based on the use of interfacial subsurfaces that, in a precise sense, migrate through the interface. That formulation yields the classical identification of surface tension with interfacial free-energy and in addition leads to a new quantity, the latent heat of migration. We find that the latent heat of migration is the negative of the entropic free-energy, a quantity ubiquitous in statistical mechanics.

2 Interfacial kinematics

When discussing the motion of the body it is most convenient to work spatially (that is, using the Eulerian description). Thus consider an evolving body which, at time t occupies a region $\mathcal{B}_t$ of three-dimensional Euclidean space, and let

$$\mathcal{S}_t \overset{\text{def}}{=} \partial\mathcal{B}_t$$

denote the boundary of the deformed body. We view $\mathcal{S}_t$ as an interface separating the body and its environment, and we write $\mathbb{n}$ for the unit normal to $\mathcal{S}_t$ directed outward from the body.

Our formulation of the basic laws for the interface $\mathcal{S}_t$ is based on the use of subsurfaces $\mathcal{A}_t$ of $\mathcal{S}_t$ that *convect with the body*.[3] The normal velocity V of $\mathcal{S}_t$ and hence $\mathcal{A}_t$ coincides with the scalar normal velocity $\mathbf{v}\cdot\mathbb{n}$ of material points,

$$V = \mathbf{v}\cdot\mathbb{n}, \tag{2.1}$$

and—letting $V_{\partial\mathcal{A}}$ denote the scalar normal velocity of the boundary *curve* $\partial\mathcal{A}_t$ in the direction of its outward unit normal[4] $\mathbb{m}$—$V_{\partial\mathcal{A}}$ must coincide with the component of the velocity $\mathbf{v}$ in the direction $\mathbb{m}$; viz.

$$V_{\partial\mathcal{A}} = \mathbf{v}\cdot\mathbb{m}. \tag{2.2}$$

We write $\mathbb{P}$ for the projection onto $\mathcal{S}_t$ defined by

$$\mathbb{P} = \mathbf{1} - \mathbb{n}\otimes\mathbb{n}; \tag{2.3}$$

$\mathbb{P}$ associates with every vector field $\mathbf{g}$ its component $\mathbf{g}_{\tan}$ tangential to $\mathcal{S}_t$:

$$\mathbf{g}_{\tan} = \mathbb{P}\mathbf{g} = \mathbf{g} - (\mathbf{g}\cdot\mathbb{n})\mathbb{n}.$$

Note that, for $\mathbf{g}$ and $\mathbf{h}$ vector fields,

$$\left.\begin{aligned} \mathbf{g} &= \mathbf{g}_{\tan} + (\mathbb{n}\cdot\mathbf{g})\mathbb{n},\\ \mathbf{g}_{\tan}\cdot\mathbf{h} &= \mathbf{g}_{\tan}\cdot\mathbf{h}_{\tan},\\ \mathbf{g}\cdot\mathbf{h} &= \mathbf{g}_{\tan}\cdot\mathbf{h}_{\tan} + (\mathbf{g}\cdot\mathbb{n})(\mathbf{h}\cdot\mathbb{n}). \end{aligned}\right\} \tag{2.4}$$

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[2] The zero-slip and prescribed temperature conditions at a solid–fluid interface were obtained previously by Kleinstein [2] using jump conditions arising from the basic laws.

[3] Such subsurfaces $\mathcal{A}_t$ are, therefore, spatial descriptions of *material surfaces* in the sense that, if $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ denotes the motion of the body, then there is a fixed material surface S such that $\mathcal{S}_t = \boldsymbol{\chi}(S, t)$. Consistent with this, given a spatial field $f(\mathbf{x}, t)$, $\dot{f}$ denotes its material time-derivative; that is, the derivative of $f(\boldsymbol{\chi}(\mathbf{X}, t), t)$ with respect to t holding $\mathbf{X}$ fixed.

[4] Note that $\mathbb{m}$ is tangent to the subsurface $\mathcal{A}_t$, but normal to its boundary curve $\partial\mathcal{A}_t$.

We write $\mathbf{v}_{\mathrm{env}}$ for the environmental velocity, which is the velocity of the environmental material at the interface. We allow for slip at the interface between the environment and the body and hence do not require that the tangential environmental velocity, $\mathbb{P}\mathbf{v}_{\mathrm{env}}$, coincide with the tangential material velocity $\mathbf{v}_{\mathrm{tan}}$. On the other hand, we rule out cavitation at the interface. Writing $\mathbf{v}$ for the velocity of the body at the interface, the normal velocity $V = \mathbf{v} \cdot \mathbb{m}$ of the body at the interface must then coincide with the normal environmental velocity $\mathbf{v}_{\mathrm{env}} \cdot \mathbb{m}$:

$$\mathbf{v}_{\mathrm{env}} \cdot \mathbb{m} = \mathbf{v} \cdot \mathbb{m} = V. \tag{2.5}$$

When convenient, we fix the time t and write $\mathcal{S}$ for $\mathcal{S}_t$ and $\mathcal{B}$ for $\mathcal{B}_t$.

3 Superficial fields, surface gradient, surface divergence

Fields such as $\mathbb{m}$ that are defined for points on $\mathcal{S}_t$—but *not* for points away from $\mathcal{S}_t$—are referred to as *superficial*. If f is a superficial field, then its conventional spatial gradient is not well-defined, since f is not defined on a three-dimensional neighborhood of $\mathcal{S}_t$. However there are many ways to extend a superficial field smoothly to a three-dimensional neighborhood of any point on $\mathcal{S}_t$. An example is the *normally constant extension* in which a superficial field is extended to be constant on normal lines, where a normal line at time t is a line through a point $\mathbf{x}$ on $\mathcal{S}_t$ parallel to $\mathbb{m}(\mathbf{x}, t)$ [3]. Moreover, given a scalar-valued superficial field f, its surface gradient $\mathrm{grad}_{\mathcal{S}} f$ is defined uniquely in terms of any smooth extension f^{e} via

$$\mathrm{grad}_{\mathcal{S}} f = \mathbb{P}\mathrm{grad}\, f^{\mathrm{e}}. \tag{3.1}$$

Then, because $\mathbb{P}$ is symmetric and $\mathbb{P}\mathbb{m} = \mathbf{0}$,

$$\mathbb{m} \cdot \mathrm{grad}_{\mathcal{S}} f = \mathbb{m} \cdot \mathbb{P}\mathrm{grad}\, f^{\mathrm{e}} = (\mathbb{P}\mathbb{m}) \cdot \mathrm{grad}\, f^{\mathrm{e}} = 0$$

and $\mathrm{grad}_{\mathcal{S}} f$ *is tangent to the interface*. Similarly, the surface gradient $\mathrm{grad}_{\mathcal{S}}\mathbb{g}$ and surface divergence $\mathrm{div}_{\mathcal{S}}\mathbb{g}$ of a vector-valued superficial field $\mathbb{g}$ are defined by

$$\mathrm{grad}_{\mathcal{S}}\mathbb{g} = (\mathrm{grad}\,\mathbb{g}^{\mathrm{e}})\mathbb{P} \qquad \text{and} \qquad \mathrm{div}_{\mathcal{S}}\mathbb{g} = \mathrm{tr}\,(\mathrm{grad}_{\mathcal{S}}\mathbb{g}) = \mathbb{P} : \mathrm{grad}\,\mathbb{g}^{\mathrm{e}}, \tag{3.2}$$

where, again, the particular features of the extension $\mathbb{g}^{\mathrm{e}}$ of $\mathbb{g}$ are irrelevant.

A useful identity, for f and $\mathbb{g}$ scalar- and vector-valued superficial fields, is the product rule

$$\mathrm{div}_{\mathcal{S}}(f\mathbb{g}) = f\,\mathrm{div}_{\mathcal{S}}\mathbb{g} + \mathbb{g}_{\mathrm{tan}} \cdot \mathrm{grad}_{\mathcal{S}} f, \tag{3.3}$$

For a superficial tensor field $\mathbb{B}$ we require that[5]

$$\mathbb{B}\mathbb{m} = \mathbf{0}; \tag{3.4}$$

if, in addition, $\mathbb{B}^{\top}\mathbb{m} = \mathbf{0}$, then we say that $\mathbb{B}$ is *fully tangential*, so that $\mathbb{B}$ maps tangent vectors to tangent vectors. An example of a fully tangential tensor field is the projection $\mathbb{P}$.

The surface divergence of a superficial tensor field $\mathbb{B}$ is defined by

$$\mathbf{a} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{B} = \mathrm{div}_{\mathcal{S}}(\mathbb{B}^{\top}\mathbf{a}) \tag{3.5}$$

for $\mathbf{a}$ any constant vector.

Each superficial tensor field $\mathbb{B}$ admits a decomposition of the form

$$\mathbb{B} = \mathbb{B}_{\mathrm{tan}} + \mathbb{m} \otimes \mathbb{b}, \tag{3.6}$$

in which $\mathbb{B}_{\mathrm{tan}} = \mathbb{P}\mathbb{B}$ *is fully tangential* and $\mathbb{b} = \mathbb{B}^{\top}\mathbb{m}$ *is tangential*. (The verification of this decomposition is straightforward: simply expand $\mathbb{P}\mathbb{B}$ using (2.3).)

The *curvature tensor* $\mathbb{K}$ defined by

$$\mathbb{K} = -\mathrm{grad}_{\mathcal{S}}\mathbb{m} \tag{3.7}$$

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[5] A superficial tensor field would generally be defined at each $\mathbf{x} \in \mathcal{S}$ as a linear transformation of the tangent space at $\mathbf{x}$ into $\mathbb{R}^3$; the requirement (3.4) allows us to consider $\mathbb{B}$ at each point as a linear transformation of $\mathbb{R}^3$ into $\mathbb{R}^3$.

is fully tangential and symmetric, and

$$K = \operatorname{tr}\mathbb{K} = \mathbb{P} : \mathbb{K} = -\operatorname{div}_{\mathcal{S}}\mathbb{n} \tag{3.8}$$

is the *total* (twice the mean) *curvature*. Then, by (2.3), we have the identity

$$\operatorname{div}_{\mathcal{S}}\mathbb{P} = K\mathbb{n}. \tag{3.9}$$

Further, the product rule (3.3) yields the useful identities

$$\operatorname{grad}_{\mathcal{S}}(V\mathbb{n}) = \mathbb{n} \otimes \operatorname{grad}_{\mathcal{S}} V - V\mathbb{K} \qquad \text{and} \qquad \operatorname{div}_{\mathcal{S}}(V\mathbb{n}) = -KV \tag{3.10}$$

involving the interfacial normal, normal velocity, and curvature. Also important is the following consequence of $(2.4)_1$:

$$\operatorname{div}_{\mathcal{S}}\mathbf{v} = \operatorname{div}_{\mathcal{S}}\mathbf{v}_{\text{tan}} - KV \tag{3.11}$$

Let $\mathbb{B}$ be a fully tangential tensor field. Then

$$\mathbb{n} \cdot \operatorname{div}_{\mathcal{S}}\mathbb{B} = \operatorname{div}_{\mathcal{S}}(\underbrace{\mathbb{B}^{\top}\mathbb{n}}_{=\mathbf{0}}) - \mathbb{B} : \operatorname{grad}_{\mathcal{S}}\mathbb{n},$$

and (3.7) yields the important identity

$$\mathbb{n} \cdot \operatorname{div}_{\mathcal{S}}\mathbb{B} = \mathbb{B} : \mathbb{K} \qquad \text{for } \mathbb{B} \text{ fully tangential.} \tag{3.12}$$

By (3.6), the superficial velocity gradient $\operatorname{grad}_{\mathcal{S}}\mathbf{v}$ has both tangential and normal parts:

$$\mathbb{P}\operatorname{grad}_{\mathcal{S}}\mathbf{v} = (\operatorname{grad}_{\mathcal{S}}\mathbf{v})_{\text{tan}} \qquad \text{and} \qquad \mathbf{n} \otimes [(\operatorname{grad}_{\mathcal{S}}\mathbf{v})^{\top}\mathbf{n}],$$

and the symmetric part of $\mathbb{P}\operatorname{grad}_{\mathcal{S}}\mathbf{v}$ represents the *superficial rate of stretch* $\mathbb{D}$:

$$\mathbb{D} = \tfrac{1}{2}(\mathbb{P}\operatorname{grad}_{\mathcal{S}}\mathbf{v} + (\operatorname{grad}_{\mathcal{S}}\mathbf{v})^{\top}\mathbb{P}). \tag{3.13}$$

Since $\mathbf{v}$ is the restriction to the interface of the bulk velocity $\mathbf{v}$, $(3.2)_1$ yields $\operatorname{grad}_{\mathcal{S}}\mathbf{v} = (\operatorname{grad}\mathbf{v})\mathbb{P}$. It, therefore, follows that $\mathbb{D}$ admits the simple alternative representation

$$\mathbb{D} = \mathbb{P}\mathbf{D}\mathbb{P}, \tag{3.14}$$

where $\mathbf{D} = \frac{1}{2}(\operatorname{grad}\mathbf{v} + (\operatorname{grad}\mathbf{v})^{\top})$ is the rate of stretch in the body.

Finally, for $\mathbb{B}$ a tangential and symmetric superficial tensor field,

$$\mathbb{B} : \operatorname{grad}_{\mathcal{S}}\mathbf{v} = \mathbb{B} : \mathbb{D}. \tag{3.15}$$

4 Integral identities

4.1 Interfacial Reynolds relation

Basic to what follows is the *Reynolds–Slattery transport relation for a surface $\mathcal{A}_t$ that convects with the body* [4,5]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{A}_t} f\,\mathrm{d}a = \int_{\mathcal{A}_t} (\dot{f} + f\operatorname{div}_{\mathcal{S}}\mathbf{v}_{\text{tan}} - fKV)\,\mathrm{d}a. \tag{4.1}$$

Here, as mentioned in Footnote 3, $\dot{f}$ is the material time-derivative of f.

Since $\mathbb{D}$ is symmetric (3.11) and (3.15) imply that

$$\begin{aligned} \mathbb{P} : \mathbb{D} &= \mathbb{P} : (\mathbb{P}\operatorname{grad}_{\mathcal{S}}\mathbf{v}) \\ &= \operatorname{div}_{\mathcal{S}}\mathbf{v} && (4.2) \\ &= \operatorname{div}_{\mathcal{S}}\mathbf{v}_{\text{tan}} - KV, && (4.3) \end{aligned}$$

which allows us to rewrite (4.1) in the more concise form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{A}_t} f\,\mathrm{d}a = \int_{\mathcal{A}_t} (\dot{f} + f\,\mathbb{P} : \mathbb{D})\,\mathrm{d}a. \tag{4.4}$$

(By (4.2), the term $f\,\mathbb{P} : \mathbb{D}$ in (4.4) can be replaced by $f\operatorname{div}_{\mathcal{S}}\mathbf{v}$.)

4.2 Surface divergence-theorem

The *surface divergence theorem* for scalar fields f and *tangential* vector fields $\mathbb{g}$ asserts that, at any fixed time and any subsurface $\mathcal{A}$ of the deformed boundary with outward unit normal $\mathbb{m}$ [6,7],

$$\left.\begin{aligned}\int\limits_{\partial\mathcal{A}} f\,\mathbb{m}\,\mathrm{d}s &= \int\limits_{\mathcal{A}} (\mathrm{grad}_{\mathcal{S}} f + f K\,\mathbb{n})\,\mathrm{d}a,\\ \int\limits_{\partial\mathcal{A}} \mathbb{g}\cdot\mathbb{m}\,\mathrm{d}s &= \int\limits_{\mathcal{A}} \mathrm{div}_{\mathcal{S}}\mathbb{g}\,\mathrm{d}a.\end{aligned}\right\} \tag{4.5}$$

Let $\mathbb{B}$ be a superficial tensor field, and let $\mathbb{h}$ be a superficial vector field. Then the *surface divergence theorem* asserts that for any subsurface $\mathcal{A}$ of $\mathcal{S}$

$$\left.\begin{aligned}\int\limits_{\partial\mathcal{A}} \mathbb{B}\mathbb{m}\,\mathrm{d}s &= \int\limits_{\mathcal{A}} \mathrm{div}_{\mathcal{S}}\mathbb{B}\,\mathrm{d}a,\\ \int\limits_{\partial\mathcal{A}} \mathbb{B}\mathbb{m}\cdot\mathbb{h}\,\mathrm{d}s &= \int\limits_{\mathcal{A}} (\mathbb{h}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{B} + \mathbb{B}\colon\mathrm{grad}_{\mathcal{S}}\mathbb{h})\,\mathrm{d}a.\end{aligned}\right\} \tag{4.6}$$

These forms of the surface divergence theorem are based on (4.5): to derive the relations in (4.6), we simply let $\mathbf{a}$ be an *arbitrary constant vector* and work with left sides

$$\int\limits_{\partial\mathcal{A}} (\mathbb{B}^{\top}\mathbf{a})\cdot\mathbb{m}\,\mathrm{d}s \qquad \text{and} \qquad \int\limits_{\partial\mathcal{A}} (\mathbb{B}^{\top}\mathbb{h})\cdot\mathbb{m}\,\mathrm{d}s,$$

using $(4.5)_2$.

5 Boundary pillboxes

Consider once again the *convecting subsurface* $\mathcal{A}_t$ of the deformed boundary $\mathcal{S}_t = \partial\mathcal{B}_t$ discussed in Sect. 4.1. We now view $\mathcal{A}_t$ as a *boundary pillbox* of infinitesimal thickness containing a portion of the boundary. The primary advantage of this view is that it allows us to isolate the physical processes in the material on the two sides of the boundary. Suppressing the argument t, the geometric boundary of $\mathcal{A}$ consists of its boundary curve $\partial\mathcal{A}$. But $\mathcal{A}$ viewed as pillbox has a pillbox boundary consisting of (Fig. 1):

- A surface $\mathcal{A}$ with unit normal $\mathbb{n}$; $\mathcal{A}$ is viewed as lying in the *environment*.
- A surface $-\mathcal{A}$ with unit normal $-\mathbb{n}$; $-\mathcal{A}$ is viewed as lying in the body adjacent to the boundary.
- A "lateral surface" represented by $\partial\mathcal{A}$ with outward unit normal $\mathbb{m}$ tangent to $\mathcal{S}$.

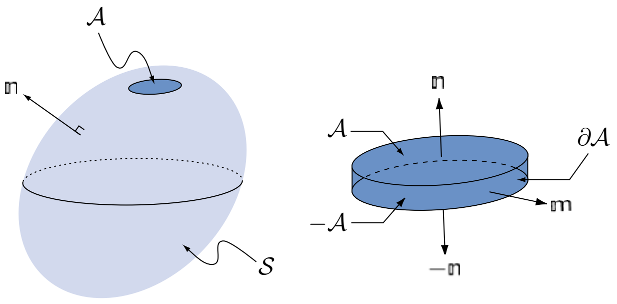

Fig. 1 Pillbox corresponding to a subsurface $\mathcal{A}$ of the boundary $\mathcal{S} = \partial\mathcal{B}$ of the region $\mathcal{B}$ of space occupied by the (deformed) body at some arbitrarily chosen time. Whereas $\mathbb{n}$ is oriented into the environment, $-\mathbb{n}$ is oriented into the body. The outward unit normal on the lateral face $\partial\mathcal{A}$ of the pillbox is denoted by $\mathbb{m}$

6 Force and moment balances for the interface

We write the following:

- $\mathbf{T}$ for the (Cauchy) stress in the body at the interface
- $\mathbf{t}_{\mathrm{env}}$ for the environmental traction exerted by the environment on the body
- $\mathbb{T}$, a superficial tensor field, for the stress within the interface

Consider a boundary pillbox $\mathcal{A} = \mathcal{A}_t$ at some fixed time t. Then $\mathbf{t}_{\mathrm{env}}$ represents the traction exerted on the pillbox surface $\mathcal{A}$, while $\mathbf{T}(-\mathbb{n}) = -\mathbf{T}\mathbb{n}$ is the traction exerted by the body on pillbox surface $-\mathcal{A}$. The force exerted on $\mathcal{A}$ by the environment and by the body is given by

$$\int\limits_{\mathcal{A}} (\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n})\,\mathrm{d}a.$$

Further, $\mathbb{T}\mathbb{m}$ represents a traction, measured per unit length, that acts along the boundary curve $\partial\mathcal{A}$. The surface stress on the portion of the interface lying within the pillbox is thus given by

$$\int\limits_{\partial\mathcal{A}} \mathbb{T}\mathbb{m}\,\mathrm{d}s \tag{6.1}$$

We neglect inertia of the interface. Balance of forces for the pillbox $\mathcal{A}$ therefore requires that

$$\int\limits_{\mathcal{A}} (\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}} \mathbb{T}\mathbb{m}\,\mathrm{d}s = \mathbf{0}. \tag{6.2}$$

Similarly, if we let

$$\mathbf{r}(\mathbf{x}) = \mathbf{x} - \mathbf{0},$$

then balance of moments for $\mathcal{A}$ requires that

$$\int\limits_{\mathcal{A}} \mathbf{r} \times (\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}} \mathbf{r} \times \mathbb{T}\mathbb{m}\,\mathrm{d}s = \mathbf{0}. \tag{6.3}$$

If we apply the surface divergence theorem $(4.6)_1$ to the term in (6.2) involving the surface stress $\mathbb{T}$, we find that

$$\int\limits_{\mathcal{A}} (\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n} + \mathrm{div}_{\mathcal{S}}\mathbb{T})\,\mathrm{d}a = \mathbf{0},$$

and, since the subsurface $\mathcal{A}$ of $\mathcal{S}$ is arbitrary, we arrive at the local force balance for the interface

$$\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n} + \mathrm{div}_{\mathcal{S}}\mathbb{T} = \mathbf{0}. \tag{6.4}$$

Consider next balance of moments (6.3). Let $\mathbf{a}$ an *arbitrary constant vector*, let $\mathbf{a}\times$ denote the tensor defined by $(\mathbf{a}\times)\mathbf{b} = \mathbf{a} \times \mathbf{b}$ for every vector $\mathbf{b}$, and note that, since $\mathrm{grad}_{\mathcal{S}}\mathbf{r} = \mathbb{P}$,

$$\mathrm{grad}_{\mathcal{S}}(\mathbf{a} \times \mathbf{r}) = (\mathbf{a}\times)(\mathrm{grad}_{\mathcal{S}}\mathbf{r})\mathbb{P} = (\mathbf{a}\times)\mathbb{P}.$$

Then, by $(4.5)_2$ and (6.4),

$$\begin{aligned}
\mathbf{a} \cdot \int\limits_{\partial\mathcal{A}} \mathbf{r} \times \mathbb{T}\mathbb{m}\,\mathrm{d}s &= \int\limits_{\partial\mathcal{A}} (\mathbf{a} \times \mathbf{r}) \cdot \mathbb{T}\mathbb{m}\,\mathrm{d}s \\
&= \int\limits_{\mathcal{A}} [\mathrm{div}_{\mathcal{S}}\mathbb{T} \cdot (\mathbf{a} \times \mathbf{r}) + \mathbb{T} : \mathrm{grad}_{\mathcal{S}}(\mathbf{a} \times \mathbf{r})]\,\mathrm{d}a \\
&= \int\limits_{\mathcal{A}} [\mathbf{a} \cdot (\mathbf{r} \times \mathrm{div}_{\mathcal{S}}\mathbb{T}) + \mathbb{T} : ((\mathbf{a}\times)\mathbb{P})]\,\mathrm{d}a \\
&= -\mathbf{a} \cdot \int\limits_{\mathcal{A}} \mathbf{r} \times (\mathbf{t}_{\mathrm{env}} - \mathbf{T}\mathbb{n})\,\mathrm{d}a + \int\limits_{\mathcal{A}} \mathbb{T} : [(\mathbf{a}\times)\mathbb{P}]\,\mathrm{d}a.
\end{aligned} \tag{6.5}$$

Next, since $\mathbb{T}$ is a superficial tensor, $\mathbb{T} = \mathbb{T}\mathbb{P}$ and hence

$$\mathbb{T} : [(\mathbf{a}\times)\mathbb{P}] = (\mathbb{T}\mathbb{P}) : (\mathbf{a}\times) = \mathbb{T} : (\mathbf{a}\times)$$

so that, by (6.3) and (6.5),

$$\int\limits_{\mathcal{A}} \mathbb{T} : (\mathbf{a}\times)\,\mathrm{d}a = 0.$$

Therefore, since $\mathcal{A}$ is arbitrary, $\mathbb{T} : (\mathbf{a}\times) = 0$ for every $\mathbf{a}$. But any skew tensor may be written in the form $\mathbf{a}\times$; thus $\mathbb{T}$ is symmetric:

$$\mathbb{T} = \mathbb{T}^{\top}. \tag{6.6}$$

It is convenient to define the body shear $\boldsymbol{\tau}$ and the environmental shear $\boldsymbol{\tau}_{\mathrm{env}}$ through

$$\left.\begin{aligned} \boldsymbol{\tau} &= (\mathbf{T}\mathbb{n})_{\mathrm{tan}}, \\ \boldsymbol{\tau}_{\mathrm{env}} &= (\mathbf{t}_{\mathrm{env}})_{\mathrm{tan}}, \end{aligned}\right\} \tag{6.7}$$

for then we may use $(2.4)_1$, (3.12), and (3.9) to decompose the local force balance into tangential and normal components

$$\left.\begin{aligned} \boldsymbol{\tau} - \boldsymbol{\tau}_{\mathrm{env}} &= \mathbb{P}\,\mathrm{div}_{\mathcal{S}}\mathbb{T} = \mathrm{div}_{\mathcal{S}}\mathbb{T} + (\mathbb{T} : \mathbb{K})\mathbb{n}, \\ \mathbb{n}\cdot\mathbf{T}\mathbb{n} - \mathbb{n}\cdot\mathbf{t}_{\mathrm{env}} &= \mathbb{n}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{T} = \mathbb{T} : \mathbb{K}. \end{aligned}\right\} \tag{6.8}$$

7 Standard forms of the first two laws for the interface

Throughout this section $\mathcal{A}_t$ is an arbitrary boundary pillbox, as discussed in Sect. 5, so that

$$\mathcal{A}_t \subset \mathcal{S}_t = \partial\mathcal{B}_t$$

and $\mathcal{A}_t$ convects with the body.

7.1 Global forms of the energy balance and entropy imbalance for a pillbox that convects with the body

We write:

- ε and η for the internal energy and entropy of the interface, measured per unit area
- ϑ for the absolute temperature of the body at the interface
- ϑ_{env} for the absolute environmental temperature at the interface (generally $\vartheta \neq \vartheta_{\mathrm{env}}$)
- $\mathbf{q}$ for the conventional heat flux in the body at the interface
- q_{env} for the heat flow into the body from the environment
- $\mathbb{q}$, a tangential vector field, for the heat flux within the interface

Then

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}_t} \varepsilon\,\mathrm{d}a \qquad \text{and} \qquad \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}_t} \eta\,\mathrm{d}a \tag{7.1}$$

represent temporal changes in the net internal energy and the net entropy of the pillbox. Further, there are flows $\mathbf{q}\cdot\mathbb{n}$ and $\mathbf{q}\cdot\mathbb{n}/\vartheta$ of heat and entropy into the pillbox from the body across the surface $-\mathcal{A}_t$, flows q_{env} and $q_{\mathrm{env}}/\vartheta_{\mathrm{env}}$ into the pillbox from the environment across the surface $\mathcal{A}_t$, and flows $-\mathbb{q}\cdot\mathbb{m}$ and $-\mathbb{q}\cdot\mathbb{m}/\vartheta$ into the pillbox from the remainder of the interface. The net flows of heat and entropy into the pillbox $\mathcal{A}_t$, therefore, have the forms

$$\int\limits_{\mathcal{A}_t} (q_{\mathrm{env}} + \mathbf{q}\cdot\mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}_t} \mathbb{q}\cdot\mathbb{m}\,\mathrm{d}s \qquad \text{and} \qquad \int\limits_{\mathcal{A}_t} \left(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q}\cdot\mathbb{n}}{\vartheta}\right)\mathrm{d}a - \int\limits_{\partial\mathcal{A}_t} \frac{\mathbb{q}\cdot\mathbb{m}}{\vartheta}\,\mathrm{d}s. \tag{7.2}$$

Our next step is to determine the power expended on the pillbox by the environment and the body. We write

- $\mathbf{v}_{\mathrm{env}}$ for the environmental velocity, which is the velocity of the environmental material at the interface.

Then consistent with the discussion given in the paragraph containing (6.2), we assume that: (i) the power expended on the pillbox by the environment and by the body is given by

$$\int\limits_{\mathcal{A}_t} (\mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v})\,\mathrm{d}a; \tag{7.3}$$

(ii) that the traction $\mathbb{T}\mathbb{m}$ acting on the pillbox $\mathcal{A}_t$ along $\partial\mathcal{A}_t$ expends power in concert with the tangential velocity $\mathbf{v}_{\mathrm{tan}}$,[6] so that

$$\int\limits_{\partial\mathcal{A}_t} \mathbb{T}\mathbb{m} \cdot \mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s \tag{7.4}$$

represents the power expended by the standard surface stress on the portion of the interface lying within the pillbox.

In view of the foregoing developments, the energy balance and entropy imbalance for the pillbox $\mathcal{A}_t$ read

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}_t} \varepsilon\,\mathrm{d}a = \int\limits_{\mathcal{A}_t} (q_{\mathrm{env}} + \mathbf{q} \cdot \mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}_t} \mathbb{q} \cdot \mathbb{m}\,\mathrm{d}s + \int\limits_{\mathcal{A}_t} (\mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}_t} \mathbb{T}\mathbb{m} \cdot \mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s \tag{7.5}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}_t} \eta\,\mathrm{d}a \geq \int\limits_{\mathcal{A}_t} \Big(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q} \cdot \mathbb{n}}{\vartheta}\Big)\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}_t} \frac{\mathbb{q} \cdot \mathbb{m}}{\vartheta}\,\mathrm{d}s, \tag{7.6}$$

respectively.

7.2 Local forms of the energy balance and entropy imbalance. Local free-energy imbalance

Applying the surface divergence theorem in the form $(4.6)_2$ to the right-most term in the energy balance (7.5) yields, since $\mathbb{T}$ is tangential and, by (6.6), symmetric,

$$\int\limits_{\partial\mathcal{A}_t} \mathbb{T}\mathbb{m} \cdot \mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s = \int\limits_{\partial\mathcal{A}_t} \mathbb{T}\mathbb{m} \cdot \mathbf{v}\,\mathrm{d}s = \int\limits_{\mathcal{A}_t} \mathrm{div}_{\mathcal{S}}(\mathbb{T}\mathbf{v})\,\mathrm{d}s = \int\limits_{\mathcal{A}_t} (\mathbf{v} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{T} + \underbrace{\mathbb{T} : \mathrm{grad}_{\mathcal{S}}\mathbf{v}}_{\mathbb{T}:\mathbb{D}})\,\mathrm{d}s. \tag{7.7}$$

Thus, applying the Reynolds–Slattery transport relation in the form (4.4) with $f = \varepsilon$ to the energy balance (7.5), we find that

$$\int\limits_{\mathcal{A}_t} (\dot{\varepsilon} + \varepsilon\,\mathbb{P} : \mathbb{D})\,\mathrm{d}a = \int\limits_{\mathcal{A}_t} (q_{\mathrm{env}} + \mathbf{q} \cdot \mathbb{n} - \mathrm{div}_{\mathcal{S}}\mathbb{q} + \mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v} + \mathbb{T} : \mathbb{D} + \mathbf{v} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{T})\,\mathrm{d}a. \tag{7.8}$$

Similarly, applying (4.4) with $f = \eta$ to the entropy imbalance (7.6), we find that

$$\int\limits_{\mathcal{A}_t} (\dot{\eta} + \eta\,\mathbb{P} : \mathbb{D})\,\mathrm{d}a \geq \int\limits_{\mathcal{A}_t} \Big[\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q} \cdot \mathbb{n}}{\vartheta} - \mathrm{div}_{\mathcal{S}}\Big(\frac{\mathbb{q}}{\vartheta}\Big)\Big]\,\mathrm{d}a. \tag{7.9}$$

Since $\mathcal{A}_t$ is arbitrary, (7.8) and (7.9) yield the local energy balance

$$\dot{\varepsilon} + \varepsilon\,\mathbb{P} : \mathbb{D} = q_{\mathrm{env}} + \mathbf{q} \cdot \mathbb{n} - \mathrm{div}_{\mathcal{S}}\mathbb{q} + \mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v} + \mathbb{T} : \mathbb{D} + \mathbf{v} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{T} \tag{7.10}$$

and the local entropy imbalance

$$\dot{\eta} + \eta\,\mathbb{P} : \mathbb{D} \geq \frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q} \cdot \mathbb{n}}{\vartheta} - \mathrm{div}_{\mathcal{S}}\Big(\frac{\mathbb{q}}{\vartheta}\Big). \tag{7.11}$$

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[6] Bear in mind that, because $\mathbb{T}$ is a tangential tensor field, $\mathbb{T}\mathbb{m}$ is a tangential vector field.

The energy balance (7.10) can be further simplified. In view of $(2.4)_3$, (2.5), (3.12), and (6.8),

$$\begin{aligned}\mathbf{t}_{\mathrm{env}}\cdot\mathbf{v}_{\mathrm{env}}-\mathbf{T}\mathbb{m}\cdot\mathbf{v}&=(\mathbf{t}_{\mathrm{env}})_{\mathrm{tan}}\cdot(\mathbf{v}_{\mathrm{env}})_{\mathrm{tan}}-(\mathbf{T}\mathbb{m})_{\mathrm{tan}}\cdot\mathbf{v}_{\mathrm{tan}}+(\mathbb{m}\cdot\mathbf{t}_{\mathrm{env}}-\mathbb{m}\cdot\mathbf{T}\mathbb{m})V\\&=\boldsymbol{\tau}_{\mathrm{env}}\cdot[(\mathbf{v}_{\mathrm{env}})_{\mathrm{tan}}-\mathbf{v}_{\mathrm{tan}}]-\mathbf{v}_{\mathrm{tan}}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{T}-V\mathbb{m}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{T},\\&=\boldsymbol{\tau}_{\mathrm{env}}\cdot[(\mathbf{v}_{\mathrm{env}})_{\mathrm{tan}}-\mathbf{v}_{\mathrm{tan}}]-\mathbf{v}\cdot\mathrm{div}_{\mathcal{S}}\mathbb{T},\end{aligned}\tag{7.12}$$

and, using this identity, (7.10) takes the form

$$\dot{\varepsilon}+\varepsilon\,\mathbb{P}\colon\mathbb{D}=q_{\mathrm{env}}+\mathbf{q}\cdot\mathbb{m}-\mathrm{div}_{\mathcal{S}}\mathbb{q}+\boldsymbol{\tau}_{\mathrm{env}}\cdot[(\mathbf{v}_{\mathrm{env}})_{\mathrm{tan}}-\mathbf{v}_{\mathrm{tan}}]+\mathbb{T}\colon\mathbb{D}.\tag{7.13}$$

Finally, subtracting ϑ times (7.11) from (7.13) while making use of the identity

$$\mathrm{div}_{\mathcal{S}}\Big(\frac{\mathbb{q}}{\vartheta}\Big)=\frac{1}{\vartheta}\mathrm{div}_{\mathcal{S}}\mathbb{q}-\frac{1}{\vartheta^2}\mathbb{q}\cdot\mathrm{grad}_{\mathcal{S}}\vartheta,\tag{7.14}$$

we arrive at the *free-energy imbalance*

$$\dot{\psi}+\eta\dot{\vartheta}\le\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}}(\vartheta_{\mathrm{env}}-\vartheta)-\frac{1}{\vartheta}\mathbb{q}\cdot\mathrm{grad}_{\mathcal{S}}\vartheta+\boldsymbol{\tau}_{\mathrm{env}}\cdot(\mathbf{v}_{\mathrm{env}}-\mathbf{v})_{\mathrm{tan}}+(\mathbb{T}-\psi\mathbb{P})\colon\mathbb{D},\tag{7.15}$$

where

$$\psi=\varepsilon-\vartheta\eta\tag{7.16}$$

denotes the free energy of the interface.

7.3 Summary of basic equations

The general relations at the boundary interface consist of the balances

$$\left.\begin{aligned}&\mathbf{t}_{\mathrm{env}}-\mathbf{T}\mathbb{m}=-\mathrm{div}_{\mathcal{S}}\mathbb{T},\\&\dot{\varepsilon}+\varepsilon\,\mathbb{P}\colon\mathbb{D}=q_{\mathrm{env}}+\mathbf{q}\cdot\mathbb{m}-\mathrm{div}_{\mathcal{S}}\mathbb{q}+\boldsymbol{\tau}_{\mathrm{env}}\cdot(\mathbf{v}_{\mathrm{env}}-\mathbf{v})_{\mathrm{tan}}+\mathbb{T}\colon\mathbb{D}.\end{aligned}\right\}\tag{7.17}$$

for force and energy, with $\mathbb{T}$ tangential and symmetric, and the free-energy imbalance

$$\dot{\psi}+\eta\dot{\vartheta}\le\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}}(\vartheta_{\mathrm{env}}-\vartheta)-\frac{1}{\vartheta}\mathbb{q}\cdot\mathrm{grad}_{\mathcal{S}}\vartheta+\boldsymbol{\tau}_{\mathrm{env}}\cdot(\mathbf{v}_{\mathrm{env}}-\mathbf{v})_{\mathrm{tan}}+(\mathbb{T}-\psi\mathbb{P})\colon\mathbb{D}.\tag{7.18}$$

These relations are supplemented by the thermodynamic identity

$$\psi=\varepsilon-\vartheta\eta\tag{7.19}$$

and the condition

$$\mathbf{v}\cdot\mathbb{m}=\mathbf{v}_{\mathrm{env}}\cdot\mathbb{m}=V\tag{7.20}$$

ruling out cavitation.

8 Constitutive equations for the interface

In applications the balances (7.17) are generally augmented by constitutive equations characterizing the interaction of the body and the environment. These constitutive equations must be consistent with the free-energy imbalance (7.18).

Interfacial elasticity, while important, is better left to a separate investigation: its inclusion would require the introduction of additional kinematics associated with surface strain and hence with a reference configuration; cf., e.g., Gurtin and Murdoch [8]. We therefore limit our discussion to situations in which *the elasticity of the interface is negligible.*[7]

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[7] Even so—with the exception of the constitutive relation $(8.8)_2$ for the dissipative stress $\mathbb{T}_{\mathrm{dis}}$, a relation most often associated with fluid interfaces—all of our results apply to both solids and fluids.

8.1 State relations. Energy balance revisited

Consistent with our neglect of interfacial elasticity, we assume that the free-energy, temperature, and entropy of the interface are related through the “state relations"

$$\psi = \hat{\psi}(\vartheta), \qquad \eta = \hat{\eta}(\vartheta) = -\frac{\mathrm{d}\hat{\psi}(\vartheta)}{\mathrm{d}\vartheta}. \tag{8.1}$$

These relations reduce the free-energy imbalance (7.18) to a *dissipation inequality*

$$\Gamma \overset{\text{def}}{=} \underbrace{\boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \mathbb{T}_{\text{dis}} : \mathbb{D}}_{\Gamma_{\text{mec}}} + \frac{q_{\text{env}}}{\vartheta_{\text{env}}}(\vartheta_{\text{env}} - \vartheta) - \frac{1}{\vartheta}\mathbb{q} \cdot \operatorname{grad}_{\mathcal{S}}\vartheta \geq 0 \tag{8.2}$$

in which

$$\mathbb{T}_{\text{dis}} \overset{\text{def}}{=} \mathbb{T} - \psi\mathbb{P} \tag{8.3}$$

is the *dissipative surface stress*, Γ is the *dissipation*, and

$$\Gamma_{\text{mec}} \overset{\text{def}}{=} \boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \mathbb{T}_{\text{dis}} : \mathbb{D} \tag{8.4}$$

is the *mechanical dissipation*.

By (7.16), the relations (8.1) give rise to a subsidiary constitutive relation

$$\varepsilon = \hat{\varepsilon}(\vartheta) = \hat{\psi}(\vartheta) + \vartheta\hat{\eta}(\vartheta) \tag{8.5}$$

for the internal energy of the interface. As a consequence of this relation and (8.1),

$$\frac{\mathrm{d}\hat{\varepsilon}(\vartheta)}{\mathrm{d}\vartheta} = \vartheta\frac{\mathrm{d}\hat{\eta}(\vartheta)}{\mathrm{d}\vartheta}, \tag{8.6}$$

and hence $\dot{\varepsilon} = \vartheta\dot{\eta}$; thus if we subtract $\psi\,\mathbb{P} : \mathbb{D}$ from both sides of $(7.17)_2$ and use (7.16), we arrive at an alternative form for the energy balance:

$$\vartheta(\dot{\eta} + \eta\,\mathbb{P} : \mathbb{D}) = q_{\text{env}} + \mathbf{q} \cdot \mathbb{m} - \operatorname{div}_{\mathcal{S}}\mathbb{q} + \boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \mathbb{T}_{\text{dis}} : \mathbb{D}. \tag{8.7}$$

8.2 Constitutive relations for the dissipative fields

Guided by the dissipation inequality (8.2), we consider constitutive relations for the environmental traction $\boldsymbol{\tau}_{\text{env}}$, the *dissipative surface stress*[8] $\mathbb{T}_{\text{dis}}$, the environmental heat flow q_{env}, and the surface heat flux $\mathbb{q}$. Specifically, we assume that these fields are linear functions of their conjugate quantities $(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}$, $\mathbb{D}$, $\vartheta_{\text{env}} - \vartheta$, and $\operatorname{grad}_{\mathcal{S}}\vartheta$, with corresponding moduli possibly dependent on temperature:

$$\left.\begin{aligned}
\boldsymbol{\tau}_{\text{env}} &= \beta(\vartheta)(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}, \\
\mathbb{T}_{\text{dis}} &= 2\alpha(\vartheta)\mathbb{D} + \lambda(\vartheta)(\operatorname{tr}\mathbb{D})\mathbb{P}, \\
q_{\text{env}} &= \kappa(\vartheta)(\vartheta_{\text{env}} - \vartheta), \\
\mathbb{q} &= -\varphi(\vartheta)\operatorname{grad}_{\mathcal{S}}\vartheta.
\end{aligned}\right\} \tag{8.8}$$

Here $\beta(\vartheta)$ is a *slip viscosity*, $\alpha(\vartheta)$ and $\lambda(\vartheta)$ represent (interfacial) *fluid viscosities*, $\kappa(\vartheta)$ is a *heat-flow modulus*, and $\varphi(\vartheta)$ is the *interfacial conductivity*. A simple calculation shows that the constitutive relations (8.8) render the dissipation (8.2) and the mechanical dissipation (8.4) of the forms

$$\Gamma = 2\alpha(\vartheta)|\mathbb{D}_0|^2 + [\lambda(\vartheta) + \alpha(\vartheta)](\operatorname{tr}\mathbb{D})^2 + \beta(\vartheta)|(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}|^2 + \kappa(\vartheta)(\vartheta_{\text{env}} - \vartheta)^2 + \varphi(\vartheta)|\operatorname{grad}_{\mathcal{S}}\vartheta|^2, \tag{8.9}$$

and

$$\Gamma_{\text{mec}} = 2\alpha(\vartheta)|\mathbb{D}_0|^2 + [\lambda(\vartheta) + \alpha(\vartheta)](\operatorname{tr}\mathbb{D})^2 + \beta(\vartheta)|(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}|^2, \tag{8.10}$$

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[8] Cf. Scriven [9], Slattery [5], and Edwards et al. [10].

with

$$\mathbb{D}_0 = \mathbb{D} - \tfrac{1}{2}(\operatorname{tr}\mathbb{D})\mathbb{P}$$

the *deviatoric stretch-rate*. Thus, since the tensor fields $(\operatorname{tr}\mathbb{D})\mathbb{P}$ and $\mathbb{D}_0$ may be specified independently, the dissipation inequality (8.9) is satisfied if and only if the moduli satisfy

$$\alpha(\vartheta) \geq 0, \qquad \lambda(\vartheta) + \alpha(\vartheta) \geq 0, \qquad \beta(\vartheta) \geq 0, \qquad \kappa(\vartheta) \geq 0, \qquad \varphi(\vartheta) \geq 0.$$

Importantly, the constitutive relation $(8.8)_2$ for the dissipative stress $\mathbb{T}_{\text{dis}}$ is frame-indifferent. To see this, let $\mathbf{Q}$ be a rotation satisfying

$$\mathbf{Q}\mathbb{m} = \mathbb{m}.$$

It then follows that

$$\begin{aligned}\mathbf{Q}\mathbb{P}\mathbf{Q}^{\top} &= \mathbf{Q}(\mathbf{1} - \mathbb{m} \otimes \mathbb{m})\mathbf{Q}^{\top}\\ &= \mathbf{Q}\mathbf{Q}^{\top} - \mathbf{Q}\mathbb{m} \otimes \mathbf{Q}\mathbb{m}\\ &= \mathbf{1} - \mathbb{m} \otimes \mathbb{m}\\ &= \mathbb{P}.\end{aligned}$$

Thus,

$$\mathbf{Q}\mathbb{P} = \mathbb{P}\mathbf{Q} \qquad \text{and} \qquad \mathbb{P}\mathbf{Q}^{\top} = \mathbf{Q}^{\top}\mathbb{P}. \tag{8.11}$$

Thus, invoking the relation (3.14) for $\mathbb{D}$ in terms of the rate of stretch $\mathbf{D}$ in the body, and bearing in mind that $\mathbf{D}$ is frame-indifferent,

$$\begin{aligned}\mathbf{Q}\mathbb{D}\mathbf{Q}^{\top} &= \mathbf{Q}\mathbb{P}\mathbf{D}\mathbb{P}\mathbf{Q}^{\top}\\ &= \mathbb{P}\mathbf{Q}\mathbf{D}\mathbf{Q}^{\top}\mathbb{P}\\ &= \mathbb{P}\mathbf{D}\mathbb{P}\\ &= \mathbb{D},\end{aligned}$$

and it follows from $(8.8)_2$ that

$$\mathbf{Q}\mathbb{T}_{\text{dis}}\mathbf{Q}^{\top} = \mathbb{T}_{\text{dis}} \tag{8.12}$$

for all rotations about the tangent plane to $\mathcal{S}$ (at any point). This establishes the frame-indifference of the constitutive equation $(8.8)_2$ for the dissipative stress $\mathbb{T}_{\text{dis}}$.

Analogous arguments yield the frame-indifference of the constitutive equations $(8.8)_1$ and $(8.8)_4$ for the environmental shear $\boldsymbol{\tau}_{\text{env}}$ and the superficial heat flux $\mathbb{q}$.

9 Boundary conditions for the traction on—and the heat flow out of—the body

The force and energy balances (6.4) and (8.7) augmented by the interfacial constitutive equations provide boundary conditions for the body. In discussing these conditions, the environmental velocity $\mathbf{v}_{\text{env}}$ and temperature ϑ_{env} are presumed known a priori; by (2.5), the former requirement necessitates that the normal velocity $V = \mathbf{v} \cdot \mathbb{m} = \mathbf{v}_{\text{env}} \cdot \mathbb{m}$ is also known a priori.

Consider the force balance (6.4). This balance is most conveniently expressed in terms of its normal and tangential parts as given in (6.8). By (3.8), $(6.8)_1$, (8.3), $(8.8)_2$, the *normal interfacial force balance* takes the form

$$\mathbb{m} \cdot \mathbf{T}\mathbb{m} - \mathbb{m} \cdot \mathbf{t}_{\text{env}} = \big[\hat{\psi}(\vartheta) + \lambda(\vartheta)(\operatorname{tr}\mathbb{D})\big]K + 2\alpha(\vartheta)\mathbb{K} : \mathbb{D}. \tag{9.1}$$

This equation represents a generalization of the classical Young–Laplace equation [11,12] to account for interfacial viscosity. Note the presence of the *full curvature tensor* $\mathbb{K}$. Similarly, the definition (8.3) of the dissipative surface stress and the constitutive equations $(8.8)_{1,2}$ for the environmental traction and for this stress reduce the force balance $(6.4)_2$ to a boundary condition for the tangential bulk traction $\boldsymbol{\tau} = (\mathbf{T}\mathbb{n})_{\tan}$:

$$\boldsymbol{\tau} = \beta(\vartheta)(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \text{grad}_{\mathcal{S}}\hat{\psi}(\vartheta) + \mathbb{P}\,\text{div}_{\mathcal{S}}(2\alpha(\vartheta)\mathbb{D} + \lambda(\vartheta)(\text{tr}\,\mathbb{D})\mathbb{P}). \tag{9.2}$$

The presence of the terms involving the superficial stretch-rate $\mathbb{D}$ render the conditions (9.1) and (9.2) most appropriate for a fluid; if we assume that the viscosities vanish, $\lambda(\vartheta) = \alpha(\vartheta) \equiv 0$, then we arrive at interface conditions

$$\mathbb{n}\cdot\mathbf{T}\mathbb{n} - \mathbb{n}\cdot\mathbf{t}_{\text{env}} = \hat{\psi}(\vartheta)K \qquad \text{and} \qquad \boldsymbol{\tau} = \beta(\vartheta)(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \text{grad}_{\mathcal{S}}\hat{\psi}(\vartheta)$$

appropriate for a solid. When surface stress and surface free energy are neglected the balance (9.2) reduces to Navier's [13] slip law

$$\boldsymbol{\tau} = \beta(\vartheta)(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}.$$

Consider next the energy balance (8.7). It is convenient to introduce the interfacial *specific heat*

$$c(\vartheta) \overset{\text{def}}{=} \frac{\mathrm{d}\hat{\varepsilon}(\vartheta)}{\mathrm{d}\vartheta}, \tag{9.3}$$

which, by (8.6), may be expressed in the form

$$c(\vartheta) = \vartheta\,\frac{\mathrm{d}\hat{\eta}(\vartheta)}{\mathrm{d}\vartheta}. \tag{9.4}$$

The identity (4.2), the energy balance (8.7), the relation (8.10) for the mechanical dissipation, and the constitutive relations $(8.1)_2$ and $(8.8)_{3,4}$ for the entropy, environmental heat flow, and superficial heat flux then yield a boundary condition

$$\mathbf{q}\cdot\mathbb{n} = \kappa(\vartheta)(\vartheta - \vartheta_{\text{env}}) + c(\vartheta)\dot{\vartheta} + \vartheta\,\hat{\eta}(\vartheta)\,\text{div}_{\mathcal{S}}\mathbf{v} - \text{div}_{\mathcal{S}}(\varphi(\vartheta)\text{grad}_{\mathcal{S}}\vartheta) - \Gamma_{\text{mec}} \tag{9.5}$$

for the bulk heat flow at the interface. These conditions, being in the form of partial differential equations, are nonclassical. By (8.10) the mechanical dissipation Γ_{mec} is quadratic in the rate of stretching $\mathbb{D}$ and interfacial slip $(\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan}$ and might, therefore, be negligible when these quantities are sufficiently small; when we neglect Γ_{mec}, we arrive at a much simpler expression

$$\mathbf{q}\cdot\mathbb{n} = \kappa(\vartheta)(\vartheta - \vartheta_{\text{env}}) + c(\vartheta)\dot{\vartheta} + \vartheta\,\hat{\eta}(\vartheta)\,\text{div}_{\mathcal{S}}\mathbf{v} - \text{div}_{\mathcal{S}}(\varphi(\vartheta)\text{grad}_{\mathcal{S}}\vartheta)$$

for the bulk heat flow at the interface.

When all but the first of the terms on the right side of (9.5) are neglected, (9.5) specializes to Newton's law [14] of cooling

$$\mathbf{q}\cdot\mathbb{n} = \kappa(\vartheta)(\vartheta - \vartheta_{\text{env}}).$$

If, more generally, we allow the modulus κ to be a function $\kappa(\vartheta, \vartheta_{\text{env}})$ of both bulk and environmental temperatures, then Newton's law of cooling includes Kirchhoff's [15] law of radiation

$$\mathbf{q}\cdot\mathbb{n} = k(\vartheta^4 - \vartheta_{\text{env}}^4),$$

where $k > 0$ is a constant.

The boundary conditions discussed above couple the interface to the environment.

10 Simple boundary conditions for nondissipative environments

In applications one is often confronted with simple boundary conditions in which interfacial dissipation vanishes and the interface itself has meager structure. To derive such boundary conditions

- we begin anew from Sect. 7.3, dropping the discussions in Sect. 8 on constitutive equations and Sect. 9 on boundary conditions.

10.1 Restrictive hypotheses. Zero-dissipation conditions

An important and useful class of boundary conditions is based on the following assumptions

$$\Gamma = 0, \qquad \mathbb{T} = \psi \mathbb{P}, \qquad \psi = \text{constant}. \tag{10.1}$$

The first of (10.1) renders the interface *dissipationless*; the remaining assumptions endow the interface with *constant free energy* (surface tension) and, furthermore, imply that

$$\mathbb{T}_{\text{dis}} = \mathbf{0} \tag{10.2}$$

and that

$$\eta \equiv 0 \qquad \text{and} \qquad \varepsilon = \psi. \tag{10.3}$$

As a consequence of (10.1), the free-energy imbalance (7.18) reduces to the *zero-dissipation condition*

$$\Gamma = \boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} + \frac{q_{\text{env}}}{\vartheta_{\text{env}}}(\vartheta_{\text{env}} - \vartheta) = 0, \tag{10.4}$$

a condition we satisfy via the relations

$$\left.\begin{aligned} \boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} &= 0, \\ q_{\text{env}}(\vartheta_{\text{env}} - \vartheta) &= 0. \end{aligned}\right\} \tag{10.5}$$

We refer to (10.5) as the *uncoupled zero-dissipation conditions*. An important consequence of (10.1) and (10.5) is that the force and energy balances (7.17) have the simple forms

$$\left.\begin{aligned} \mathbf{T}\mathbb{m} - \psi K \mathbb{m} &= \mathbf{t}_{\text{env}}, \\ \mathbf{q} \cdot \mathbb{m} &= -q_{\text{env}}. \end{aligned}\right\} \tag{10.6}$$

(The energy balance reduces to $\varepsilon \mathbb{P} : \mathbb{D} = \mathbb{T} : \mathbb{D}$, which by $(10.4)_2$ and $(10.3)_2$ holds trivially.) Note that the force balance $(10.6)_1$ is independent of surface tension ψ on any flat subsurface of the boundary, since the total curvature K vanishes on flat subsurfaces.

Hereafter, we suppress the argument t. It is most convenient to state boundary conditions for an arbitrary subsurface $\mathcal{A}$ of the deformed boundary $\mathcal{B}$ (at some arbitrarily given time). Depending on the physical circumstances one is trying to characterize: $\mathcal{A}$ may equal $\partial\mathcal{B}$; or $\mathcal{A}$ may be a proper subsurface of $\partial\mathcal{B}$, allowing for the prescription of other conditions on $\partial\mathcal{B}\backslash\mathcal{A}$.

10.2 Simple boundary conditions

Our uncoupling of the zero dissipation conditions allows us to consider, separately:

(i) simple mechanical boundary conditions, which are restrictions on **T** and **v** consistent with

$$\left.\begin{aligned} \boldsymbol{\tau}_{\text{env}} \cdot (\mathbf{v}_{\text{env}} - \mathbf{v})_{\tan} &= 0, \\ \mathbf{T}\mathbb{m} - \psi K \mathbb{m} &= \mathbf{t}_{\text{env}}; \end{aligned}\right\} \tag{10.7}$$

(ii) simple thermal boundary conditions, which are restrictions on ϑ and **q** consistent with

$$\left.\begin{aligned} q_{\text{env}}(\vartheta_{\text{env}} - \vartheta) &= 0, \\ \mathbf{q} \cdot \mathbb{m} &= -q_{\text{env}}. \end{aligned}\right\} \tag{10.8}$$

Note that (10.7) provides *two* mechanical conditions, while (10.8) provides *two* thermal conditions. But experience has shown that exactly *one* mechanical boundary condition and exactly *one* thermal boundary condition is needed for the solution of coupled thermomechanical boundary-value problems. Indeed, the extra conditions in (10.7) and (10.8) are essentially irrelevant: each extra condition should be considered as an equation for an unused environmental field. This view is clarified in more detail below.

We begin by stating some simple mechanical boundary conditions that are widely used in the formulation and solution of boundary-value problems.

- **Velocity condition** This boundary condition requires that

$$\mathbf{v} = \mathbf{v}_{\text{env}} \quad \text{on } \mathcal{A}, \tag{10.9}$$

with environmental velocity $\mathbf{v}_{\text{env}}$ *prescribed* on $\mathcal{A}$. When $\mathbf{v}_{\text{env}} = \mathbf{0}$, so that

$$\mathbf{v} = \mathbf{0} \quad \text{on } \mathcal{A}, \tag{10.10}$$

then the velocity condition is referred to as a *zero-slip condition* and the surface $\mathcal{A}$ is said to be *fixed*.

Boundary conditions, such as (10.9), are best explained within the rubric of boundary-value problems. For a boundary-value problem the velocity condition would be viewed as one in which the environmental velocity $\mathbf{v}_{\text{env}}$ is given a priori, a view that begs the question as to the status of the environmental traction $\mathbf{t}_{\text{env}}$. This traction would be determined, *if needed* (and generally it is not!) from the resulting solution using $(10.7)_2$. Granted this, both of the equations (10.7) would be satisfied. A similar discussion applies to each of the boundary conditions discussed below. It is readily shown that, for each such mechanical condition, each of the environmental fields not discussed may be determined from the bulk fields $\mathbf{v}$, $\mathbf{T}$, ϑ, and $\mathbf{q}$ so as to ensure satisfaction of the balance and uncoupled zero dissipation conditions stated in (10.7); and similarly for the simple thermal boundary conditions (10.8).

- **Traction condition** This boundary condition requires that

$$\mathbf{T}\mathbb{m} - \psi K \mathbb{m} = \mathbf{t}_{\text{env}} \quad \text{on } \mathcal{A}, \tag{10.11}$$

with environmental traction $\mathbf{t}_{\text{env}}$ *prescribed* on $\mathcal{A}$. When $\mathbf{t}_{\text{env}} = \mathbf{0}$, so that

$$\mathbf{T}\mathbb{m} = \psi K \mathbb{m} \quad \text{on } \mathcal{A}, \tag{10.12}$$

then the traction condition is referred to as a *free-surface condition*.

- **Mixed condition**[9] This boundary condition requires that

$$\left.\begin{aligned}(\mathbf{T}\mathbb{m})_{\tan} &= \boldsymbol{\tau}_{\text{env}}\\ \mathbf{v}\cdot\mathbb{m} &= V_{\text{env}}\end{aligned}\right\} \quad \text{on } \mathcal{A}, \tag{10.13}$$

with environmental shear $\boldsymbol{\tau}_{\text{env}}$ and normal environmental velocity

$$V_{\text{env}} \overset{\text{def}}{=} \mathbf{v}_{\text{env}} \cdot \mathbb{m}$$

prescribed on $\mathcal{A}$. When $\boldsymbol{\tau}_{\text{env}} = \mathbf{0}$, so that

$$(\mathbf{T}\mathbb{m})_{\tan} = \mathbf{0} \quad \text{on } \mathcal{A}, \tag{10.14}$$

then the traction condition is referred to as a *zero-shear condition*. In this case the body may slide freely with respect to the environmental material.

We next list two choices for the thermal boundary conditions, each of great importance.

- **Temperature condition** This boundary condition requires that

$$\vartheta = \vartheta_{\text{env}} \quad \text{on } \mathcal{A}, \tag{10.15}$$

with environmental temperature ϑ_{env} *prescribed* on $\mathcal{A}$. When $\vartheta_{\text{env}} =$ constant, then the surface $\mathcal{A}$ is said to be in *thermal equilibrium*.

- **Heat flow condition** This boundary condition requires that

$$\mathbf{q}\cdot\mathbb{m} = -q_{\text{env}} \quad \text{on } \mathcal{A}, \tag{10.16}$$

with environmental heat flow q_{env} *prescribed* on $\mathcal{A}$. When $q_{\text{env}} = 0$, so that

$$\mathbf{q}\cdot\mathbb{m} = \mathbf{0} \quad \text{on } \mathcal{A}, \tag{10.17}$$

then this condition is referred to as a *flux-free condition* and the surface $\mathcal{A}$ is said to be *thermally isolated*.

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[9] There is a second mixed condition, of little importance, in which the normal environmental traction and the tangential environmental velocity are prescribed.

11 Addendum: an alternative formulation of the first two laws

11.1 Migrating boundary pillboxes

In the materials-science literature surface tension is often viewed as a scalar tensile force that expends power in conjunction with temporal changes in surface area. On the other hand, in our discussion of the first two laws in Sect. 7.1 surface tension was tacitly included as part of the total surface stress $\mathbb{T}$, so that, by (7.4), the traction corresponding to this surface tension necessarily expends power in conjunction with the tangential material velocity $\mathbf{v}_{\tan}$. In this section we present an alternative formulation of the first two laws that is consistent with the materials-science view of surface tension, but at the same time equivalent to the formulation presented in Sect. 7.1. This alternative formulation—developed by Gurtin [16] to treat phase transformations—is based on the use of interfacial subsurfaces $\mathcal{A}(t)$ that (in contrast to the boundary pillboxes $\mathcal{A}_t$ of the type discussed in Sect. 5) need not convect with the body: such subsurfaces $\mathcal{A}(t)$ of $\mathcal{S}_t$ have boundary curves $\partial\mathcal{A}(t)$ that generally *migrate relative to the material*. Throughout what follows

- we view such subsurfaces $\mathcal{A}(t)$ as *migrating boundary pillboxes*.

Consider an arbitrary migrating boundary pillbox $\mathcal{A}(t)$. Let $V_{\partial\mathcal{A}}(\mathbf{x}, t)$ denote the scalar normal velocity of the boundary *curve* $\partial\mathcal{A}(t)$ in the direction of its outward unit normal $\mathbb{m}(\mathbf{x}, t)$; cf. (2.2). Bearing in mind that $\partial\mathcal{A}(t)$ generally migrates relative to the material, we refer to the relative normal velocity

$$V_{\partial\mathcal{A}}^{\mathrm{mig}} \overset{\mathrm{def}}{=} V_{\partial\mathcal{A}} - \mathbf{v}\cdot\mathbb{m} \tag{11.1}$$

as the migrational velocity of $\partial\mathcal{A}(t)$; $V_{\partial\mathcal{A}}^{\mathrm{mig}}$ represents the rate at which $\partial\mathcal{A}(t)$ evolves with respect to the deforming surface $\mathcal{S}_t$ (or, said another way, the rate at which $\partial\mathcal{A}(t)$ evolves relative to $\partial\mathcal{B}_t$); in contrast, when $\partial\mathcal{A}(t)$ convects with $\mathcal{S}_t$ it follows that $V_{\partial\mathcal{A}} = \mathbf{v}\cdot\mathbb{m}$ and $V_{\partial\mathcal{A}}^{\mathrm{mig}} = 0$.

Important to what follows is our assumption that $\partial\mathcal{A}(t)$ be allowed to migrate arbitrarily within the interface. Granted this, $V_{\partial\mathcal{A}}$ and hence $V_{\partial\mathcal{A}}^{\mathrm{mig}} = V_{\partial\mathcal{A}} - \mathbf{v}\cdot\mathbb{m}$ may be arbitrarily specified; we therefore assume, without loss in generality, that

$$V_{\partial\mathcal{A}}^{\mathrm{mig}} \quad \text{is arbitrary.} \tag{11.2}$$

The arbitrary nature of $V_{\partial\mathcal{A}}^{\mathrm{mig}}$ necessitates a modified version of the Reynolds–Slattery transport theorem [3]: for $\mathcal{A}(t)$ an arbitrary time-dependent subsurface of the interface $\mathcal{S}_t$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}(t)} \varphi\,\mathrm{d}a = \int\limits_{\mathcal{A}(t)} \big(\dot{\varphi} + \varphi\,\mathrm{div}_{\mathcal{S}}\mathbf{v}_{\tan} - \varphi K V\big)\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}(t)} \varphi V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s. \tag{11.3}$$

11.2 Global forms of the energy balance and entropy imbalance for a migrating boundary pillbox

Classically, the first and second laws for a migrating boundary pillbox $\mathcal{A}(t)$ have the forms

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}(t)} \varepsilon\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \varepsilon V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s &= \int\limits_{\mathcal{A}(t)} (q_{\mathrm{env}} + \mathbf{q}\cdot\mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \mathbb{q}\cdot\mathbb{m}\,\mathrm{d}s \\ &+ \int\limits_{\mathcal{A}(t)} (\mathbf{t}_{\mathrm{env}}\cdot\mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n}\cdot\mathbf{v})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}(t)} \mathbb{T}\mathbb{m}\cdot\mathbf{v}_{\tan}\,\mathrm{d}s\end{aligned} \tag{11.4}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}(t)} \eta\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \eta V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s \ge \int\limits_{\mathcal{A}(t)} \Big(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q}\cdot\mathbb{n}}{\vartheta}\Big)\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \frac{\mathbb{q}\cdot\mathbb{m}}{\vartheta}\,\mathrm{d}s. \tag{11.5}$$

In what follows, we derive the classical relation $\sigma = \psi$ identifying surface tension with interfacial free-energy. Moreover, we identify a new quantity, the *latent heat of migration* Q, which we show to have the simple form $Q = \vartheta\eta$—the quantity $-Q$, therefore, coincides with the entropic free-energy, a quantity ubiquitous in statistical mechanics. To achieve this, we begin with the first two laws for a migrating boundary pillbox $\mathcal{A}(t)$ in their elemental form [16]:

$$\left.\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\left\{\begin{matrix}\text{internal energy}\\ \text{of } \mathcal{A}(t)\end{matrix}\right\} &= \left\{\begin{matrix}\text{heat flow}\\ \text{into } \mathcal{A}(t)\end{matrix}\right\} + \left\{\begin{matrix}\text{power expended}\\ \text{on } \mathcal{A}(t)\end{matrix}\right\},\\ \frac{\mathrm{d}}{\mathrm{d}t}\left\{\begin{matrix}\text{entropy}\\ \text{of } \mathcal{A}(t)\end{matrix}\right\} &\geq \left\{\begin{matrix}\text{entropy flow}\\ \text{into } \mathcal{A}(t)\end{matrix}\right\}.\end{aligned}\right\} \tag{11.6}$$

These statements of the basic thermodynamic laws may seem platitudes, but they are not. For example, (11.6) as stated cannot *explicitly* accommodate the inflows

$$\int\limits_{\partial\mathcal{A}(t)} \varepsilon V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}a \qquad \text{and} \qquad \int\limits_{\partial\mathcal{A}(t)} \eta V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}a. \tag{11.7}$$

of energy and entropy induced by the migration of $\partial\mathcal{A}(t)$: in the present formulation such inflows are characterized *implicitly by effective flows of heat and entropy* induced by the migration of interfacial material across $\partial\mathcal{A}(t)$. Specifically, the formulation we present here is based on a nonclassical treatment of the migrating boundary curve $\partial\mathcal{A}(t)$—a treatment that separately characterizes expenditures of power and flows of heat and entropy associated with the transfer of material across $\partial\mathcal{A}(t)$ due to its migration.

Turning to a description of the expended power, we consider the surface stress $\mathbb{T}$ as the sum of a surface stress $\mathbb{S}$ that does not involve surface tension and a stress $\sigma\mathbb{P}$ due to a scalar surface tension σ:

$$\mathbb{T} = \sigma\mathbb{P} + \mathbb{S}. \tag{11.8}$$

We assume that the total surface stress $\mathbb{T}$ is consistent with the force and moment balances for the interface as established in §6, but we no longer assume that the total stress $\mathbb{T}$ expends power over the tangential component of the material velocity $\mathbf{v}_{\mathrm{tan}}$ (cf. (7.4)); in fact, in our current view the tractions $\sigma\mathbb{m}$ and $\mathbb{S}\mathbb{m}$ have dissimilar power-conjugate velocities.

Based on the primitive view of surface tension as a force that performs work in conjunction with changes in surface area, we suppose that the surface tension acting on the pillbox $\mathcal{A}(t)$ along $\partial\mathcal{A}(t)$ expends power in conjunction with temporal changes in the local area induced by the migration of $\partial\mathcal{A}(t)$. The normal velocity $V_{\partial\mathcal{A}}$ of the boundary curve $\partial\mathcal{A}(t)$ represents this rate, measured per unit length; therefore,

$$\int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}\,\mathrm{d}s$$

represents the power expended by surface tension on the portion of the interface lying within the pillbox. On the other hand, we assume that the traction $\mathbb{S}\mathbb{m}$ should be power-conjugate to the tangential material velocity $\mathbf{v}_{\mathrm{tan}}$; therefore,

$$\int\limits_{\partial\mathcal{A}(t)} \mathbb{S}\mathbb{m}\cdot\mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s$$

represents the power expended by the surface stress on the portion of the interface lying within the pillbox. Thus the sum

$$\int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}\,\mathrm{d}s + \int\limits_{\partial\mathcal{A}(t)} \mathbb{S}\mathbb{m}\cdot\mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s \tag{11.9}$$

represents the power expended by the total traction $\mathbb{T}\mathbb{m}$ along $\partial\mathcal{A}(t)$. Next, by $(2.4)_2$ and (11.1), the power expended by surface tension admits a decomposition into standard and migrational parts.

$$\begin{aligned}\int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}\,\mathrm{d}s &= \int\limits_{\partial\mathcal{A}(t)} \sigma\mathbf{v}\cdot\mathbb{m}\,\mathrm{d}s + \int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s\\ &= \underbrace{\int\limits_{\partial\mathcal{A}(t)} (\sigma\mathbf{v}_{\mathrm{tan}})\cdot\mathbb{m}\,\mathrm{d}s}_{\text{standard power}} + \underbrace{\int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s}_{\text{migrational power}}.\end{aligned} \tag{11.10}$$

Thus we can rewrite (11.9) in the form

$$\underbrace{\int\limits_{\partial\mathcal{A}(t)} \overbrace{(\mathbb{S}\mathbb{m} + \sigma\,\mathbb{m})}^{\mathbb{T}\mathbb{m}} \cdot \mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s}_{\text{standard power}} + \underbrace{\int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s}_{\text{migrational power}}\,. \tag{11.11}$$

We have yet to include the power expended on the upper and lower faces of the pillbox; since these faces are locally stationary the integrand of this power expenditure is simply (7.3) with $\partial\mathcal{A}_t$ replaced by $\partial\mathcal{A}(t)$; thus, by (11.11), the net power expended on the pillbox $\mathcal{A}(t)$ is given by

$$\int\limits_{\mathcal{A}(t)} (\mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}(t)} \mathbb{T}\mathbb{m} \cdot \mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s + \int\limits_{\partial\mathcal{A}(t)} \sigma V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s. \tag{11.12}$$

Consider next the flows of heat and entropy. We let q_{mig} denote the *migrational heat flow* measured per unit length and, consistent with standard discussions, let $q_{\mathrm{mig}}/\vartheta$ denote the corresponding *migrational entropy flow*, so that

$$\int\limits_{\partial\mathcal{A}(t)} q_{\mathrm{mig}}\,\mathrm{d}s \qquad \text{and} \qquad \int\limits_{\partial\mathcal{A}(t)} \frac{q_{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s, \tag{11.13}$$

represent net flows of migrational heat and entropy across $\partial\mathcal{A}(t)$. Next, the migrational heat flow q_{mig} should vanish when the migrational velocity vanishes—in fact, consistent with (11.7), q_{mig} should be proportional to the migrational velocity $V_{\partial\mathcal{A}}^{\mathrm{mig}}$ of $\partial\mathcal{A}$ and hence of the form

$$q_{\mathrm{mig}} = Q V_{\partial\mathcal{A}}^{\mathrm{mig}}.$$

The migational flows of heat and entropy across $\partial\mathcal{A}(t)$ are therefore given by

$$\int\limits_{\partial\mathcal{A}(t)} Q V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s \qquad \text{and} \qquad \int\limits_{\partial\mathcal{A}(t)} \frac{Q V_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s; \tag{11.14}$$

We make no other assumptions regarding the migrational flows of heat and entropy. We refer to the scalar field Q as a *latent heat of migration*, because $Q V_{\partial\mathcal{A}}^{\mathrm{mig}}$ represents an effective heat flow induced by the migration of the boundary curve $\partial\mathcal{A}(t)$.

As a consequence of (11.14), the net flows of heat and entropy into the pillbox $\mathcal{A}(t)$ have the forms

$$\underbrace{\int\limits_{\mathcal{A}(t)} (q_{\mathrm{env}} + \mathbf{q} \cdot \mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \mathbb{q} \cdot \mathbb{m}\,\mathrm{d}s}_{\text{standard heat flow}} + \underbrace{\int\limits_{\partial\mathcal{A}(t)} Q V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s}_{\text{migrational heat flow}}$$

and

$$\underbrace{\int\limits_{\mathcal{A}(t)} \Big(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q} \cdot \mathbb{n}}{\vartheta}\Big)\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}} \frac{\mathbb{q} \cdot \mathbb{m}}{\vartheta}\,\mathrm{d}s}_{\text{standard entropy flow}} + \underbrace{\int\limits_{\partial\mathcal{A}} \frac{Q V_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s}_{\text{migrational entropy flow}} \quad .$$

The energy balance and entropy imbalance for a migrating boundary pillbox $\mathcal{A}(t)$ are, therefore, given by

$$\begin{aligned} \underbrace{\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\mathcal{A}(t)} \varepsilon\,\mathrm{d}a}_{\text{internal-energy rate}} = {} & \underbrace{\int\limits_{\mathcal{A}(t)} (q_{\mathrm{env}} + \mathbf{q} \cdot \mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} (\mathbb{q} \cdot \mathbb{m} - Q V_{\partial\mathcal{A}}^{\mathrm{mig}})\,\mathrm{d}s}_{\text{heat flow}} \\ & + \underbrace{\int\limits_{\mathcal{A}(t)} (\mathbf{t}_{\mathrm{env}} \cdot \mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n} \cdot \mathbf{v})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}(t)} (\mathbb{T}\mathbb{m} \cdot \mathbf{v}_{\mathrm{tan}} + \sigma V_{\partial\mathcal{A}}^{\mathrm{mig}})\,\mathrm{d}s}_{\text{power expended}} \end{aligned} \tag{11.15}$$

and

$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\mathcal{A}(t)} \eta \,\mathrm{d}a}_{\text{entropy rate}} \geq \underbrace{\int\limits_{\mathcal{A}(t)} \Big(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q}\cdot\mathbb{n}}{\vartheta}\Big)\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \frac{\mathbb{q}\cdot\mathbb{m} - QV_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s}_{\text{entropy flow}}\,. \tag{11.16}$$

Importantly,

- *the migrational versions* (11.15) *and* (11.16) *of the first two laws reduce to the standard versions* (7.5) *and* (7.6) *when* $\mathcal{A}(t) = \mathcal{A}_t$*, so that* $V_{\partial\mathcal{A}}^{\mathrm{mig}} = 0$.

The migrational formulation of the first two laws is therefore consistent with the standard formulation.

11.3 Surface tension equals interfacial free-energy. Latent heat of migration equals the negative of the entropic free-energy

Our next step is to determine the precise form of the latent heat of migration Q. Applying the transport relation (11.3) with $\varphi = \varepsilon$ and $\varphi = \eta$ to (11.15) and (11.16), we find that

$$\begin{aligned}\int\limits_{\mathcal{A}(t)} \big(\dot{\varepsilon} + \varepsilon\,\mathrm{div}_{\mathcal{S}}\mathbf{v}_{\mathrm{tan}} - \varepsilon K V\big)\,\mathrm{d}a &= \int\limits_{\mathcal{A}(t)} (q_{\mathrm{env}} + \mathbf{q}\cdot\mathbb{n})\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \mathbb{q}\cdot\mathbb{m}\,\mathrm{d}s \\ &+ \int\limits_{\mathcal{A}(t)} (\mathbf{t}_{\mathrm{env}}\cdot\mathbf{v}_{\mathrm{env}} - \mathbf{T}\mathbb{n}\cdot\mathbf{v})\,\mathrm{d}a + \int\limits_{\partial\mathcal{A}(t)} \mathbb{T}\mathbb{m}\cdot\mathbf{v}_{\mathrm{tan}}\,\mathrm{d}s + \int\limits_{\partial\mathcal{A}(t)} (Q + \sigma - \varepsilon)V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s\end{aligned} \tag{11.17}$$

and

$$\int\limits_{\mathcal{A}(t)} (\dot{\eta} + \eta\,\mathrm{div}_{\mathcal{S}}\mathbf{v}_{\mathrm{tan}} - \eta K V)\,\mathrm{d}a \geq \int\limits_{\mathcal{A}(t)} \Big(\frac{q_{\mathrm{env}}}{\vartheta_{\mathrm{env}}} + \frac{\mathbf{q}\cdot\mathbb{n}}{\vartheta}\Big)\,\mathrm{d}a - \int\limits_{\partial\mathcal{A}(t)} \frac{\mathbb{q}\cdot\mathbb{m}}{\vartheta}\,\mathrm{d}s + \int\limits_{\partial\mathcal{A}(t)} \frac{(Q - \vartheta\eta)V_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s. \tag{11.18}$$

At this point we use the presumption that $\partial\mathcal{A}(t)$ be allowed to evolve arbitrarily, so that (11.2) is satisfied. The integrals in (11.17) and (11.18) involving the term $V_{\partial\mathcal{A}}^{\mathrm{mig}}$ must therefore vanish,

$$\int\limits_{\partial\mathcal{A}(t)} (Q + \sigma - \varepsilon)V_{\partial\mathcal{A}}^{\mathrm{mig}}\,\mathrm{d}s = 0, \qquad \int\limits_{\partial\mathcal{A}(t)} \frac{(Q - \vartheta\eta)V_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\,\mathrm{d}s = 0,$$

for all $V_{\partial\mathcal{A}}^{\mathrm{mig}}$, so that

$$Q + \sigma - \varepsilon = 0, \qquad Q = \vartheta\eta. \tag{11.19}$$

The relation

$$Q = \vartheta\eta \tag{11.20}$$

shows that the latent heat of migration Q coincides, modulo sign, with a quantity referred to in statistical mechanics as the *entropic free-energy*. The relation $Q = \vartheta\eta$ also has a formal interpretation: when material is added to a pillbox across its boundary, the entropy transferred, $\eta\,\mathrm{d}s$, induces a transfer of heat of amount $Q\,\mathrm{d}s = \vartheta\eta\,\mathrm{d}s$, or more simply $\mathrm{d}Q = \vartheta\,\mathrm{d}\eta$, a relation ubiquitous in classical thermodynamics.

Finally, by (11.19), recalling the definition (7.16) of interfacial free energy $\psi = \varepsilon - \vartheta\eta$, we arrive at the classical result: *surface tension equals interfacial free-energy*,

$$\sigma = \psi. \tag{11.21}$$

The results (11.20) and (11.21) show that the assumed forms (11.14) for the migrational flows of heat and entropy across $\partial\mathcal{A}(t)$ were not chosen capriciously. Indeed, using (11.20) and (11.21) in (11.17) and (11.18) and utilizing the modified Reynolds–Slattery transport theorem (11.3) yields the classical statements (11.4) and (11.5) of the first two laws for a migrating boundary pillbox. Thus, granted (11.20) and (11.21), (11.17) and (11.18) are equivalent to (11.4) and (11.5).

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