

Thermodynamics of moving Gibbs dividing surfaces

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A systematic continuum approach is proposed to develop models of moving interfaces. The approach uses a zero-mass Gibbs dividing surface as an approximation of real three-dimensional interfacial region, introduces quantities representing the net action of two bulk phases on the interface, and employs the second law of thermodynamics to provide required constitutive equations. To demonstrate the approach, a general thermodynamic model is developed for two-dimensional moving interfaces. [S1063-651X(97)11102-3]

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I. INTRODUCTION

Moving interfaces arise in a variety of natural and industrial processes. Examples are growth boundaries of crystal, ice, and grain, and melting boundaries of ice, snow, and metal. They also appear in the multiphase flows and moving boundary problems. The correct description of their motion is thus of considerable practical importance. Because of the complexities of the problem [1], initial attempts to describe physical processes have relied on descriptive models of a more or less intuitive or empirical nature [2–4]. These models are generally limited in application to particular problems and usually have a narrow range of validity. The formulation of these models typically begins with some empirical assumptions regarding kinematics of moving interfaces. As well, most of them are kinematic rather dynamic models in nature.

A second possible approach to modeling the moving interfaces can be referred to as molecular models. In this method, the statistical theory is used to obtain a phenomenological description of interfaces from a molecular point of view. This method has been successfully used to model static fluid interfaces [5–9]. However, we are not aware of any work on the moving interfaces.

A third approach employs continuum mechanics [10–15]. In this approach, a moving interface is viewed as a separate two-dimensional material surface with possible different constitutive equations from those applicable outside the interfacial region. Associated with the surface are the usual thermodynamic quantities, which are continuous along the surface but may be discontinuous across the surface. The classical conservation laws of continuum mechanics along with the constitutive equations govern the motion of the interface, resulting in a relatively general dynamic model.

Of the three methods, the continuum mechanical approach appears to provide the best framework to advance the understanding of the moving interfaces. However, previous works in this group appear to suffer three fundamental defects, resulting in a set of complex equations. Specification of a number of additional constitutive equations is also required to complete the model. First, these works fail to select a proper Gibbs dividing surface as the representative of the real three-dimensional region [16,17]. In fact, most works do not even mention what kind of Gibbs dividing surface is used. Typically, a material surface with γ as the surface density is used

to represent the real three-dimensional region, resulting in a complicated set of equations. In the application of such models, γ is usually set to zero to simplify the model [10]. Associated with this, the relation between the Gibbs dividing surface used and the classical *surface tension* surface is not clear.

Second, these works have immediately focused on particular types of material surfaces such as Newtonian surface fluids, and imposed constitutive relations for such particular surfaces to relate capillary force to the strain in the surface by introducing some parameters such as surface dilational viscosity and surface shear viscosity which are difficult to determine. Thus, early in the derivations, assumptions about constitutive relations restrict the equations developed to certain materials or special cases. The steps to extend the equations to more general situations are usually rather obscure. Furthermore, the justification for such assumptions is an open question. Third, these works modeled the action of two bulk phases on the interface for each side of the interface rather than modeling the net effect of two bulk phases. In modeling each side, the bulk constitutive equations are used in the neighborhood of the phase interface to relate stress to the kinematic quantity of the bulk phase for some particular material without justification. This, once again, limits the model developed to some particular cases.

The motivation for the present work comes from the desire to provide a systematic, continuum approach for developing models of moving interfaces in which the three defects are avoided. The approach is based on two fundamental assumptions. First, a real three-dimensional (3D) interfacial region may be approximated by a zero-mass Gibbs dividing surface. The cumulative effects associated with this replacement are taken into account by the assignment to the dividing surface of excess quantities. The justification of this approximation and the existence of such surfaces have been well described in [16–18]. The advantage of this choice can be seen in Sec. 2.2. It is worthy to note that the classical concept of equilibrium surface tension is also based on this kind of dividing surface [16–17]. Hereafter when we say the phase interface, we mean this zero-mass Gibbs dividing surface. Second, we assume that all thermodynamic quantities are continuous on the interfaces although they may be discontinuous across the interfaces. This is a reasonable assumption on the physical grounds of practical situations, and is used in all continuum approaches.

To demonstrate the approach, we develop one thermodynamic model for the moving interfaces. The model consists of three basic parts: the conservation laws, an interfacial version of the second law of thermodynamics, and constitutive equations. The second law is used to obtain thermodynamically sound constitutive equations that relate the dynamic quantities to the kinematic ones. The conservation laws and the constitutive equations, with some kinematic relations from the differential geometry, form the equations governing the motion of interfaces.

In developing the model, we made the following two assumptions to highlight the crucial aspects of the approach. First, we restrict our attention to the 2D interface motions to avoid the geometrical complications associated with the motion of surfaces in 3D space. By this assumption, a moving interface becomes a moving curve in 2D space whose motion must satisfy some classical fundamental laws. Secondly, we assume that the motion of the bulk phases can be neglected compared with the motion of the interface. This happens when the volumes of the bulk phases are large enough. By this assumption, some mathematical results will be simplified. Unlike the two fundamental assumptions, all these assumptions are only for the sake of simplicity. The approach is systematic in the sense that these simplifying assumptions may be relaxed if more general results are desired.

II. THERMODYNAMIC MODEL

A. Kinematics

To develop a dynamic model for the interface, we need to know its kinematics first. This is well developed in the field of differential geometry because our 2D moving interface is a moving curve in 2D space. Here we just list some results from the differential geometry that will be used in our model [19,20]. Geometry relations:

$$\mathbf{t} = \mathbf{r}_s, \quad (1)$$

$$k = \alpha_s, \quad (2)$$

$$\mathbf{t}_s = k\mathbf{n}, \quad (3)$$

$$\mathbf{n}_s = -k\mathbf{t}. \quad (4)$$

Kinematic relations:

$$u_s = -kv, \quad (5)$$

$$\alpha_t + u\alpha_s = v_s, \quad (6)$$

$$k_t + uk_s = v_{ss} + k^2v. \quad (7)$$

In Eqs. (1)–(7), \mathbf{r} is position vector, s is arch length, \mathbf{n} is the unit normal vector, α is the angle between \mathbf{n} and \mathbf{e}_1 , k is curvature, which is the derivative of α with respect to s [Eq. (2)], \mathbf{t} is a unit tangent, which is the derivative of \mathbf{r} with respect to s , and u and v are the tangential (along \mathbf{t}) and the normal (along \mathbf{n}) components of interface velocity vector \mathbf{v} (Fig. 1). Hereafter, the subscript s means the derivative with respect to s holding time t fixed, and the subscript t represents the derivative with respect to t holding s fixed. Thus Eqs. (3) and (4) relate \mathbf{t} , \mathbf{n} , and k at any point of the inter-

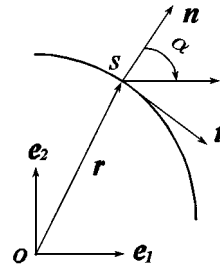


FIG. 1. A moving interface.

face. Equations (5)–(7) relate u , v , and k at any point of the interface. In other words, they relate the motion of an interface with its shape.

B. Governing laws

What we know about the motion of an interface is its satisfaction of classical laws: conservation of mass, linear momentum, and rotational momentum, and the first and second laws of thermodynamics. Here the rotational momentum is also called angular momentum or moment of momentum. The definition of our interface, i.e., the zero-mass Gibbs interface, has already ensured the mass conservation. Thus we only need to use the conservation of linear and rotational momenta and the first and second laws of thermodynamics to restrict the motion of the interface.

1. Conservation of linear and rotational momenta

Consider an infinitesimal subinterface i as shown in Fig. 2(a). The forces acting on i are either internal traction, which acts at two end points of i and comes from the cumulative effect associated with the replacement of a real 3-D interfacial region by a Gibbs dividing surface, or external forces, which act on every point of i and come from the action of each of the two bulk phases. The former we denote by the capillary force $\mathbf{c}(s,t)$. The net effect of the latter we characterize by an interactive force $\mathbf{a}(s,t)$ [per unit arc length, Fig. 2(b)] and an interactive moment $\mathbf{m}(s,t)$ [per unit arc length, Fig. 2(b)] because the motion of the interface depends on the resulting or combined forces, not on each single force. The introduction of \mathbf{a} and \mathbf{m} is unique to this approach in the sense that the previous approaches in the literature modeled these forces on either side of i separately. Since the interface has zero mass, the other force fields such as the gravitational force field do not contribute any force to i .

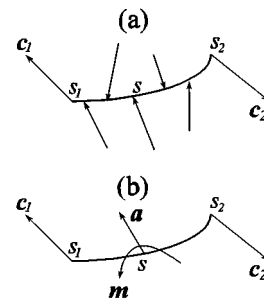


FIG. 2. An infinitesimal subinterface i .

Applying the conservation laws of linear and rotational momenta to i yields

$$\int_i \mathbf{a} ds + \int_{\partial i} \mathbf{c} = \mathbf{0}, \quad (8)$$

$$\int_i \mathbf{m} ds + \int_i \mathbf{r} \times \mathbf{a} ds + \int_{\partial i} \mathbf{r} \times \mathbf{c} = \mathbf{0}, \quad (9)$$

where ∂i represents the boundary of i . For the 2D case, it consists of two end points of i . Thus $\int_{\partial i} \xi = \xi(s_2, t) - \xi(s_1, t)$. Also, $\int_i \xi ds = \int_{s_1(t)}^{s_2(t)} \xi(s, t) ds$.

Note that our interface has zero mass; the rate of change in the linear and rotational momenta of i vanish. This leads to a simple right side of Eqs. (8) and (9). To obtain a local form of Eqs. (8) and (9), change the integrations over ∂i to the integrations over i by the divergence theorem, which can be invoked because of our continuous assumption of all quantities along i . Then the validity of Eqs. (8) and (9) for all i , with the continuous assumption of all quantities along i , allows us to appeal the localization theorem to obtain

$$\mathbf{a} + \mathbf{c}_s = \mathbf{0}, \quad (10)$$

$$\mathbf{m} + \mathbf{r}_s \times \mathbf{c} = \mathbf{0}. \quad (11)$$

A component form of Eqs. (10) and (11) can be obtained by applying Eqs. (1)–(4) and decomposing \mathbf{a} and \mathbf{c} along \mathbf{t} and \mathbf{n} . The result is as follows:

$$\sigma_s + \tau k + f = 0, \quad (12)$$

$$\tau_s - \sigma k + g = 0, \quad (13)$$

$$\sigma = -m, \quad (14)$$

in which f and g are the normal and tangential components of \mathbf{a} while σ and τ are the normal and tangential components of \mathbf{c} . Note that σ causes surface shear and τ causes surface tension.

2. The first and second laws of thermodynamics

The dynamics of the interface is determined by three interfacial fields: interactive force $\mathbf{a}(s, t)$, capillary force $\mathbf{c}(s, t)$, and interactive moment $\mathbf{m}(s, t)$, which are interrelated through the conservation laws [Eqs. (12)–(14)]. The thermodynamics of the interface is described by three scalar-valued interfacial fields defined on the interface for all time, i.e., the interfacial energy $\psi(\mathbf{x}, t)$, the interfacial entropy $\iota(\mathbf{x}, t)$ and the apparent heat flux $\vartheta(\mathbf{x}, t)$. There exists a fundamental question regarding the nature of heat conduction. The classical theory (the Fourier law) regards heat conduction as a diffusion process, which leads to a paradox, namely, an infinite velocity of heat propagation for a time duration. The duration is of the order 10^{-8} – 10^{-12} s for homogeneous substance [21] and 10^{-3} – 10^3 s for nonhomogeneous materials [22,23]. This paradox was first observed by Cattaneo [24]. Since then, several theories have been developed to eliminate it. The theory of *second sound*, for example, assumes that heat moves as a wave rather than a diffusion process to eliminate the *paradox of instantaneous propagation of ther-*

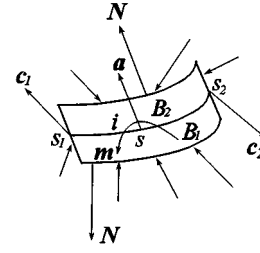


FIG. 3. A two-phase control volume B .

mal disturbances. A review of the literature in this area can be found in [25]. To avoid this uncertainty (i.e., which theory is more exact to what takes place in reality), we use both heat flux field and temperature field as the thermodynamic quantities instead of just temperature. It is up to the user to provide the constitutive relation to relate heat flux to temperature.

Consider a two-phase control volume B consisting of B_1 of phase 1, B_2 of phase 2, and interface i (Fig. 3), and let $e(\mathbf{x}, t)$ and $S(\mathbf{x}, t)$ be the energy and entropy of bulk phases per unit area. Then,

$$\int_{B_1+B_2} e(\mathbf{x}, t) da + \int_i \psi ds, \quad (15)$$

$$\int_{B_1+B_2} S(\mathbf{x}, t) da + \int_i \iota ds \quad (16)$$

are the internal energy and the internal entropy of B .

Let $\mathbf{q}(\mathbf{x}, t)$ and $T(\mathbf{x}, t)$ be the bulk heat flux and the bulk absolute temperature, respectively. Then

$$\int_{\partial B} \mathbf{q} \cdot \mathbf{N} ds, \quad (17)$$

$$\int_{\partial B} \frac{\mathbf{q}}{T} \cdot \mathbf{N} ds \quad (18)$$

represent the net heat and thermal entropy flux out of B by bulk heat conduction across ∂B , respectively. Here \mathbf{N} is the outward unit normal vector of ∂B .

Neglecting the heat conduction along the interface, the heat and thermal entropy flux through ∂i are those resulting from the tangential motion of the edge of i . Suppose that the temperature T is continuous across the interface (but we allow the other bulk fields to suffer jump discontinuities across the interface), they can be written as

$$\int_{\partial i} \vartheta u \quad (19)$$

and

$$\int_{\partial i} T^{-1} \vartheta u. \quad (20)$$

For the case that the motion of the bulk material can be neglected comparing with the motion of the interface, the power expended on B by the bulk forces acting on ∂B is negligible. As well, the interactive force \mathbf{a} and moment \mathbf{m} do

not expend power on B since they are internal to B by noting that they come from the mechanical action on i of each of two bulk phases. Therefore, the only source of power for B comes from the capillary forces on ∂i , which can be written as

$$\int_{\partial i} \mathbf{c} \cdot \mathbf{v}. \quad (21)$$

The first law of thermodynamics requires the conservation of energy for B , yielding

$$\frac{d}{dt} \left\{ \int_{B_1+B_2} e da + \int_i \psi ds \right\} = - \int_{\partial B} \mathbf{q} \cdot \mathbf{N} ds + \int_{\partial i} \vartheta u + \int_{\partial i} \mathbf{c} \cdot \mathbf{v}. \quad (22)$$

The second law of thermodynamics requires that the entropy generation, which is the sum of the change of entropy of B and the outflow of entropy from B minus the thermal entropy flux, is never less than zero (note that the work exchange does not cause change in entropy). This leads to

$$\frac{d}{dt} \left\{ \int_{B_1+B_2} S da + \int_i \iota ds \right\} \geq - \int_{\partial B} T^{-1} \mathbf{q} \cdot \mathbf{N} ds + \int_{\partial i} T^{-1} \vartheta u, \quad (23)$$

which must hold for all two-phase control volume B .

To obtain an interfacial form of the first and second laws of thermodynamics, we shrink B to i by letting $B_1 \rightarrow 0$ and $B_2 \rightarrow 0$. This yields

$$\begin{aligned} \frac{d}{dt} \int_i \psi ds + \int_{\partial i} u \psi = \int_i [e] v ds - \int_i [\mathbf{q}] \cdot \mathbf{n} ds \\ + \int_{\partial i} \vartheta u + \int_{\partial i} \mathbf{c} \cdot \mathbf{v}, \end{aligned} \quad (24)$$

$$\frac{d}{dt} \int_i \iota ds + \int_{\partial i} u \iota \geq \int_i [S] v ds - \int_i T^{-1} \mathbf{q} \cdot \mathbf{n} ds + \int_{\partial i} T^{-1} \vartheta u, \quad (25)$$

which are valid for all moving subinterfaces i . Here $[e]$ is the jump in e across the interface, etc., and v is the normal velocity component of the interface.

The interfacial first and second laws (24) and (25) represent the first and the second laws for a subinterface i . $\int_i \psi ds$ and $\int_i \iota ds$ are the energy and entropy of i while $\int_{\partial i} u \psi$ and $\int_{\partial i} u \iota$ represent the outflow rate of interfacial energy and entropy from i . $\int_i [e] v ds$ and $\int_i [S] v ds$ represent flows of bulk energy and bulk entropy into i while $-\int_i [\mathbf{q}] \cdot \mathbf{n} ds$ and $-\int_i T^{-1} [\mathbf{q}] \cdot \mathbf{n} ds$ account for heat and thermal entropy flux to i by bulk material through heat conduction. $\int_{\partial i} \vartheta u$ and $\int_{\partial i} T^{-1} \vartheta u$ represent heat and thermal entropy flux to i by the tangential motion of ∂i . $\int_{\partial i} \mathbf{c} \cdot \mathbf{v}$ is the power expended on i by the capillary force.

Note that

$$\begin{aligned} \frac{d}{dt} \int_i \psi ds &= \int_{\partial i} u \psi + \int_i \psi_t(s, t) ds = \int_{\partial i} u \psi + \int_i (\psi^0 - u \psi_s) ds \\ &= \int_{\partial i} u \psi + \int_i \psi^0 ds - \int_i u \psi_s ds = \int_i (\psi^0 + \psi u_s) ds \\ &= \int_i (\psi^0 - \psi k v) ds \end{aligned} \quad (26)$$

in which Eq. (5) is used, and superscript 0 denotes the full time derivative.

Also

$$\int_{\partial i} \mathbf{c} \cdot \mathbf{v} = \int_{\partial i} \tau u + \int_{\partial i} \sigma v = \int_{\partial i} \tau u + \int_i (\sigma_s v + \sigma v_s) ds \quad (27)$$

in which the divergence theorem is used. Using Eq. (12) and $v_s = \alpha^0$ (angular velocity), Eq. (27) can be written as

$$\int_{\partial i} \mathbf{c} \cdot \mathbf{v} = \int_{\partial i} \tau u - \int_i (f v + \tau k v - \sigma \alpha^0) ds. \quad (28)$$

Applying Eqs. (26) and (28) to Eqs. (24) and (25) yields

$$\begin{aligned} \int_i \{ \psi^0 - \sigma \alpha^0 - (\psi - \tau) k v + (f - [e]) v + [\mathbf{q}] \cdot \mathbf{n} \} ds \\ + \int_{\partial i} (\psi - \vartheta - \tau) u = 0, \end{aligned} \quad (29)$$

$$\int_i \{ \iota^0 - \iota k v - [S] v + T^{-1} [\mathbf{q}] \cdot \mathbf{n} \} ds + \int_{\partial i} (\iota - T^{-1} \vartheta) u \geq 0 \quad (30)$$

for all subinterfaces i .

Note that Eqs. (29) and (30) must hold for arbitrary ∂i and t ; it is obvious that

$$\psi = \vartheta + \tau, \quad (31)$$

$$\iota = T^{-1} \vartheta, \quad (32)$$

which represents energy balance and entropy at the edge of the subinterface. Equation (31) also states that the interfacial energy in terms of per unit arc length is equal to the sum of the apparent heat flux and surface tension.

Combining Eq. (31) with Eq. (32) gives

$$\tau = F, \quad (33)$$

with

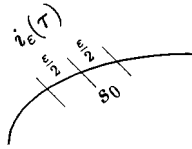
$$F = \psi - T \iota \quad (34)$$

as the Helmholtz free energy of the interface.

By Eqs. (31) and (32), Eqs. (29) and (30) reduce to

$$\int_i Y ds = 0, \quad \forall i \quad (35)$$

$$\int_i \Xi ds \geq 0, \quad \forall i \quad (36)$$

FIG. 4. A subinterface i_ε .

where

$$Y = \psi^0 - \sigma\alpha^0 - (\psi - \tau)kv + (f - [e])v + [\mathbf{q}] \cdot \mathbf{n} \quad (37)$$

and

$$\Xi = \iota^0 - \iota kv - [S]v + T^{-1}[\mathbf{q}] \cdot \mathbf{n}. \quad (38)$$

To obtain a local form of Eqs. (35) and (36), consider a subinterface $i_\varepsilon(\tau)$ at arbitrary instant τ , which has an arch length ε (≥ 0) centered at s_0 (Fig. 4).

Let

$$I_{1_\varepsilon} = \left| Y(s_0, \tau) - \frac{1}{\varepsilon} \int_{i_\varepsilon} Y(s, \tau) ds \right|, \quad (39)$$

$$I_{2_\varepsilon} = \left| \Xi(s_0, \tau) - \frac{1}{\varepsilon} \int_{i_\varepsilon} \Xi(s, \tau) ds \right|. \quad (40)$$

Then

$$I_{1_\varepsilon} \geq 0, \quad (41)$$

$$I_{2_\varepsilon} \geq 0. \quad (42)$$

Since $Y(s, \tau)$ and $\Xi(s, \tau)$ are continuous on s by our fundamental assumption,

$$\begin{aligned} I_{1_\varepsilon} &= \left| \frac{1}{\varepsilon} \int_{i_\varepsilon} [Y(s_0, \tau) - Y(s, \tau)] ds \right| \\ &\leq \frac{1}{\varepsilon} \int_{i_\varepsilon} \max_{s \in i_\varepsilon} |Y(s_0, \tau) - Y(s, \tau)| ds \\ &= \max_{s \in i_\varepsilon} |Y(s_0, \tau) - Y(s, \tau)|, \\ I_{2_\varepsilon} &= \left| \frac{1}{\varepsilon} \int_{i_\varepsilon} [\Xi(s_0, \tau) - \Xi(s, \tau)] ds \right| \\ &\leq \frac{1}{\varepsilon} \int_{i_\varepsilon} \max_{s \in i_\varepsilon} |[\Xi(s_0, \tau) - \Xi(s, \tau)]| ds \\ &= \max_{s \in i_\varepsilon} |[\Xi(s_0, \tau) - \Xi(s, \tau)]|, \end{aligned}$$

which tend to zero as $\varepsilon \rightarrow 0$. Hence we have

$$I_{1_\varepsilon} \leq 0, \quad (43)$$

$$I_{2_\varepsilon} \leq 0 \quad (44)$$

as $\varepsilon \rightarrow 0$.

To satisfy Eqs. (41)–(44), we have that

$$Y(s_0, \tau) = \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} \int_{i_\varepsilon} Y(s, \tau) ds \quad (45)$$

and

$$\Xi(s_0, \tau) = \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} \int_{i_\varepsilon} \Xi(s, \tau) ds, \quad (46)$$

which yield, after using Eqs. (35) and (36),

and

$$Y(s_0, \tau) = 0, \quad (47)$$

$$\Xi(s_0, \tau) \geq 0. \quad (48)$$

Since s_0, τ are arbitrary, we have

$$Y(s, \tau) = 0, \quad (49)$$

$$\Xi(s, \tau) \geq 0, \quad (50)$$

i.e.,

$$\psi^0 - \sigma\alpha^0 - (\psi - \tau)kv + (f - [e])v + [\mathbf{q}] \cdot \mathbf{n} = 0, \quad (51)$$

$$\iota^0 - \iota kv - [S]v + T^{-1}[\mathbf{q}] \cdot \mathbf{n} \geq 0. \quad (52)$$

By the third law of thermodynamics, $T > 0$. Inequality (52) can thus be rewritten as

$$T\iota^0 - T\iota kv - T[S]v + [\mathbf{q}] \cdot \mathbf{n} \geq 0. \quad (53)$$

To eliminate the vector-valued \mathbf{q} , which is a quantity associated with the bulk field, subtracting Eq. (53) from Eq. (51) yields another form of the second law of thermodynamics

$$F^0 - \sigma\alpha^0 + \iota T^0 + (f - [\eta])v \leq 0, \quad (54)$$

where η is the bulk Helmholtz free energy, i.e.,

$$\eta = e - TS. \quad (55)$$

C. Constitutive equations

Equations (12)–(14) and (51) form the conservation equations of the thermodynamic model. To be truly useful for the description of the moving interfaces, they must be supplemented by constitutive equations to relate f , g , $\sigma(m)$, $\tau(F)$, ψ , and \mathbf{q} to the kinematic and thermal quantities of the interface. Such constitutive equations are usually provided through some empirical laws such as Fourier law of heat conduction for heat flux and Newton law of stress for Newtonian fluids. At present, we have no experiments by means of which we can study the constitutive equations in the neighborhood of an interface. The previous works then intuitively imposed some constitutive equations similar to those applicable in bulk phases by introducing concepts such as Newtonian surface fluids [10]. In the present work, we use the second law of thermodynamics [inequality (54)] to provide the required constitutive equations. The justification comes from the fact that the motion of the interface is controlled not only by the conservation laws of mass, linear

momentum, rotational momentum, and energy, but also by the other fundamental laws such as the second law of thermodynamics.

An examination of the inequality (54) shows that the second law of thermodynamics does not place any restriction on ψ and g explicitly. However, by Eqs. (13) and (34), we can obtain the required constitutive equations for ψ and g once we have constitutive equations of $F(\tau)$, σ , f , and ι . The constitutive equation of \mathbf{q} can be provided by several theories. The classical Fourier law, for example, states that

$$\mathbf{q} = -\mathbf{K}\nabla T, \quad (56)$$

where \mathbf{K} is the conductivity tensor, and ∇ is the gradient.

The inequality (54) indicates that the proper independent variables are α , v , and T . Consequently, we suppose, as interfacial constitutive equations, that F , σ , f , and ι depend smoothly on the orientation of the interface through a dependence on α , on the kinematics of the interface through a dependence on v and on the thermal behavior through a dependence on T , i.e.,

$$F = F(\alpha, v, T), \quad \sigma = \sigma(\alpha, v, T), \quad f = f(\alpha, v, T), \\ \iota = \iota(\alpha, v, T). \quad (57)$$

These, with the aid of Eqs. (13), (14), (31), and (34), induce additional constitutive equations for τ , g , m , ϑ , and ψ .

The second law of thermodynamics (54) requires

$$(F_\alpha - \sigma)\alpha^0 + F_v v^0 + (F_T + \iota)T^0 + (f - [\eta])v \leq 0 \quad (58)$$

for all moving subinterfaces that satisfy the conservation laws. Since the fields α , v , T , α^0 , v^0 , and T^0 can have arbitrary values at any point and time, we take $\alpha^0 = 0$, $v^0 \neq 0$, $T^0 = 0$, and $v = 0$. Then Eq. (58) reduces to

$$F_v(\alpha, v, T)v^0 \leq 0, \quad \forall v^0 \neq 0. \quad (59)$$

This implies that

$$F = F(\alpha, T). \quad (60)$$

Similarly, we have

$$\sigma = F_\alpha(\alpha, T), \quad (61)$$

$$\iota = -F_T(\alpha, T). \quad (62)$$

Applying Eqs. (60)–(62) into Eq. (58) yields

$$\{f(\alpha, v, T) - [\eta]\}v \leq 0, \quad \forall \alpha, v, \text{ and } T. \quad (63)$$

Let

$$\phi(v) = [\eta] - f(\alpha, v, T). \quad (64)$$

Thus

$$\phi(v)v \geq 0, \quad (65)$$

which implies that $\phi(v)v$ has a minimum at $v = 0$. This requires

$$\left. \frac{d(\phi v)}{dv} \right|_{v=0} = \phi(0) + v\phi'(v)|_{v=0} = 0,$$

which gives

$$\phi(0) = 0. \quad (66)$$

Hence,

$$\nu(\alpha, v, T) = \frac{\phi(v)}{v} \quad (67)$$

is well defined. This concludes that

$$\phi(v) = \nu(\alpha, v, T)v,$$

i.e.,

$$f(\alpha, v, T) = [\eta] - \nu(\alpha, v, T)v. \quad (68)$$

Note that $\phi(v)$ and v always have the same sign [Eq. (65)]; Eq. (67) concludes that

$$\nu(\alpha, v, T) \geq 0. \quad (69)$$

Conversely, Eqs. (60)–(62), (68), and (69) yield Eq. (58) in all processes.

By Eqs. (2), (13), (33), and (61), we have

$$g = \iota(\alpha, T)T_s, \quad (70)$$

which is not zero if temperature varies along the interface. Also, Eq. (34) yields

$$\psi = F(\alpha, T) - TF_T(\alpha, T). \quad (71)$$

Equations (60)–(62), (68), and (71) show that (1) F , σ , ι , and ψ cannot depend on v explicitly, (2) surface shear is always equal to the derivative of F with respect to α , and (3) the interfacial entropy ι is always equal to the derivative of F with respect to T . These are important because they imply that (1) $\tau(F)$, σ , ι , and ψ in the dynamic situation assume their values in the static situation (this will significantly simplify the experiments to determine them), (2) a gradient of F or τ will cause surface shear, and (3) the variation of F or τ with temperature T will result in an interfacial entropy.

By Eqs. (32), (51), (60)–(62), and (68), the left side of Eq. (30) reduces to $\int_i \nu v^2$ so that νv^2 is the total entropy generation per unit length due to the irreversibility of the process. Like conductivity and viscosity, ν is to be determined through experiments. However, for small values of v , we can approximate $\nu(\alpha, v, T)$ by $\nu(\alpha, 0, T)$. On the other hand, we can impose other principles such as frame indifference to obtain the form of dependence of ν on α , v , and T . It is our belief that all the details concerning constitutive equations can be obtained through imposing enough fundamental laws.

By collecting all results, we have the conservation equations (12)–(14), (51) and the constitutive equations (32), (33), (60)–(62), and (68)–(71) for the moving interfaces. All these, with the kinematic relations (5)–(7), form a completed thermodynamic model of the moving interfaces. They can be used to predict and control the motion, shape, and characteristics of the moving interfaces. They can also be employed as

the microscopic model for interfaces in the multiphase flows, and as the boundary conditions in moving and free boundary problems.

III. CONCLUDING REMARKS

A systematic, continuum approach is set up to develop the thermodynamic model of the moving interfaces. The approach differs from the others mainly in three aspects: (1) using zero-mass Gibbs interfaces as the approximation of the real 3-D interfacial region; (2) introducing \mathbf{a} and \mathbf{m} to reflect the net action of two bulk phases on the interface; and (3) employing the second law of thermodynamics to derive the required constitutive equations.

The proposed approach is used to develop a thermodynamic model for two-dimensional moving interfaces. The

model consists of three basic parts: the conservation laws, the second law of thermodynamics, and constitutive equations. The conservation laws, the constitutive equations, and some kinematic relations from the differential geometry together form the governing equations of moving interfaces. Such equations can be used to predict and control the motion, shape, and characteristics of interfaces appearing in various natural and industrial processes.

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