Thermodynamic Approach to Interfacial Transport Phenomena: Single-Component Systems

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Balancing extensive quantities at interfaces in terms of excess densities is a subtle problem because these densities change with the precise location of the dividing surface within the interfacial region. We propose to handle such ambiguities for moving interfaces by introducing a gauge degree of freedom associated with the location of the dividing surface and by studying all the normal velocities associated with different excess densities. Unambiguous interfacial balance equations can then be obtained directly from the differences between normal velocities. By assuming local equilibrium, considering the interfacial entropy balance, and identifying the entropy production rate at the interface, we are naturally led to thermodynamically consistent constitutive assumptions for the fluxes characterizing transport in the interface and for the boundary conditions characterizing transport across the interface. The usefulness and generality of the proposed approach is illustrated in the context of several examples. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 1424–1433, 2014
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Introduction

It is well established that models based on transport phenomena are essential for developing a deep understanding of chemical and biological processes and for their efficient design and operation. The cornerstone of transport phenomena are balance equations for mass, momentum, and energy. When expressed in differential form, the balance equations apply to all points within a given phase; for multiphase systems, each phase is governed by its own set of balance equations. A detailed treatment of transport phenomena has been elaborated in the famous textbook of Bird et al.[1] Communication between distinct phases takes place at interfaces in the form of boundary conditions, which are usually formulated by assuming the phases are in equilibrium at the interface, and using two-dimensional forms of the balance equations for mass, momentum, and energy.

It will be useful to provide a brief review of the transport phenomena equations for bulk phases. This review will serve as a rough outline of the approach to be developed in subsequent sections and will establish the notation we shall use. Let us consider the balance equations for a given phase comprised of a single component, which can be formulated by considering a stationary region in space with fixed volume. The balance equation for mass density ρ, or continuity equation, can be written as follows

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (v\rho) \tag{1}$$

The balance equation for momentum density $M = \rho v$ can, neglecting external forces, be written as

$$\frac{\partial M}{\partial t} = -\nabla \cdot (vM + \pi) \tag{2}$$

where π is the flux of momentum relative to that convected by the velocity v, or pressure tensor. The balance equation for angular momentum implies the pressure tensor is symmetric: $\pi = \pi^{\mathrm{T}}$. Note that it is more common to refer to the product ρv as a mass flux, and it is rare to refer to it as momentum density and assign to it a separate variable M as we have done in (2). For our purposes, there is no difference between the momentum density M and the mass flux ρv, but we will find it convenient to use the former in clarifying the structure of balance equations. The balance equation for total energy density e, again neglecting external forces, takes the form

$$\frac{\partial e}{\partial t} = -\nabla \cdot (ve + j_q + \pi \cdot v) \tag{3}$$

where j_q is the (diffusive) flux of energy relative to that convected with v. Typically, one is interested in the balance equation for internal energy density $u = e - \frac{1}{2}\rho v^2$, which is obtained by subtracting from (3) the balance equation for kinetic energy density, which is obtained by forming the scalar product of v with (2). This leads to the following balance equation for the internal energy density

$$\frac{\partial u}{\partial t} = -\nabla \cdot (vu + j_q) - \pi : \nabla v \tag{4}$$

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The above balance equations* are not a solvable set of equations, as the number of unknowns they involve is larger than the number of equations.

It is worthwhile to notice the structure of the balance equations in (1)–(4): the left-hand sides express the time rate of change of a density at a fixed point, and terms of the form $-\nabla \cdot (..)$ on the right-hand sides express the net flux of a density to the point, which consist of a convective part associated with $\boldsymbol{v}$, and a diffusive part relative to $\boldsymbol{v}$.[†] The presence of terms not of the form $\nabla \cdot (..)$, which are source terms, indicates the balance equation governs the density of a quantity that is not conserved. Hence, mass, momentum, and total energy are conserved quantities, while internal energy is not.

One approach to resolve the under-determined state of the balance equations for mass, momentum, and energy is via thermodynamics. To do so, we assume there exists at each point a local thermodynamic equilibrium state and introduce the thermodynamic potential for internal energy density $u = u(s, \rho)$, where s is the entropy density. The balance equation for entropy density can be written as

$$\frac{\partial s}{\partial t} = -\nabla \cdot (\boldsymbol{v}s + \boldsymbol{j}_s) + \sigma \tag{5}$$

where $\boldsymbol{j}_s$ is the diffusive entropy flux and σ is a source term, which must be nonnegative. From the thermodynamic potential, we have Gibbs fundamental form: $du = Tds + \hat{\mu}d\rho$, where the temperature is defined as $T = (\partial u / \partial s)_\rho$ and chemical potential per unit mass as $\hat{\mu} = (\partial u / \partial \rho)_s$. Also, from the extensivity of mass, energy, and entropy, we have the Euler equation: $p + u = Ts + \hat{\mu}\rho$, where p is pressure. Using these results, it possible to write the entropy source term as

$$\sigma = \boldsymbol{j}_q \cdot \nabla \left(\frac{1}{T}\right) - \frac{1}{T}\boldsymbol{\tau} : \nabla \boldsymbol{v} \tag{6}$$

To arrive at this equation, we have decomposed the pressure tensor in the form: $\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau}$, where $\boldsymbol{\tau}$, which inherits the symmetry of $\boldsymbol{\pi}$, is the pressure on top of the local equilibrium pressure, or "extra stress." We have also identified the famous irreversible entropy flux that is proportional to heat flux: $\boldsymbol{j}_s = \boldsymbol{j}_q / T$.

It is of interest to express the fundamental form and Euler equations in terms of total energy. Since $e = u + \frac{1}{2}\rho v^2$, the fundamental form can be written as

$$de = Tds + \left(\hat{\mu} - \frac{1}{2}v^2\right)d\rho + \boldsymbol{v} \cdot d\boldsymbol{M} \tag{7}$$

and the Euler equation takes the form

$$e + p = sT + \left(\hat{\mu} - \frac{1}{2}v^2\right)\rho + \boldsymbol{v} \cdot \boldsymbol{M} \tag{8}$$

The expressions in (7) and (8) identify $\boldsymbol{v}$ as an intensive thermodynamic variable.

The simplest way to ensure the entropy source term in (6) is nonnegative is to make it a quadratic form by choosing

the force-flux relations to be linear. For the energy flux, we have

$$\boldsymbol{j}_q = -\lambda \nabla T \tag{9}$$

where λ is the thermal conductivity, and for the extra pressure tensor

$$\boldsymbol{\tau} = -\eta \left[\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T - \frac{2}{3}(\nabla \cdot \boldsymbol{v})\boldsymbol{\delta}\right] \tag{10}$$

where η is the shear viscosity (note that for convenience we have excluded a contribution from bulk viscosity). The famous constitutive equations in (9) and (10) are known as Fourier's law and Newton's law of viscosity, respectively. Combining (9) and (10) with the balance equations in (2) and (4) and using (1) gives the following

$$\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) = \eta\nabla^2\boldsymbol{v} + \frac{1}{3}\eta\nabla(\nabla \cdot \boldsymbol{v}) - \left(\frac{\partial p}{\partial \rho}\right)_T \nabla\rho - \left(\frac{\partial p}{\partial T}\right)_\rho \nabla T \tag{11}$$

$$\rho\hat{c}_{\hat{v}}\left(\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \nabla T\right) = \lambda\nabla^2 T - T\left(\frac{\partial p}{\partial T}\right)_\rho (\nabla \cdot \boldsymbol{v})$$
$$+ \eta\left[\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T - \frac{2}{3}(\nabla \cdot \boldsymbol{v})\boldsymbol{\delta}\right] : \nabla \boldsymbol{v} \tag{12}$$

where we have taken η and λ to be constant. The volumetric properties of the bulk phase fluid are obtained from an equation of state $\rho = \rho(T, p)$, and $\hat{c}_{\hat{v}}$ (constant-volume specific heat) is obtained from a second-order derivative of the thermodynamic potential. The equations in (1), (11), and (12) are a set of three equations that govern ρ, $\boldsymbol{v}$, and T. Note that the equation governing ρ is first order and those governing $\boldsymbol{v}$ and T are second order. Hence, at the interface between two interacting bulk phases, one boundary condition is required relating the densities of the two phases, and two boundary conditions each are required relating the velocities and temperatures of the two phases.

Our goal is to formulate balance equations for interfaces that separate bulk phases. Interfacial balance equations are essential for prescribing boundary conditions at phase interfaces. A number questions immediately come to mind. For example, how does one formulate balance equations at surfaces that in general are not stationary, and do interfaces themselves possess fields analogous to the mass, momentum, and energy densities used to describe bulk phases? Also, how does one handle the large differences in densities that exist near the interface? A number of approaches have been used to address some of these issues in the formulation of balance equations for interfaces. Typically, these approaches are based on the idea of an interface with a small, but finite, thickness, and then taking the limit of vanishing thickness. Extensive treatments of this and similar types of approaches can be found in several books.[3–5] A nonequilibrium thermodynamic description of interfaces based on the Gibbs[6] approach has been developed by Bedeaux et al.[7,8] and the implications of local equilibrium at interfaces has been explored recently.[9] The approach we use here is based more on intuition and the experience gained from developing transport equations for bulk phases using thermodynamics as a guide. To illustrate this nonstandard approach, we consider one-component systems. The formulation of interface balance equations for multicomponent systems will be discussed in a future publication.

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*It is more common[1] to write balance equations using per unit mass quantities rather than as per unit volume (densities). For a density a, the per unit mass (specific) quantity is given by $\hat{a} = a/\rho$.

†A detailed discussion of the inconsistencies resulting from the inclusion of a diffusive mass flux in single component systems can be found elsewhere.[2] Hence, throughout this development we take $\boldsymbol{j}_\rho = \boldsymbol{0}$.

Dividing Surfaces and Normal Velocities

Suppressing two lateral dimensions, the idealization of an interface as a surface of discontinuity between two bulk phases is illustrated in Figure 1. Instead of a continuous density profile that changes within a few nanometers from the value of one bulk phase to the value of another bulk phase, we assume that the two bulk phases touch in the surface of discontinuity. The precise choice of the location of this *dividing surface* within the interfacial region is not unique. A possible procedure to fix the position is to postulate that the total masses obtained by integrating the two profiles in Figure 1 are exactly equal. Whereas this definition looks quite natural, things are not really so simple. For example, for a multicomponent system, the proposed construction works only for one selected species of particles. For any other species, we expect an excess mass density at the interface, which is defined as the mass obtained from the true continuous profile minus the mass from the discontinuous idealization per unit area. Such excess densities, which can be associated with all extensive properties, depend on the precise location of the interface. Note that these excess quantities are accumulated in the interface; therefore, a corresponding surface density should be defined as the amount of the quantity per unit area instead of the amount per unit volume occurring naturally in the usual bulk density. Whereas excess densities are ambiguous under small displacements of the interface, relationships between excess densities may be unambiguous, thus containing important physical information. We call a small displacement of the interface, which leads to changes of the various excess densities, a *gauge transformation*. We refer to properties that are not affected by the precise location of the interface as *gauge invariant*. The gauge degree of freedom is a result of the Gibbs phase rule, which implies that one physical degree of freedom is lost for the coexistence of two phases. For three coexisting phases, we would have two gauge degrees of freedom for the contact line.

In the words of Gibbs,[6] "It will be observed that the position of this [dividing] surface is as yet to a certain extent arbitrary." Excess quantities "are determined partly by the state of the physical system which we are considering, and partly by the various imaginary surfaces by means of which these quantities have been defined."
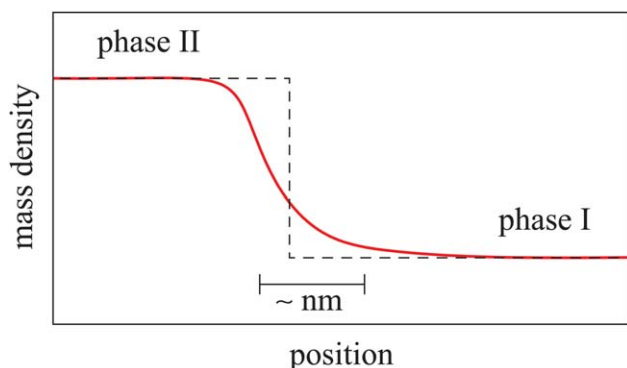

Figure 1. True continuous density profile (continuous line) and an idealized profile for two bulk phases touching in a surface of discontinuity (dashed line).

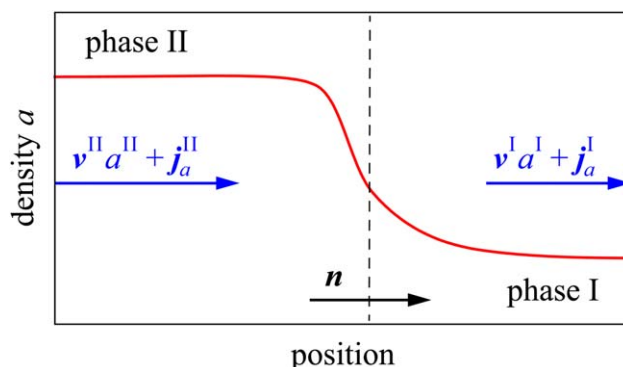[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Density profile of a conserved quantity; as a consequence of a net accumulation of that quantity in the interfacial region, the dividing surface for $a^s=0$ (dashed line) moves to the right.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We are interested in nonstationary interfaces that interact with the two bulk phases with which they are in contact. This situation is shown schematically in Figure 2 where we arbitrarily choose the unit normal $\boldsymbol{n}$ to the surface so that it points into phase I and out of phase II. What happens if we move the dividing surface in Figure 2 by a distance ℓ to the right? Of course, the integral under the continuous curve does not change. The integral under the dashed profile increases by $\ell(\rho^{II}-\rho^I)$, where ρ^I and ρ^{II} are the mass densities of the two bulk phases at the interface. Hence, displacing the dividing surface a distance ℓ results in a change in the excess mass density $\rho^s \rightarrow \rho^s+\ell(\rho^I-\rho^{II})$, which is a gauge transformation. Note that ℓ times volume density has the proper dimensions of a surface density. For any excess density a^s, we have the gauge transformation

$$a^s \rightarrow a^s+\ell(a^I-a^{II}) \tag{13}$$

If the interface is not planar, then the gauge transformation is generalized to the following

$$a^s \rightarrow a^s+\ell(a^I-a^{II}-a^s\mathbf{V}_\parallel \cdot \boldsymbol{n}) \tag{14}$$

where $\mathbf{V}_\parallel$ is the surface gradient, or surface Nabla, operator.[‡]

We are interested in balance equations for the excess densities of mass ρ^s, momentum $\boldsymbol{M}^s$, internal energy u^s, and entropy s^s. As we just discussed, all these quantities are ambiguous, because they depend on the choice of the dividing surface. To obtain unambiguous equations, we would need to look at the evolution of quantities like u^s in the gauge fixed by $\rho^s=0$. To avoid the need to consider two balances simultaneously, we start with a simpler question: How can we determine the velocity of the evolving surface for which a particular excess density vanishes at all times?

For any density a of a conserved extensive quantity, we consider the surface for which the corresponding excess density vanishes, $a^s=0$, and study the motion of this particular surface. For the special case of a planar homogeneous interface, the normal velocity v_{na}^s of the surface defined by $a^s=0$ at all times is given by

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[‡]$\mathbf{V}_\parallel$ can formally be written as the projection of $\mathbf{V}$ onto a surface with unit normal $\boldsymbol{n}$, $\mathbf{V}_\parallel=(\boldsymbol{\delta}-\boldsymbol{nn}) \cdot \mathbf{V}=\boldsymbol{\delta}_\parallel \cdot \mathbf{V}$; note, however, that for fields only defined in the interface, the full $\mathbf{V}$ is undefined, whereas differentiations in tangential directions are possible. Also note that $\mathbf{V}_\parallel \cdot \boldsymbol{n}=-2H$, where H is the mean curvature of the surface.

$$v_{na}^s(a^{II}-a^I)=\boldsymbol{n}\cdot(\boldsymbol{v}^{II}a^{II}+\boldsymbol{j}_a^{II}-\boldsymbol{v}^Ia^I-\boldsymbol{j}_a^I) \qquad (15)$$

The right-hand side of (15) represents the flux of a coming from the bulk phases into the interfacial region, split into the convective contribution $\boldsymbol{v}a$ and the diffusive contribution $\boldsymbol{j}_a$ known from the balance equations for each bulk phase. If, as suggested in Figure 2, the net effect is an inflow of a into the interfacial region, the bulk phase with the higher value of a expands at the expense of that with the lower value of a, where the required positive value of the normal velocity v_{na}^s is given by (15).

For an inhomogeneous interface, the surface defined by a^s $=0$ is no longer planar and its normal velocity may be affected by transport processes taking place within the interface. We hence generalize (15) to

$$v_{na}^s(a^{II}-a^I)=\boldsymbol{n}\cdot(\boldsymbol{v}^{II}a^{II}+\boldsymbol{j}_a^{II}-\boldsymbol{v}^Ia^I-\boldsymbol{j}_a^I)-\nabla_{\|}\cdot\boldsymbol{j}_a^s \qquad (16)$$

where the tangential vector field $\boldsymbol{j}_a^s$ is the interface analogue of the bulk conductive fluxes $\boldsymbol{j}_a^I,\boldsymbol{j}_a^{II}$. Note that a convection term in the interface would not make any sense in the present discussion because we look at the surface with $a^s=0$. Source terms can be included for densities such as entropy (and species mass for multicomponent systems).

By applying (16) to the exchange of mass and momentum between the bulk and the interfacial region, we obtain

$$v_{n\rho}^s(\rho^{II}-\rho^I)=\boldsymbol{n}\cdot(\boldsymbol{v}^{II}\rho^{II}-\boldsymbol{v}^I\rho^I) \qquad (17)$$

and

$$v_{nM}^s(\boldsymbol{M}^{II}-\boldsymbol{M}^I)=\boldsymbol{n}\cdot(\boldsymbol{v}^{II}\boldsymbol{M}^{II}+\boldsymbol{\pi}^{II}-\boldsymbol{v}^I\boldsymbol{M}^I-\boldsymbol{\pi}^I)-\nabla_{\|}\cdot\boldsymbol{\pi}^s \qquad (18)$$

where the symmetric momentum flux tensor $\boldsymbol{\pi}^s$ is purely transverse. In writing (17), we have, based on the lesson from bulk phases, taken $\boldsymbol{j}_\rho^s=\boldsymbol{0}$.

The Interface Velocity

We have just seen that there are a multitude of interface normal velocities corresponding to different dividing surfaces where one of the extensive excess densities is zero. Are any of these velocities special, and is it possible to identify $\boldsymbol{v}^s$, the full velocity vector of the interface? To answer these questions, we define $\boldsymbol{v}^s=\boldsymbol{M}^s/\rho^s$ to be the gauge invariant velocity of the interface. The gauge condition $\rho^s=0$ implies that also $\boldsymbol{M}^s$ must vanish for this gauge. Using this definition and applying the gauge transformation in (13) for $a^s=\rho^s$ and $a^s=\boldsymbol{M}^s$, we obtain

$$\frac{\boldsymbol{M}^I-\boldsymbol{M}^{II}}{\rho^I-\rho^{II}}=\boldsymbol{v}^s \qquad (19)$$

which is a nonequilibrium Clapeyron equation for the relative jumps of the momentum density vector and mass density.[9,10]

Taking the normal projection of (19) we obtain

$$\boldsymbol{n}\cdot(\boldsymbol{v}^I-\boldsymbol{v}^s)\rho^I=\boldsymbol{n}\cdot(\boldsymbol{v}^{II}-\boldsymbol{v}^s)\rho^{II} \qquad (20)$$

which, when compared to (17) indicates $v_{n\rho}^s=\boldsymbol{n}\cdot\boldsymbol{v}^s$. If we identify $v_{nM}^s=\boldsymbol{n}\cdot\boldsymbol{v}^s$, then (18) can be written as

$$\boldsymbol{n}\cdot[(\boldsymbol{v}^I-\boldsymbol{v}^s)\boldsymbol{M}^I+\boldsymbol{\pi}^I]=\boldsymbol{n}\cdot[(\boldsymbol{v}^{II}-\boldsymbol{v}^s)\boldsymbol{M}^{II}+\boldsymbol{\pi}^{II}]-\nabla_{\|}\cdot\boldsymbol{\pi}^s \qquad (21)$$

Equations 20 and 21 are known as the *jump mass balance* and *jump momentum balance*, respectively, which are easily obtained by more standard methods.[3-5]

From the definition of $\boldsymbol{v}^s$ in (19), it is possible to write the following

$$\boldsymbol{v}^I-\boldsymbol{v}^s=-\frac{\rho^{II}}{\rho^{II}-\rho^I}(\boldsymbol{v}^{II}-\boldsymbol{v}^I) \qquad (22)$$

and

$$\boldsymbol{v}^{II}-\boldsymbol{v}^s=-\frac{\rho^I}{\rho^{II}-\rho^I}(\boldsymbol{v}^{II}-\boldsymbol{v}^I) \qquad (23)$$

which show the velocity differences for each phase depend on the same jumps in velocity and density. Using (22) and (23), the jump momentum balance (21) can be rewritten in the alternative form

$$\left(\frac{1}{\rho^I}-\frac{1}{\rho^{II}}\right)^{-1}\boldsymbol{n}\cdot(\boldsymbol{v}^{II}-\boldsymbol{v}^I)(\boldsymbol{v}^{II}-\boldsymbol{v}^I)=\boldsymbol{n}\cdot(\boldsymbol{\pi}^{II}-\boldsymbol{\pi}^I)-\nabla_{\|}\cdot\boldsymbol{\pi}^s \qquad (24)$$

Equation 24 relates jumps in the pressure tensor to jumps in velocity and reciprocal density (that is, specific volume).

Note that there is no jump balance for the energy that would be analogous to the jump balances (20) and (21) for mass and momentum. The reason is that v_{ne}^s is different from $v_{n\rho}^s=v_n^s=\boldsymbol{n}\cdot\boldsymbol{v}^s$. Although the difference between these velocities must be small because the distance between the surfaces with $\rho^s=0$ and $e^s=0$ is of the order of the interfacial thickness, this difference is exactly what matters for the evolution of the interfacial energy in the gauge $\rho^s=0$. The physical relevance of the small difference $v_{ne}^s-v_{n\rho}^s$ is a consequence of the fact that we are dealing with ambiguous variables, each of which can be made to vanish by a proper choice of the dividing surface within the interfacial region, but one cannot make all these small excess quantities vanish simultaneously.

We next introduce a splitting of the velocity $\boldsymbol{v}^s$ into translational and deformational parts, $\boldsymbol{v}_{tr}^s$ and $\boldsymbol{v}_{def}^s$, which is motivated by the wish to introduce partial time derivatives of fields living in the interface. We are then faced with the problem of defining a time derivative at a "fixed" position although the interface is moving. Such a concept requires a given mapping of equivalent points of the interface at different times.[4] Instead of a global mapping, we equivalently introduce the velocity $\boldsymbol{v}_{tr}^s$ associated with a trajectory of equivalent points (see Figure 3) and write

$$\boldsymbol{v}^s=\boldsymbol{v}_{tr}^s+\boldsymbol{v}_{def}^s \qquad (25)$$

The conditions that equivalent points follow the interface and that the deformation takes place within the interface are expressed by

$$\boldsymbol{n}\cdot\boldsymbol{v}_{tr}^s=\boldsymbol{n}\cdot\boldsymbol{v}^s, \quad \boldsymbol{n}\cdot\boldsymbol{v}_{def}^s=0 \qquad (26)$$

The minimalist way of "following the interface" is given by the normal-parallel splitting

$$\boldsymbol{v}_{tr}^s=\boldsymbol{n}\boldsymbol{n}\cdot\boldsymbol{v}^s=v_n^s\boldsymbol{n}, \quad \boldsymbol{v}_{def}^s=(\boldsymbol{\delta}-\boldsymbol{n}\boldsymbol{n})\cdot\boldsymbol{v}^s=\boldsymbol{v}_{\|}^s \qquad (27)$$

Whereas we mostly assume the splitting (27), other choices are possible. A simple situation in which we would choose a different splitting is given by the uniform motion of a nondeforming interface; in that situation we would clearly choose $\boldsymbol{v}_{tr}^s=\boldsymbol{v}^s$, so that $\boldsymbol{v}_{def}^s=\boldsymbol{0}$. An important ingredient in the general splitting expressed in (25) and (26) is that uniform motion affects only $\boldsymbol{v}_{tr}^s$ so that our equations are Galilean invariant.
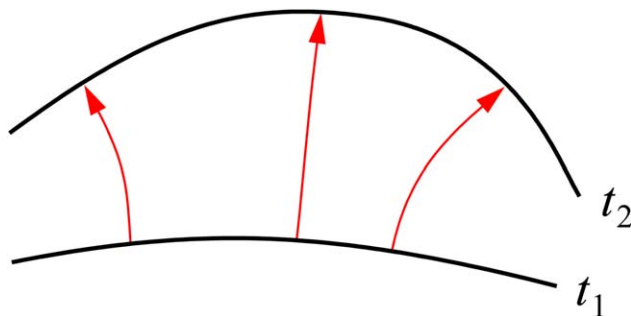
Figure 3. Instead of mapping equivalent points of a continuously deforming interface at two times t_1 and t_2 (thick lines), we can alternatively look at the trajectories associated with equivalent points (thin arrows) and their time derivatives providing the translational velocity field v_{tr}^s.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We are now in a position to introduce a surface partial time derivative by following the interface without deformation, symbolically expressed as

$$\frac{\partial^s}{\partial t} = \frac{\partial}{\partial t} + v_{tr}^s \cdot \nabla_{\parallel} \qquad (28)$$

Note that Eq. 28 is merely a formal equation because strictly speaking the partial derivative on the right-hand side has no meaning. This equation is only meant to express the idea that for a surface partial time derivative we need to follow the equivalent points in the spirit of a substantial or material time derivative. For the splitting in (27), the partial time derivative in (28) is taken at a position within the interface that is "as constant as possible."

Energy and Entropy Evolution Equations

As pointed out before, the normal velocity v_{na}^s associated with the density of some extensive surface density a^s can be different from $v_{n\rho}^s = v_{nM}^s = v_n^s$. This difference can be translated into a rate of change of the excess density for the gauge with $\rho^s = 0$. The rate of change of a^s at a fixed position on the interface can be expressed as follows

$$\frac{\partial^s a^s}{\partial t} = \left(v_{na}^s - v_n^s\right)\left(a^{II} - a^I\right) - \nabla_{\parallel} \cdot \left(v_{def}^s a^s\right) - a^s \nabla_{\parallel} \cdot v_{tr}^s \qquad (29)$$

According to (16), $v_{na}^s(a^{II} - a^I)$ is the amount of an extensive quantity that accumulates in the interfacial region; in (29), the effect of the moving reference surface is subtracted. The last two terms in (29) correspond to convection in the interface and to a relative change of surface area, which leads to an inverse relative change of any surface density.[§]

By applying (16) to the total energy density e, we find

$$v_{ne}^s(e^{II} - e^I) = n \cdot (v^{II}e^{II} + j_q^{II} + \pi^{II} \cdot v^{II} - v^I e^I - j_q^I - \pi^I \cdot v^I)$$
$$- \nabla_{\parallel} \cdot (j_q^s + \pi^s \cdot v^s) \qquad (30)$$

For the entropy balance one should take into account that the passage of entropy from the bulk into the interfacial region, as well as a flow j_s^s within the interface, both naturally accompanied by an additional entropy production rate

[§]Note that only for the normal-parallel splitting in (27) we can write: $\nabla_{\parallel} \cdot (v_{def}^s a^s) + a^s \nabla_{\parallel} \cdot v_{tr}^s = \nabla_{\parallel} \cdot (v^s a^s)$.

σ^s resulting from dissipative processes in and around the interface

$$v_{ns}^s(s^{II} - s^I) = n \cdot \left(v^{II}s^{II} + \frac{j_q^{II}}{T^{II}} - v^I s^I - \frac{j_q^I}{T^I}\right) - \nabla_{\parallel} \cdot j_s^s + \sigma^s \qquad (31)$$

By applying (29) to the total energy density and using (30), we arrive at

$$\frac{\partial^s e^s}{\partial t} = n \cdot [(v^{II} - v^s)e^{II} + j_q^{II} + \pi^{II} \cdot v^{II} - (v^I - v^s)e^I - j_q^I - \pi^I \cdot v^I]$$
$$- \nabla_{\parallel} \cdot (v_{def}^s e^s + j_q^s + \pi^s \cdot v^s) - e^s \nabla_{\parallel} \cdot v_{tr}^s \qquad (32)$$

Note that we have used the reference velocity v^s corresponding to the gauge $\rho^s = 0$. Similarly, applying (29) to the entropy density, (31) can be rewritten as an entropy balance equation

$$\frac{\partial^s s^s}{\partial t} = n \cdot \left[(v^{II} - v^s)s^{II} + \frac{j_q^{II}}{T^{II}} - (v^I - v^s)s^I - \frac{j_q^I}{T^I}\right]$$
$$- \nabla_{\parallel} \cdot \left(v_{def}^s s^s + j_s^s\right) - s^s \nabla_{\parallel} \cdot v_{tr}^s + \sigma^s \qquad (33)$$

again in the gauge fixed by the condition $\rho^s = 0$.

It is worthwhile to make some observations about the structure of the interface balance equations we have just formulated. More specifically, let us compare the balance equations for energy and entropy in the bulk, (3) and (5), with their interfacial counterparts in (32) and (33). The left-hand sides express the time rate of change of a density—at a fixed point in space for the bulk equations; at a fixed point on the surface for the interface equations. Notice that going from the bulk to the interface, terms corresponding to divergences of fluxes $-\nabla \cdot (..)$ appear in two forms: one is a surface divergence $-\nabla_{\parallel} \cdot (..)$ and the second as a difference $n \cdot [(..)^{II} - (..)^I]$, where motion of the surface is subtracted off the convective part. Terms of the form $a^s \nabla_{\parallel} \cdot v_{tr}^s$ in (32) and (33), which do not have counterparts in the bulk, describe changes in an excess density due to changes in surface area. The absence of time derivatives and convective transport within the interface in (20) and (21) is a consequence of these being formulated in the gauge where $\rho^s = 0$.

Local Equilibrium Assumption

In addition to the jump balance for mass and momentum, we now have evolution equations for the energy and entropy densities that characterize the physics of the interface. Up to this point, our discussion about interfaces has been based entirely on balancing and gauge transformations. We now introduce the idea of local equilibrium thermodynamics to relate the excess energy and entropy densities to temperature and interfacial tension.

Analogous to bulk systems, one can write the Euler equation and fundamental form for the interface in global equilibrium[9]

$$u^s = Ts^s + \gamma + \hat{\mu}\rho^s \qquad (34)$$

and

$$du^s = Tds^s + \hat{\mu}d\rho^s \qquad (35)$$

where $\gamma = -p^s$ is the interfacial tension, which does not appear in (35). Whereas these fundamental equations for interfaces look very similar to those for bulk phases, it should be noted that they relate the well-defined intensive quantities T, γ, $\hat{\mu}$,

and the ambiguous or gauge variant excess densities u^s, s^s, ρ^s. The ambiguity of the excess densities is related to the fact that, according to the Gibbs phase rule, one independent physical variable is lost because of the coexistence of two phases. If we still use the same set of variables in (34) and (35), there must exist one ambiguous degree of freedom for the interfaces between coexisting bulk phases.

To formulate the gauge invariance of the interfacial tension, we write (34) as follows

$$\gamma = e^s - T^s s^s - \left(\hat{\mu}^s + \frac{1}{2} v^{s2}\right)\rho^s \qquad (36)$$

Gauge invariance of γ can then be expressed in the following form resulting from the transformation law in (14)

$$e^{II} - e^I - T^s(s^{II} - s^I) - \left(\hat{\mu}^s + \frac{1}{2} v^{s2}\right)(\rho^{II} - \rho^I) = -\gamma \boldsymbol{\nabla}_\| \cdot \boldsymbol{n} \quad (37)$$

which one can recognize as a nonequilibrium generalization of the Young–Laplace equation. At equilibrium, $v^I = v^{II} = v^s = \boldsymbol{0}$, $T^I = T^{II} = T^s$, and $\hat{\mu}^I = \hat{\mu}^{II} = \hat{\mu}^s$, so that (37) reduces to the following: $p^{II} - p^I = \gamma \boldsymbol{\nabla}_\| \cdot \boldsymbol{n}$. This result is also obtained from the jump momentum balance (21) for a system at equilibrium. Note that (37) also guarantees the gauge invariance of the fundamental form for total excess energy, which is given by: $e^s = u^s + \frac{1}{2}\rho^s v^{s2}$. Hence, using (35) and $v^s = \boldsymbol{M}^s/\rho^s$, we obtain

$$de^s = T^s ds^s + \left(\hat{\mu}^s - \frac{1}{2} v^{s2}\right)d\rho^s + v^s \cdot d\boldsymbol{M}^s \qquad (38)$$

which is clearly the surface analog of (7). The gauge invariance condition (37) hence is of a crucial importance for our development of interface balance equations under the local equilibrium assumption.

As a next step, we use the fundamental form (38) to determine the entropy production rate σ^s occurring in the interfacial entropy balance equation (33). As we have already established the gauge invariance of (38), we can now apply it in the gauge $\rho^s = 0$, which gives

$$\frac{\partial^s e^s}{\partial t} = T^s \frac{\partial^s s^s}{\partial t} \qquad (39)$$

Substitution of (32) and (33) in (39) and assuming $j_s^s = j_q^s/T^s$, we obtain the following expression for the entropy production rate

$$\begin{aligned}
\sigma^s &= \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1} \boldsymbol{n} \cdot \left\{\frac{1}{\rho^{II}}\left[(e^{II} - T^s s^{II} - v^s \cdot \boldsymbol{M}^{II})\boldsymbol{\delta} + \boldsymbol{\pi}^{II}\right]\right.\\
&\quad \left. - \frac{1}{\rho^I}[(e^I - T^s s^I - v^s \cdot \boldsymbol{M}^I)\boldsymbol{\delta} + \boldsymbol{\pi}^I]\right\} \cdot (v^{II} - v^I)\\
&\quad + j_q^{II} \cdot \boldsymbol{n}\left(\frac{1}{T^s} - \frac{1}{T^{II}}\right) - j_q^I \cdot \boldsymbol{n}\left(\frac{1}{T^s} - \frac{1}{T^I}\right)\\
&\quad + j_q^s \cdot \boldsymbol{\nabla}_\| \frac{1}{T^s} - \frac{1}{T^s}\boldsymbol{\tau}^s : \boldsymbol{\nabla}_\| v^s
\end{aligned}$$

$$(40)$$

This result has been simplified by the following decomposition of the surface pressure tensor: $\boldsymbol{\pi}^s = -\gamma\boldsymbol{\delta}_\| + \boldsymbol{\tau}^s$, where $\boldsymbol{\tau}^s$ is the transverse excess surface stress tensor. Recall that the isotropic part of the pressure tensor is positive for bulk phases, whereas the "isotropic" contribution for the interface is negative. Note that the entropy production rate in (40) contains only gauge-invariant surface quantities T^s and v^s.

It is convenient to rewrite the entropy production rate in (40), using (22) and (23) and the Euler relation to eliminate entropy, in the equivalent form

$$\begin{aligned}
\sigma^s &= \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\left[T^s\left(\frac{\hat{\mu}^{II}}{T^{II}} - \frac{\hat{\mu}^I}{T^I}\right) + \frac{1}{2}\frac{\rho^I + \rho^{II}}{\rho^I - \rho^{II}}(v^{II} - v^I)^2\right.\\
&\quad \left. + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot \boldsymbol{n}\right](v^{II} - v^I) \cdot \boldsymbol{n}\\
&\quad + \frac{1}{T^s}\left(\frac{1}{\rho^{II}} - \frac{1}{\rho^I}\right)^{-1}\boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{II}}{\rho^{II}} - \frac{\boldsymbol{\tau}^I}{\rho^I}\right) \cdot (v^{II} - v^I)_\|\\
&\quad + [(v^{II} - v^s)h^{II} + j_q^{II}] \cdot \boldsymbol{n}\left(\frac{1}{T^s} - \frac{1}{T^{II}}\right)\\
&\quad - [(v^I - v^s)h^I + j_q^I] \cdot \boldsymbol{n}\left(\frac{1}{T^s} - \frac{1}{T^I}\right)\\
&\quad + j_q^s \cdot \boldsymbol{\nabla}_\| \frac{1}{T^s} - \frac{1}{T^s}\boldsymbol{\tau}^s : \boldsymbol{\nabla}_\| v^s
\end{aligned}$$

$$(41)$$

Note that in the above expression we have also decomposed the velocity jump into normal and tangential components.

We have chosen the gauge $\rho^s = 0$, where $e^s = u^s$, so that the evolution equation for u^s is taken over from (32)

$$\begin{aligned}
\frac{\partial^s u^s}{\partial t} &= \boldsymbol{n} \cdot [(v^{II} - v^s)e^{II} + j_q^{II} + \boldsymbol{\pi}^{II} \cdot v^{II} - (v^I - v^s)e^I - j_q^I - \boldsymbol{\pi}^I \cdot v^I]\\
&\quad - \boldsymbol{\nabla}_\| \cdot (v_{def}^s u^s + j_q^s + \boldsymbol{\pi}^s \cdot v^s) - u^s \boldsymbol{\nabla}_\| \cdot v_{tr}^s
\end{aligned}$$

$$(42)$$

It is important to note that, contrary to the procedure used to derive (4) for a bulk phase, (42) is not obtained by subtracting from the total energy the mechanical energy. For this reason, important elements of structural consistency discussed earlier are lost between (4) and (42). Note that the balance equation in (42) has also been obtained by an alternative method.[4] A commonly used approximate form of (42), obtained when interfacial terms are neglected, is the *jump energy balance*

$$\begin{aligned}
&\boldsymbol{n} \cdot \left[(v^I - v^s)\left(h^I + \frac{1}{2}\rho^I v^{I2}\right) + j_q^I + \boldsymbol{\tau}^I \cdot v^I\right]\\
&= \boldsymbol{n} \cdot \left[(v^{II} - v^s)\left(h^{II} + \frac{1}{2}\rho^{II} v^{II2}\right) + j_q^{II} + \boldsymbol{\tau}^{II} \cdot v^{II}\right]
\end{aligned} \qquad (43)$$

where $h = u + p$ is the enthalpy density.

Before proceeding to the formulation of constitutive equations, we note that the jump momentum balance (21), or (24), can using $\boldsymbol{\pi}^s = -\gamma\boldsymbol{\delta}_\| + \boldsymbol{\tau}^s$ be rewritten as follows

$$\begin{aligned}
&\left(\frac{1}{\rho^I} - \frac{1}{\rho^{II}}\right)^{-1}\boldsymbol{n} \cdot (v^{II} - v^I)(v^{II} - v^I) = \boldsymbol{n} \cdot (\boldsymbol{\tau}^{II} - \boldsymbol{\tau}^I)\\
&\quad + (p^{II} - p^I)\boldsymbol{n} - \gamma(\boldsymbol{\nabla}_\| \cdot \boldsymbol{n})\boldsymbol{n} + \boldsymbol{\nabla}_\|\gamma - \boldsymbol{\nabla}_\| \cdot \boldsymbol{\tau}^s
\end{aligned} \qquad (44)$$

This form of the jump momentum balance shows the Young–Laplace equation in the second and third terms on the right-hand side, and the fourth term is the tangential force due to variations of the interfacial tension, which is known as the Marangoni force.

Constitutive Equations

In Introduction, we discussed how an analysis of the entropy production can be used to formulate constitutive equations. We here use the same idea for the entropy production in and at the interface. The simplest way to

guarantee that the entropy production is nonnegative is to make each of the contributions in (41) nonnegative. The result for the constitutive assumptions will depend on our particular way of writing the entropy production rate.

The last two terms on the right-hand side of (41), which are clear analogs of the force-flux products in (6), are entropy production terms resulting from transport within the interface. To ensure these terms are nonnegative, we assume linear expressions for $\boldsymbol{j}_q^{\mathrm{s}}$ and $\boldsymbol{\tau}^{\mathrm{s}}$

$$\boldsymbol{j}_q^{\mathrm{s}} = -\lambda^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} T^{\mathrm{s}} \tag{45}$$

where λ^{s} is the thermal conductivity of the interface, and

$$\boldsymbol{\tau}^{\mathrm{s}} = -\eta^{\mathrm{s}} \left[(\boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{\delta}_{\parallel} + \boldsymbol{\delta}_{\parallel} \cdot (\boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}})^T - (\boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}^{\mathrm{s}}) \boldsymbol{\delta}_{\parallel} \right] \tag{46}$$

where η^{s} is the viscosity of the interface. The transport coefficients λ^{s} and η^{s} for the interface must, of course, be nonnegative. The expression in (46) is a special case of the Boussinesq interfacial fluid model; as with the bulk, alternative interfacial rheological constitutive equations are possible.[3,11] The diffusive transport (conduction) of energy within an interface described by (45) does not appear to have been investigated and is usually neglected.

The remaining terms in (41) can also be recognized as force-flux products that account for entropy produced due to transport between the bulk phases and interface. Note that the forces are expressed in terms of differences rather than gradients, and that the term involving the jump in tangential components of velocity is of a different tensorial order than all other terms. We hence handle this term separately, which can be made nonnegative using the following expression

$$(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})_{\parallel} = \boldsymbol{\xi}_{\parallel} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}} \right) \cdot \boldsymbol{n} \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}} \right)^{-1} \tag{47}$$

where $\boldsymbol{\xi}_{\parallel}$ is a transverse mobility coefficient tensor characterizing slip. The entropy source terms in (41) involving the jump in normal velocity components and temperature jumps all have the same tensorial order (scalar). The most general approach to ensure nonnegative entropy production is to allow coupling of force-flux pairs in the form of Onsager relations. Here, we choose, somewhat arbitrarily, to exclude couplings between mass and energy in formulating constitutive equations for an interface. Hence, we write the following constitutive equation for the normal component of velocity

$$(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}}) \cdot \boldsymbol{n} = \xi_n \left[T^{\mathrm{s}} \left(\frac{\hat{\mu}^{\mathrm{II}}}{T^{\mathrm{II}}} - \frac{\hat{\mu}^{\mathrm{I}}}{T^{\mathrm{I}}} \right) + \frac{1}{2} \frac{\rho^{\mathrm{I}} + \rho^{\mathrm{II}}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}} (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})^2 \right. \\ \left. + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}} \right) \cdot \boldsymbol{n} \right] \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}} \right)^{-1} \tag{48}$$

where ξ_n is a coefficient characterizing the phase conversion process. For the energy flux-temperature difference terms in (41), we ensure nonnegativity by assuming the following constitutive equations

$$T^{\mathrm{I}} - T^{\mathrm{s}} = -R_{\mathrm{K}}^{\mathrm{Is}} [(\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{I}} + \boldsymbol{j}_q^{\mathrm{I}}] \cdot \boldsymbol{n} \tag{49}$$

$$T^{\mathrm{II}} - T^{\mathrm{s}} = R_{\mathrm{K}}^{\mathrm{IIs}} [(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{II}} + \boldsymbol{j}_q^{\mathrm{II}}] \cdot \boldsymbol{n} \tag{50}$$

where the Kapitza resistances $R_{\mathrm{K}}^{\mathrm{Is}}$ and $R_{\mathrm{K}}^{\mathrm{IIs}}$ characterize heat flow through the interface.[††] It is important to emphasize that less ambiguous, and more general, constitutive equations could be obtained by including cross effects. Constitutive equations having forms similar to those in (47)–(50) have been developed using a different approach.[5]

It is natural that the difference in chemical potential divided by temperature between the bulk phases occurs in the phase conversion rate in (48), with some mechanical modifications. If $\xi_n = 0$, there is no mass transfer across the interface, and from (22) and (23) we have

$$\boldsymbol{v}^{\mathrm{I}} \cdot \boldsymbol{n} = \boldsymbol{v}^{\mathrm{II}} \cdot \boldsymbol{n} = \boldsymbol{v}^{\mathrm{s}} \cdot \boldsymbol{n} \tag{51}$$

which means the normal components of velocity are continuous across the interface. The slip law (47) may be considered as purely mechanical, and it involves bulk properties only. If $\boldsymbol{\xi}_{\parallel} = \boldsymbol{0}_{\parallel}$, then, we have the *no-slip condition*

$$\boldsymbol{v}_{\parallel}^{\mathrm{II}} = \boldsymbol{v}_{\parallel}^{\mathrm{I}} \tag{52}$$

and the tangential components of velocity are continuous across the interface. If heat is produced in the interface, the constitutive assumptions (49) and (50) allow heat to flow into both bulk phases. If there is no resistance to heat flow $R_{\mathrm{K}}^{\mathrm{Is}} = R_{\mathrm{K}}^{\mathrm{IIs}} = 0$, then, we have

$$T^{\mathrm{I}} = T^{\mathrm{II}} = T^{\mathrm{s}} \tag{53}$$

or continuity of temperature at the interface. Although our derivation of all constitutive boundary conditions relies heavily on the local equilibrium assumption, one does not notice that in (47), which is independent of the state of the interface. The interfacial temperature T^{s} appears in (48)–(50), however, and the local equilibrium assumption obviously plays a crucial role.

As in the bulk, the evolution for T^{s} comes from the balance equation for internal energy. Using (21)–(23), we can write (42) as follows

$$\frac{\partial^{\mathrm{s}} u^{\mathrm{s}}}{\partial t} = -\boldsymbol{\nabla}_{\parallel} \cdot (\boldsymbol{v}_{\mathrm{def}}^{\mathrm{s}} u^{\mathrm{s}} + \boldsymbol{j}_q^{\mathrm{s}}) - u^{\mathrm{s}} \boldsymbol{\nabla}_{\parallel} \cdot \boldsymbol{v}_{\mathrm{tr}}^{\mathrm{s}} - \boldsymbol{\pi}^{\mathrm{s}} : \boldsymbol{\nabla}_{\parallel} \boldsymbol{v}^{\mathrm{s}} \\ + \boldsymbol{n} \cdot [(\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{II}} + \boldsymbol{j}_q^{\mathrm{II}} - (\boldsymbol{v}^{\mathrm{I}} - \boldsymbol{v}^{\mathrm{s}}) h^{\mathrm{I}} - \boldsymbol{j}_q^{\mathrm{I}}] \\ + (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})_{\parallel} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}} \right) \cdot \boldsymbol{n} \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}} \right)^{-1} \\ + (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}}) \cdot \boldsymbol{n} \left[\frac{1}{2} \frac{\rho^{\mathrm{I}} + \rho^{\mathrm{II}}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}} (\boldsymbol{v}^{\mathrm{II}} - \boldsymbol{v}^{\mathrm{I}})^2 \right. \\ \left. + \boldsymbol{n} \cdot \left(\frac{\boldsymbol{\tau}^{\mathrm{II}}}{\rho^{\mathrm{II}}} - \frac{\boldsymbol{\tau}^{\mathrm{I}}}{\rho^{\mathrm{I}}} \right) \cdot \boldsymbol{n} \right] \left(\frac{1}{\rho^{\mathrm{II}}} - \frac{1}{\rho^{\mathrm{I}}} \right)^{-1} \tag{54}$$

Note the similarity between (4) and the first line of (54). The forth term on the right-hand side of (54) is a source due to a discontinuity in the tangential velocity (slip), and the last term is a source due to a discontinuity in the normal velocity (phase change). The temperature of the interface T^{s} follows most conveniently from the excess energy density u^{s} in the gauge $\rho^{\mathrm{s}} = 0$, which from (34) and (35) give $u^{\mathrm{s}} = \gamma - T^{\mathrm{s}} d\gamma / dT^{\mathrm{s}}$. Substitution for u^{s} along with (45) and (46) in (54) gives

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[††]The Kapitza resistance is usually introduced via the temperature difference rather than the difference of inverse temperatures.

$$-T^s \frac{d^2\gamma}{dT^{s2}}\left(\frac{\partial^s T^s}{\partial t}+\boldsymbol{v}^s_{\text{def}}\cdot\boldsymbol{\nabla}_\| T^s\right)=\lambda^s\nabla_\|^2 T^s+T^s\frac{d\gamma}{dT^s}\boldsymbol{\nabla}_\|\cdot\boldsymbol{v}^s_{\text{def}}$$

$$+\eta^s\left[(\boldsymbol{\nabla}_\|\boldsymbol{v}^s)\cdot\boldsymbol{\delta}_\|+\boldsymbol{\delta}_\|\cdot(\boldsymbol{\nabla}_\|\boldsymbol{v}^s)^T-(\boldsymbol{\nabla}_\|\cdot\boldsymbol{v}^s)\boldsymbol{\delta}_\|\right]:\boldsymbol{\nabla}_\|\boldsymbol{v}^s$$

$$+\gamma\boldsymbol{\nabla}_\|\cdot\boldsymbol{v}^s_{\text{tr}}+\boldsymbol{n}\cdot[(\boldsymbol{v}^{\text{II}}-\boldsymbol{v}^s)h^{\text{II}}+\boldsymbol{j}_q^{\text{II}}-(\boldsymbol{v}^{\text{I}}-\boldsymbol{v}^s)h^{\text{I}}-\boldsymbol{j}_q^{\text{I}}]$$

$$+(\boldsymbol{v}^{\text{II}}-\boldsymbol{v}^{\text{I}})_\|\cdot\left(\frac{\boldsymbol{\tau}^{\text{II}}}{\rho^{\text{II}}}-\frac{\boldsymbol{\tau}^{\text{I}}}{\rho^{\text{I}}}\right)\cdot\boldsymbol{n}\left(\frac{1}{\rho^{\text{II}}}-\frac{1}{\rho^{\text{I}}}\right)^{-1}$$

$$+(\boldsymbol{v}^{\text{II}}-\boldsymbol{v}^{\text{I}})\cdot\boldsymbol{n}\left[\frac{1}{2}\frac{\rho^{\text{I}}+\rho^{\text{II}}}{\rho^{\text{I}}-\rho^{\text{II}}}(\boldsymbol{v}^{\text{II}}-\boldsymbol{v}^{\text{I}})^2\right.$$

$$\left.+\boldsymbol{n}\cdot\left(\frac{\boldsymbol{\tau}^{\text{II}}}{\rho^{\text{II}}}-\frac{\boldsymbol{\tau}^{\text{I}}}{\rho^{\text{I}}}\right)\cdot\boldsymbol{n}\right]\left(\frac{1}{\rho^{\text{II}}}-\frac{1}{\rho^{\text{I}}}\right)^{-1}$$

$$(55)$$

where we have taken λ^s to be constant. Notice the similarity between (55) and (12), and one might identify the factor $-T^s\frac{d^2\gamma}{dT^{s2}}=T^s\frac{ds^s}{dT^s}$ as the heat capacity per unit area of the interface. A similar, but somewhat less general, evolution equation for interfacial temperature has been proposed.[12]

The jump mass balance (20) provides a relationship between ρ^{I} and ρ^{II}. The constitutive equations in (47) and (48) provide a boundary condition relating $\boldsymbol{v}^{\text{I}}$ and $\boldsymbol{v}^{\text{II}}$. The second boundary condition for velocity is given by the jump momentum balance (21) that, through the pressure tensor, relate both the pressure and gradient of velocity in each phase. The interfacial velocity $\boldsymbol{v}^s$ defined in (19) is determined from the bulk phase densities and velocities. Boundary conditions for T^{I} and T^{II} in terms of T^s and $\boldsymbol{v}^s$ are given in (49) and (50). The second boundary condition relating T^{I}, T^{II}, and T^s and their gradients is given in (55). Note that the gauge invariance condition (37) remains as an additional condition for the jumps of bulk densities involving the state of the interface; only at global equilibrium is this result redundant with (21). This condition expresses the validity or approximate validity of the local equilibrium assumption and needs to be checked separately.

Examples

Here, we consider several examples to demonstrate how boundary conditions can be formulated from the interface balance and constitutive equations developed in the previous sections. Let the interface separating Phases I and II be a spherical surface having unit normal $\boldsymbol{n}=\boldsymbol{\delta}_r$ and location $r=R$ (see Figure 4). For convenience, we take the density in each phase to be uniform so that we can write $\rho^{\text{I}}=\rho$ and $\rho^{\text{II}}=\bar{\rho}$, where ρ and $\bar{\rho}$ can still depend on time. Velocity and tem-
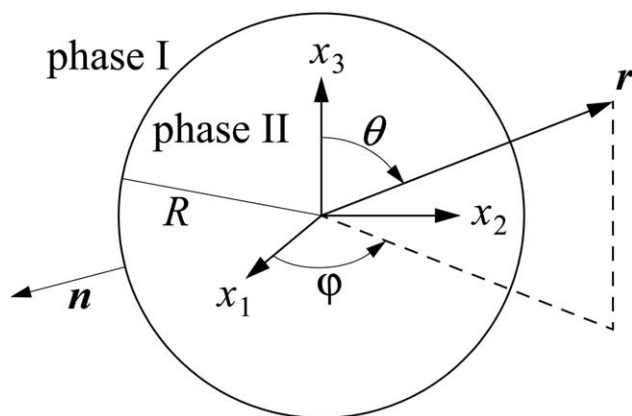

Figure 4. Schematic of spherical interface with unit normal n separating Phases I and II.

perature fields in each phase will be denoted as follows: $\boldsymbol{v}^{\text{I}}=\boldsymbol{v}(R), \boldsymbol{v}^{\text{II}}=\bar{\boldsymbol{v}}(R)$ and $T^{\text{I}}=T(R), T^{\text{II}}=\bar{T}(R)$, which emphasizes that fields in the bulk phases are evaluated at the interface. (The dependence of these fields on angular variables and/or time is not expressed explicitly.)

Momentum and energy transfer

We first consider a stationary ($\boldsymbol{v}^s\cdot\boldsymbol{n}=0$) and nondeforming ($\boldsymbol{v}^s_{\text{def}}=\boldsymbol{0}$) interface across which there is no mass transfer, and assume symmetry about the x_3-coordinate so that velocity and temperature fields are independent of ϕ. This situation occurs when a uniform velocity or temperature gradient is imposed far from the sphere. In the absence of mass transfer, the normal velocities are constrained by (51) and the jump mass balance is trivially satisfied. Hence, we have the boundary condition

$$v_r(R)=\bar{v}_r(R) \qquad (56)$$

For this case, the normal component of the jump momentum balance (44) gives

$$p(R)-2\eta\frac{\partial v_r}{\partial r}(R)=\bar{p}(R)-2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}(R)-2\frac{\gamma}{R} \qquad (57)$$

If we further assume γ is constant, the transverse component of (44) simplifies to the following: $\boldsymbol{n}\cdot\boldsymbol{\tau}^{\text{I}}\cdot\boldsymbol{\delta}_\|=\boldsymbol{n}\cdot\boldsymbol{\tau}^{\text{II}}\cdot\boldsymbol{\delta}_\|$; using (10), we can write the following boundary condition for the tangential velocity

$$\eta\left[\frac{\partial v_\theta}{\partial r}(R)-\frac{v_\theta(R)}{R}\right]=\bar{\eta}\left[\frac{\partial\bar{v}_\theta}{\partial r}(R)-\frac{\bar{v}_\theta(R)}{R}\right] \qquad (58)$$

where η and $\bar{\eta}$ are the viscosities of Phases I and II, respectively. To formulate a second boundary condition for the tangential velocity, we use the constitutive equation in (47) with an isotropic mobility coefficient given by $\boldsymbol{\xi}_\|=\xi_{\text{slip}}\boldsymbol{\delta}_\|$. Combining this with the transverse component of the jump momentum balance we obtain: $(\boldsymbol{v}^{\text{II}}-\boldsymbol{v}^{\text{I}})_\|=\xi_{\text{slip}}\boldsymbol{\delta}_\|\cdot\boldsymbol{\tau}^{\text{I}}\cdot\boldsymbol{n}$. Using (10), the relevant component of this result gives the boundary condition

$$v_\theta(R)-\bar{v}_\theta(R)=\xi_{\text{slip}}\eta\left[\frac{\partial v_\theta}{\partial r}(R)-\frac{v_\theta(R)}{R}\right] \qquad (59)$$

which is the well-known Navier-slip law. The product $\xi_{\text{slip}}\eta$ appearing in (59) is sometimes referred to as the "slip length," which is useful in describing flows of rarified gases and non-Newtonian fluids in contact with solid surfaces. It is remarkable that, in our approach, the Navier-slip law arises directly from an analysis of the entropy production at the interface.

We now examine thermal effects and formulate boundary conditions for temperature. For the case under consideration, the temperature equation (55) simplifies, using (9) and (59), to the following

$$\lambda\frac{\partial T}{\partial r}(R)=\bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R)-\frac{1}{\xi_{\text{slip}}}\left[v_\theta(R)-\bar{v}_\theta(R)\right]^2 \qquad (60)$$

where λ and $\bar{\lambda}$ are the thermal conductivities of Phases I and II, respectively. The remaining temperature boundary conditions are obtained from (49) and (50), which when combined with (60), gives the following

$$T(R)-\bar{T}(R)=(R_{\text{K}}^{\text{Is}}+R_{\text{K}}^{\text{IIs}})\lambda\frac{\partial T}{\partial r}(R)+\frac{R_{\text{K}}^{\text{IIs}}}{\xi_{\text{slip}}}\left[v_\theta(R)-\bar{v}_\theta(R)\right]^2 \qquad (61)$$

The boundary condition in (60) shows that frictional heating due to imperfect slip leads to a discontinuity in energy flux,

and the boundary condition in (61) shows that interfacial resistances and slip can lead to a discontinuity in temperature, at an interface. For this example, we require two boundary conditions each for the two components of velocity and temperature fields in the bulk (for a total of six), which are given in (56)–(61). No boundary condition for the mass density is required because we have assumed uniform density in the bulk phases.

Mass and energy transfer

For our second example, we consider a homogeneous and nondeforming ($v^s_{def}=0$) interface at which there is mass transfer (phase change). The interface velocity has only a normal component $v^s \cdot n = dR/dt$. Here, we assume spherical symmetry so that fields depend only on radial position r and velocity in the bulk phases is purely radial. This example is applicable to the growth or collapse of a spherical particle or bubble in an otherwise stationary fluid. The jump mass balance (20) takes the form

$$v_r(R)-\frac{dR}{dt}=\epsilon\left(\bar{v}_r(R)-\frac{dR}{dt}\right) \qquad (62)$$

where $\epsilon=\bar{\rho}/\rho$ is the ratio of densities. The normal component of the jump momentum balance (44) can, neglecting inertia (left-hand side), be written as

$$p(R)-2\eta\frac{\partial v_r}{\partial r}(R)=\bar{p}(R)-2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}(R)-2\frac{\gamma}{R} \qquad (63)$$

where we have again taken the bulk phases to be Newtonian fluids. For this case, the temperature equation (55), neglecting kinetic energy effects and using (62), simplifies to the following

$$-T^s\frac{d^2\gamma}{dT^{s2}}\frac{\partial^s T^s}{\partial t}=2\frac{\gamma}{R}\frac{dR}{dt}+\lambda\frac{\partial T}{\partial r}(R)-\bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R)$$
$$+\left(\bar{v}_r(R)-\frac{dR}{dt}\right)\left[\bar{h}(R)-\epsilon h(R)-2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}(R)+2\epsilon\eta\frac{\partial v_r}{\partial r}(R)\right] \qquad (64)$$

Particularly interesting is the first term on the right-hand side of (64), which expresses a heating of the interface for expansion of the bubble against the interfacial tension, or cooling for a shrinking bubble. From (49) and (50), we can write the following temperature boundary conditions

$$T(R)-T^s=-R_K^{Is}\left[\left(\bar{v}_r(R)-\frac{dR}{dt}\right)\epsilon h(R)-\lambda\frac{\partial T}{\partial r}(R)\right] \qquad (65)$$

$$\bar{T}(R)-T^s=R_K^{IIs}\left[\left(\bar{v}_r(R)-\frac{dR}{dt}\right)\bar{h}(R)-\bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R)\right] \qquad (66)$$

To complete the formulation, we must find an expression for the velocity difference appearing in (62) and (64)–(66). The constitutive equation in (48) gives the following expression for the rate of phase change

$$\bar{v}_r(R)-\frac{dR}{dt}=\frac{\xi_n}{(1-\epsilon)^2}\left[\bar{\rho}T^s\left(\frac{\bar{\hat{\mu}}(R)}{\bar{T}(R)}-\frac{\hat{\mu}(R)}{T(R)}\right)-2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}(R)\right.$$
$$\left.+2\epsilon\eta\frac{\partial v_r}{\partial r}(R)\right] \qquad (67)$$

As expected, we see in (67) that the rate of phase change is proportional to the difference in the ratio of chemical poten-

tial to temperature, modified by viscous stresses, between the bulk phases. For this example, we require two boundary conditions each for the radial velocity and temperature fields in the bulk, plus one each for the interfacial position and temperature (for a total of six), which are given in (62)–(67).

Marangoni effect

In our final example, we consider steady flow around a spherical bubble or liquid drop driven by a gradient of interfacial tension. We take the interface to be stationary ($v^s \cdot n=0$) and assume symmetry about the x_3-coordinate. In the absence of mass transfer, from (51), we have the boundary condition

$$v_r(R)=\bar{v}_r(R) \qquad (68)$$

and the normal component of the jump momentum balance (44) again gives

$$p(R)-2\eta\frac{\partial v_r}{\partial r}(R)=\bar{p}(R)-2\bar{\eta}\frac{\partial\bar{v}_r}{\partial r}(R)-2\frac{\gamma}{R} \qquad (69)$$

For convenience, we take $\eta^s=0$ so that (44) gives: $n \cdot \tau^I \cdot \delta_\| = n \cdot \tau^{II} \cdot \delta_\| + \nabla_\| \gamma$, which leads to the following:

$$\eta\left[\frac{\partial v_\theta}{\partial r}(R)-\frac{v_\theta(R)}{R}\right]=\bar{\eta}\left[\frac{\partial\bar{v}_\theta}{\partial r}(R)-\frac{\bar{v}_\theta(R)}{R}\right]-\frac{d\gamma}{dT^s}\frac{1}{R}\frac{\partial T^s}{\partial\theta} \qquad (70)$$

For this example, we again take the mobility coefficient to be isotropic and use (47) to obtain a second boundary condition for the tangential velocity

$$v_\theta(R)-\bar{v}_\theta(R)=\xi_{slip}\eta\left[\frac{\partial v_\theta}{\partial r}(R)-\frac{v_\theta(R)}{R}\right]+\frac{\xi_{slip}}{1-\epsilon}\frac{d\gamma}{dT^s}\frac{1}{R}\frac{\partial T^s}{\partial\theta} \qquad (71)$$

where $\epsilon=\bar{\rho}/\rho$. The slip law (59) is modified by the stress resulting from spatial variations of the interfacial tension. The boundary conditions in (70) and (71) require the interfacial temperature, which from (55) can be written as

$$-T^s\frac{d^2\gamma}{dT^{s2}}\frac{(v^s_{def})_\theta}{R}\frac{\partial T^s}{\partial\theta}=T^s\frac{d\gamma}{dT^s}\frac{1}{R\sin\theta}\frac{\partial}{\partial\theta}[(v^s_{def})_\theta\sin\theta]$$
$$+\frac{\lambda^s}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T^s}{\partial\theta}\right)+\lambda\frac{\partial T}{\partial r}(R)-\bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R)$$
$$+\frac{1}{\xi_{slip}}[v_\theta(R)-\bar{v}_\theta(R)]^2+[v_\theta(R)-\bar{v}_\theta(R)]\frac{1}{1-\epsilon}\frac{d\gamma}{dT^s}\frac{1}{R}\frac{\partial T^s}{\partial\theta} \qquad (72)$$

From (49) and (50), we can write the following temperature boundary conditions

$$T(R)-T^s=R_K^{Is}\lambda\frac{\partial T}{\partial r}(R) \qquad (73)$$

$$\bar{T}(R)-T^s=-R_K^{IIs}\bar{\lambda}\frac{\partial\bar{T}}{\partial r}(R) \qquad (74)$$

Finally, from (19) and (71), we have the following expression for the interfacial velocity

$$(v^s_{def})_\theta=v_\theta(R)+\xi_{slip}\left(\frac{1}{\bar{\rho}}-\frac{1}{\rho}\right)^{-1}\left(\eta\left[\frac{\partial v_\theta}{\partial r}(R)-\frac{v_\theta(R)}{R}\right]\right.$$
$$\left.+\frac{1}{1-\epsilon}\frac{d\gamma}{dT^s}\frac{1}{R}\frac{\partial T^s}{\partial\theta}\right) \qquad (75)$$

Hence, the velocity and temperature fields in the bulk are coupled through the boundary conditions in (70)–(72). For

our final example, we require two boundary conditions each for the two components of velocity and temperature fields in the bulk plus one each for the interfacial velocity and temperature (for a total of eight), which are given in (68)–(75).

Summary

The description of systems comprised of two or more bulk phases involves equations governing density, velocity, and temperature fields in each phase, and boundary conditions at interfaces that separate the bulk phases. The well-known evolution equations for bulk fields are based on conservation equations for mass, momentum, and energy, supplemented by constitutive equations whose form is guided by thermodynamics. Boundary conditions, which describe the interaction between bulk phases, are formulated from equations that express the same conservation laws as in the bulk.

The formulation of balance and constitutive equations for interfaces, however, involves a number subtle issues. In particular, the identification of excess densities relevant for the description of an interface is ambiguous. In previous work, these ambiguities are avoided by allowing all excess densities to exist, or by excluding them entirely. The result of the latter approach are so-called jump balances. In the present work, we have handled this ambiguity using the principle of gauge invariance. Following this nonstandard approach, we have formulated a physically consistent set of equations describing interfaces that express mass, momentum, and energy conservation. In addition, we have used thermodynamics to guide in the formulation of constitutive equations for transport both within the interface and between the interface and bulk phases. For the latter, we have chosen to exclude coupling between mass and energy transport. Included in these results are expressions for tangential velocity differences having the Navier-slip law form and for temperature jumps in terms of Kaptiza resistances. However, more general constitutive assumptions in terms of a matrix of Onsager coefficients would also be possible. Recently, a generalized nonequilibrium thermodynamic framework has been developed for interfaces that is not restricted to linear constitutive equations.[13] The most appropriate form of the constitutive equations, including possible cross effects, needs to be found experimentally.

We have presented examples that illustrate how the complete set of conservation and constitutive equations can be used to formulate boundary conditions for interfaces at which mass, momentum, and energy transport occur simultaneously. These boundary conditions involve interesting couplings between mass, momentum, and energy transport that result from slip and interfacial thermal resistance.

Literature Cited

1. Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*, 2nd ed. New York: Wiley, 2001.
2. Öttinger HC, Struchtrup H, Liu M. Inconsistency of a dissipative contribution to the mass flux in hydrodynamics. *Phys Rev E*. 2009; 80:056303.
3. Edwards DA, Brenner H, Wasan DT. *Interfacial Transport Processes and Rheology. Butterworth-Heinemann Series in Chemical Engineering*. Boston, MA: Butterworth-Heinemann, 1991.
4. Slattery JC, Sagis L, Oh E-S. *Interfacial Transport Phenomena*, 2nd ed. New York: Springer, 2007.
5. Gatignol R, Prud'homme R. *Mechanical and Thermodynamical Modeling of Fluid Interfaces. Series on Advances in Mathematics for Applied Sciences*, 1st ed., Vol. 58. Singapore: World Scientific Publishing, 2001.
6. Gibbs JW. *Thermodynamnics, Vol. 1. The Scientific Papers of J. Willard Gibbs*. Woodbridge, CT: Ox Bow, 1993.
7. Bedeaux D, Albano AM, Mazur P. Boundary conditions and nonequilibrium thermodynamics. *Physica A*. 1976;82:438–462.
8. Bedeaux D. Nonequilibrium thermodynamics and statistical physics of surfaces. *Adv Chem Phys*. 1986;64:47–109.
9. Savin T, Glavatskiy KS, Kjelstrup S, Öttinger HC, Bedeaux D. Local equilibrium of the Gibbs interface in two-phase systems. *Europhys Lett*. 2012;97:40002.
10. Öttinger HC, Bedeaux D, Venerus DC. Nonequilibrium thermodynamics of transport through moving interfaces with application to bubble growth and collapse. *Phys Rev E*. 2009;80:021606.
11. Sagis LMC. Dynamic properties of interfaces in soft matter: experiments and theory. *Rev Mod Phys*. 2011;83:1367–1403.
12. Prosperetti A. Boundary conditions at a liquid-vapor interface. *Meccanica*. 1979;14:34–47.
13. Sagis LMC, Öttinger HC. Dynamics of multiphase systems with complex microstructure. I. Development of the governing equations through nonequilibrium thermodynamics. *Phys Rev E*. 2013;88: 022149.