Theory for solvent, momentum, and energy transfer between a surfactant solution and a vapor atmosphere

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We develop a complete set of equations governing the evolution of a sharp interface separating a volatile-solvent/nonvolatile-surfactant solution from a vapor atmosphere. In addition to a sorption isotherm equation and the conventional balances for mass, linear momentum, and energy, these equations include an alternative to the Hertz-Knudsen-Langmuir equation familiar from conventional theories of evaporation and condensation. This additional equation arises from a consideration of configurational forces within a thermodynamical framework. While the notion of configurational forces is well developed and understood for the description of materials that, like crystalline solids, possess natural reference configurations, very little has been done regarding their role in materials, such as viscous fluids, that do not possess preferred reference states. We therefore provide comprehensive developments of configurational forces, the balance of configurational momentum, and configurational thermodynamics. Our treatment does not require a choice of reference configuration. The general evolution equations arising from our theory account for the thermodynamic structure of the solution and the interface and for sources of dissipation related to the transport of surfactant, momentum, and heat in the solution and within the interface along with the transport of solute, momentum, kinetic energy, and heat across the interface. Moreover, the equations account for the Soret and Dufour effects in the solution and on the interface and for observed discontinuities of the temperature and chemical potential across the interface. Due to the complexity of these equations, we provide approximate equations which we compare to equations preexistent in the literature.

I. INTRODUCTION

Continuum theories for tranformations between the liquid and vapor phases of a fluid typically impose an interfacial equation in addition to those of kinematical origin and those deriving from the balances for mass, momentum, and energy. Known as the Hertz-Knudsen-Langmuir equation, that additional interface equation dictates how a difference between the interfacial temperatures of the liquid and vapor phases drives evaporation or condensation. Specifically, on writing **u** for the velocity of the liquid, n for the unit orientation of the interface (directed into the vapor), V for the scalar normal velocity of the interface in the direction of n, ϑ for the (absolute) temperature of the liquid, and ϑ_s for the equilibrium saturation temperature of the vapor phase, the Hertz-Knudsen-Langmuir equation can be expressed as

$$\beta V^{\mathrm{mig}} = -\ell\left\{\frac{\vartheta}{\vartheta_s}-1\right\}, \qquad (1)$$

where $V^{\mathrm{mig}} = V - \mathbf{u}\cdot\mathrm{n}$ is the migrational velocity of the interface relative to the liquid, $\beta > 0$ is a modulus associated with the kinetics of attachment and detachment at the interface, and $\ell > 0$ is the latent heat of vaporization. Consistent with intuitive expectations, (1) predicts evaporation when the interfacial temperature of the liquid phase exceeds the equilibrium saturation temperature and condensation when the interfacial temperature of the liquid phase is less than the equilibrium saturation temperature.

Schrage [1] and Knacke and Stranski [2] review the experimental and theoretical developments leading up to the Hertz-Knudsen-Langmuir equation, including the seminal contributions of Hertz [3], Knudsen [4], and Langmuir [5]. The conventional derivation of the Hertz-Knudsen-Langmuir equation involves arguments from the kinetic theory of gases; a careful discussion of the hypotheses underlying this derivation is given by Cammenga [6]. Of prominent importance among these hypotheses is the assumption that the mechanisms underlying evaporation and condensation depend only on the states of the liquid and vapor phases and are independent of mass, momentum, and energy transfer. Despite the neglect of these effects, the Hertz-Knudsen-Langmuir equation is, as Koffman, Plesset, and Lees [7] observe, often used without justification in continuum problems involving mass, momentum, and energy transfer.

The purpose of this paper is to develop, from basic considerations, a complete set of equations governing the evolution of a sharp interface separating a solution—consisting of a volatile solvent and a nonvolatile surfactant—from a vapor atmosphere, with focus on providing a generalization of (1) that accounts properly for transport. In so doing we account for distributions of surfactant molecules, molecular fluxes, viscous stresses, and heat fluxes in bulk and on the surface. However, we neglect the mass of the interface and also impose a no-slip condition requiring that tangential components of the solution and vapor velocities at the interface coincide. Specifically, writing $\mathbf{u}_v$ for the velocity of the vapor at the interface, this condition can be expressed as

$$\mathbf{u} - \mathbf{u}_v = (\mathbf{u} \cdot \mathrm{n} - \mathbf{u}_v \cdot \mathrm{n})\mathrm{n}. \qquad (2)$$

Our approach to developing the equations resembles closely that taken by Anderson *et al.* [8] in their theory for two-fluid phases undergoing transformation, the primary difference being due to the need to treat surfactant transport. To incorporate this phenomenon, we follow Danov *et al.* [9] and model the surfactant as a single unconstrained species. Whereas the theory of Anderson *et al.* [8] provides a detailed treatment of both fluid phases, we focus primarily on the liquid phase and treat the vapor phase as a reservoir in which the density and temperature take uniform values ρ_v and ϑ_v. This results in a theory that is one sided in the sense of that utilized by Burelbach, Bankoff and Davis [10] in their work on the evaporation and condensation of pure liquid films.

By allowing the temperature of the solution at the interface to differ from that of the vapor, our theory therefore encompasses the recent experiments of Fang and Ward [11], who observe that, during evaporation, the temperature of the vapor phase in a region very close to the interface may actually exceed that of the liquid phase. Specifically, we obtain a generalized Hertz-Knudsen-Langmuir Eq. (1) in which the role of the equilibrium saturation temperature ϑ_s is replaced by the uniform temperature ϑ_v of the vapor at the interface. Most importantly, various additional terms entering our equation allow for evaporation to occur when the interfacial temperature of the liquid phase is less than that of the vapor phase (and similarly for condensation).

Another important feature of our theory concerns the properties of the chemical potential of the surfactant at the interface. Specifically, because we assume that the surfactant is nonvolatile, the chemical potential of the surfactant in the vapor is necessarily trivial. Consistent with the results of Røsjorde *et al.* [12,13], our theory therefore allows the chemical potential of the surfactant to be discontinuous across the interface.

Like the theory of Anderson *et al.* [8], our theory requires a consideration of the mechanics and thermodynamics of configurational forces. For applications involving solid-state phenomena the understanding that configurational forces may be needed to describe defects has been clear since the groundbreaking studies of Peach and Koehler [14], Eshelby [15–18], and Herring [19]. These studies are performed within a variational framework where configurational forces arise on considering variations which allow the defect to move while holding fixed the positions of material particles. However, studies based on variational arguments are inherently unable to characterize dissipation, a drawback that is particularly limiting when dealing with fluids, because of the prominence of viscous stresses. Moreover, any variationally based introduction of configurational forces must necessarily be predicated on an underlying constitutive framework and, therefore, restricted to a particular class of materials.

To circumvent these restrictions, we adopt the point of view advanced by Gurtin and Struthers [20], who use an argument based on invariance under observer changes to conclude that a configurational force balance should join the standard force balance as a basic law of continuum physics. (The work of Gurtin and Struthers [20] is somewhat obscure; better references for the underlying ideas are Gurtin [21,22].)

Here the operative word is "basic." Basic laws are by their very nature independent of constitutive assumptions; when placed within a thermodynamic framework such laws allow one to use the now standard procedures of continuum thermodynamics to develop suitable constitutive theories.

The organization and central results of our paper are as follows. In Secs. II and III we revisit a familiar topic: the bulk material away from the interface. This allows for a discussion of the first and second laws of thermodynamics in forms that account explicitly for power expended by configurational forces. Although the configurational and standard forms of these laws are equivalent, this simple setting provides a useful vehicle for discussing the basic structure of these laws, a structure not at all transparent when discussing phase interfaces. Once this basic framework is established, we turn to our stated goal: to develop a complete set of equations governing the evolution of a sharp interface separating a volatile-solvent/nonvolatile-surfactant solution from a vapor atmosphere.

Following a review of the kinematics of the interface given in Sec. IV, the interfacial balances for mass, surfactant molecules, linear and angular momenta, and configurational momentum are developed in Sec. V. The local versions of these laws are

$$\varrho V^{\mathrm{mig}} = \varrho_v V_v^{\mathrm{mig}} = -J, \qquad (3a)$$

$$\mathring{n}^{\mathrm{x}} - n^{\mathrm{x}}(KV - \mathrm{div}_S \mathbf{u}_{\mathrm{tan}}) = -\mathrm{div}_S \mathrm{j} + \mathbf{j} \cdot \mathrm{n} - nV^{\mathrm{mig}}, \quad (3b)$$

$$\mathrm{div}_S \mathbb{T} = \mathbf{T}\mathrm{n} + \frac{J^2}{\varrho_v}\mathrm{n}, \qquad (3c)$$

$$\mathbb{T} = \mathbb{T}^{\mathrm{T}}, \qquad (3d)$$

$$\mathrm{div}_S \mathbb{C} + \mathrm{f} = \mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v}\mathrm{n}, \qquad (3e)$$

where ϱ and ϱ_v are the mass densities of the solution and vapor, V_v^{mig} is the migrational velocity of the interface relative to the vapor, J is the mass flow across the interface in the direction n, n and n^{x} are the bulk and interfacial molecular densities of the surfactant, $K = -\mathrm{div}_S \mathrm{n}$ is the total curvature of the interface, $\mathbf{u}_{\mathrm{tan}}$ is the tangential component of the velocity $\mathbf{u}$ of the solution, $\mathbf{j}$ and j are the bulk and interfacial fluxes of surfactant molecules, $\mathbf{T}$ and $\mathbb{T}$ are the bulk and interfacial Cauchy stress tensors, $\mathbf{C}$ and $\mathbb{C}$ are the bulk and interfacial configurational stress tensors, f is the internal configurational force density, div_S is the surface divergence on the interface, and a superposed circle denotes the normal time derivative following the migration of the interface through the solution (more precisely, the migrationally normal time derivative as introduced by Cermelli, Fried, and Gurtin [23]). In (3c) and (3e), the terms involving J^2 reflect the role of inertia and issue from the assumption that the mass density of the vapor is negligibly small in comparison to that of the solution. This approximation is used also by Burelbach, Bankoff, and Davis [10] and Danov *et al.* [9].

The external power expended on a subset of the interface by both standard and configurational forces is discussed in

Sec. VI. The final form for this power expenditure shows that no expense of power is associated with the tangential motion of the interface. This result is to be expected, since only the normal motion of the interface is intrinsic. On these grounds, we reason that the tangential component of the internal configurational density $\mathbb{f}$ must be indeterminate in the sense in which that term is used in classical mechanics. As a consequence of this result, we may conclude that only the normal component of the configurational momentum balance (3e) is relevant to the theory. This normal configurational momentum balance reads

$$\mathbb{C}_{\tan}\!:\!\mathbb{K} + \operatorname{div}_{\mathcal{S}}\mathbb{c} + f = \mathrm{n} \cdot \mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v}, \tag{4}$$

where $\mathbb{C}_{\tan}$ is the tangential component of the interfacial configurational stress $\mathbb{C}$, $\mathbb{K} = \operatorname{grad}_{\mathcal{S}}\mathrm{n}$ is the interfacial curvature tensor, $\mathbb{c}$ is the configurational shear, and $f = \mathbb{f} \cdot \mathrm{n}$ is the normal component of the force density $\mathbb{f}$.

The first and second laws of thermodynamics at the interface are developed in Sec. VII. The local versions of these laws are

$$\dot{\varepsilon}^{\mathrm{x}} - \vartheta\eta^{\mathrm{x}}(KV - \operatorname{div}_{\mathcal{S}}\mathbf{u}_{\tan})$$
$$= \mu\mathring{n}^{\mathrm{x}} - \mathrm{j}\cdot\operatorname{grad}_{\mathcal{S}}\mu - \mathbb{C}_{\tan}\!:\!\mathbb{D} - fV^{\mathrm{mig}} + \mathbb{c}\cdot\operatorname{grad}_{\mathcal{S}}V^{\mathrm{mig}}$$
$$- \operatorname{div}_{\mathcal{S}}\mathbb{h} + \mathbf{q}\cdot\mathrm{n} - \vartheta\eta V^{\mathrm{mig}} + q, \tag{5a}$$

$$\vartheta\mathring{\eta}^{\mathrm{x}} - \vartheta\eta^{\mathrm{x}}(KV - \operatorname{div}_{\mathcal{S}}\mathbf{u}_{\tan}) \geqslant \operatorname{div}_{\mathcal{S}}\frac{\mathbb{h}}{\vartheta} + \mathbf{q}\cdot\mathrm{n} - \vartheta\eta V^{\mathrm{mig}} + \frac{\vartheta}{\vartheta_v}q, \tag{5b}$$

where ε^{x} is the interfacial internal energy density, μ is the chemical potential of the surfactant measured relative to that of the solution, $\mathbb{C}_{\tan} = \mathbb{P}\mathbb{C}$ (with $\mathbb{P} = \mathbf{1} - \mathrm{n}\otimes\mathrm{n}$) is the tangential component of $\mathbb{C}$, $\mathbb{D}$ is the interfacial rate of stretch, $\mathbb{h}$ is the interfacial heat flux, $\mathbf{q}$ is the bulk heat flux, η and η^{x} are the bulk and interfacial entropy densities, ϑ and ϑ_v are the absolute temperatures of the solution and the vapor, and q is the heat flow from the solution to the vapor. Our formulation of the first two laws is predicated on the assumption that the surfactant chemical potential μ and the absolute temperature ϑ of the solution are smooth up to the interface and that the surface limits of these fields are equal to the surfactant chemical potential and absolute temperature on the interface. Of crucial importance is the observation that *the assumption that the surfactant chemical potential μ and the absolute temperature ϑ of the solution are smooth up to the interface does not rule out discontinuities between the interfacial limits of the chemical potential and the temperature of the solution and the corresponding interfacial limits in the vapor.*

Along with local versions of the basic laws, our development up until this point yields an interfacial counterpart of Eshelby's relation for the bulk configurational stress tensor **C**. In our setting, the bulk Eshelby relation has the form

$$\mathbf{C} = \left\{\omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2\right\}\mathbf{1} - \mathbf{T}, \quad \omega = \psi - n\mu, \tag{6}$$

where ω, ψ, and $\mathbf{T}$ denote the grand canonical potential density, the free-energy density, and the Cauchy stress tensor of the solution. Analogously, we find that the interfacial configurational stress tensor has the form

$$\mathbb{C} = \omega^{\mathrm{x}}\mathbb{P} - \mathbb{T} + \mathrm{n}\otimes\mathbb{c}, \quad \omega^{\mathrm{x}} = \psi^{\mathrm{x}} - n^{\mathrm{x}}\mu, \tag{7}$$

where ω^{x} is the interfacial grand canonical potential density, ψ^{x} is the interfacial free-energy density, and $\mathbb{T}$ is the interfacial Cauchy stress tensor. Because we neglect the mass of the interface, (7) contains no counterpart of the kinetic energy term entering (6). The bulk and interfacial Eshelby tensors (6) and (7) enter the configurational momentum balance and therefore play an important role in determining the form taken by our generalized Hertz-Knudsen-Langmuir equation. A derivation of the bulk result is provided in Sec. III. This derivation is performed independent of any particular constitutive equations and relies solely on a simple invariance argument. The derivation of (7) follows from the same notion of invariance. However, because that proof is complicated, its essential steps are relegated to the Appendix.

In Sec. VIII we present various alternative forms for the balances (3c) and (3e) of standard and configurational momentum. In particular, as a consequence of the representations (6) and (7), the normal configurational momentum balance (4) becomes

$$\mathbb{C}_{\tan}\!:\!\mathbb{K} + \operatorname{div}_{\mathcal{S}}\mathbb{c} + f = \omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2 - \mathrm{n}\cdot\mathbf{T}\mathrm{n} - \frac{J^2}{\varrho_v}. \tag{8}$$

Also, using the representations (6) and (7) in the normal component of the sum of (3c) and (3e) yields the normal combined momentum balance

$$\omega^{\mathrm{x}}K + \operatorname{div}_{\mathcal{S}}\mathbb{c} + f = \omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2, \tag{9}$$

which can be imposed instead of the normal configurational momentum balance (8) or, alternatively, instead of the normal component of the standard momentum balance (3c).

The local version of the second laws as derived in Sec. VII combines with the various interfacial balances to yield a dissipation inequality. Any choice of constitutive equations consistent with that dissipation inequality is thermodynamically compatible. If, in particular, we were to take the dissipation to be quadratic, we would obtain equations coupling the various effects underlying the interfacial transport of surfactant, momentum, and heat with the migration of the interface relative to the solution. In Sec. IX, we develop a relatively simple class of constitutive equations in which these classical transport mechanisms are decoupled from the migration of the interface. Specifically, in addition to equations of state of the classical form

$$\psi^{\mathrm{x}} = \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta), \tag{10a}$$

$$\mu = \frac{\partial\hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial n^{\mathrm{x}}}, \tag{10b}$$

$$\eta^{\mathrm{x}} = -\frac{\partial\hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial\vartheta}, \tag{10c}$$

we restrict our attention to the linear, isotrotropic relations

$$\mathbb{j} = -m \ \mathrm{grad}_{\mathcal{S}}\mu + m_s \ \mathrm{grad}_{\mathcal{S}}\vartheta, \tag{11a}$$

$$\mathbb{h} = -l_d \ \mathrm{grad}_{\mathcal{S}}\mu + l \ \mathrm{grad}_{\mathcal{S}}\vartheta, \tag{11b}$$

$$\mathbb{C}_{\mathrm{tan}} = -(\kappa + \zeta)(\mathrm{tr}\ \mathbb{D})\mathbb{P} - 2\nu\mathbb{D}_0, \tag{11c}$$

$$\mathbb{e} = -\alpha \ \mathrm{grad}_{\mathcal{S}}V^{\mathrm{mig}}, \tag{11d}$$

$$f = -\beta V^{\mathrm{mig}}, \tag{11e}$$

$$q = -\lambda(\vartheta - \vartheta_v), \tag{11f}$$

in which the surfactant mobility m, Soret coefficient m_s, Dufour coefficient k_d, thermal conductivity k, dilatational viscosity $\kappa + \zeta \geqslant 0$, rotational viscosity $\alpha \geqslant 0$, shear viscosity $\zeta \geqslant 0$, kinetic coefficient $\beta \geqslant 0$, and heat transfer coefficient $\lambda \geqslant 0$ may depend on $(n^{\mathrm{x}}, \vartheta)$. In (11a), $\mathbb{D}_0 = \mathbb{D} - \frac{1}{2}(\mathrm{tr}\mathbb{D})\mathbb{P}$ is the deviatoric component of the interfacial rate of stretch. Consistent with the work of Bedeaux and Kjelstrup [24], which indicates that, in settings involving interfacial transport, it is generally incorrect to neglect the Soret and Dufour effects, those effects are accounted for in (11a) and (11b). In view of (7), the theory also determines auxiliary constitutive equations for the Cauchy interfacial stress and the interfacial grand canonical potential density:

$$\mathbb{T} = \{\omega^{\mathrm{x}} + (\kappa + \zeta)\mathrm{tr}\ \mathbb{D}\}\mathbb{P} + 2\zeta\mathbb{D}_0,$$

$$\omega^{\mathrm{x}} = \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta) - n^{\mathrm{x}}\frac{\partial\hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial n^{\mathrm{x}}}. \tag{12}$$

The first equation of (12), which was proposed by Scriven [25], implies that the surface tension $\sigma = \frac{1}{2}\mathrm{tr}\mathbb{T}$ has the form

$$\sigma = \omega^{\mathrm{x}} + (\kappa + \zeta)\mathrm{tr}\ \mathbb{D} \tag{13}$$

and therefore consists of an equilibrium contribution coincident with the interfacial grand canonical potential density and a dissipative contribution associated with the interfacial rate of dilation.

In Sec. X we discuss sorption isotherms. Our considerations here stem from the hypothesis that the surfactant chemical potential μ and the absolute temperature ϑ of the solution are smooth up to the interface. Supposing that ψ and ψ^{x} are given by equations of state of the form $\psi = \hat{\psi}(n, \vartheta)$ and $\psi^{\mathrm{x}} = \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)$, this hypothesis yields the interfacial condition

$$\mu = \frac{\partial\hat{\psi}(n, \vartheta)}{\partial n} = \frac{\partial\hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial n^{\mathrm{x}}}. \tag{14}$$

We argue that $\hat{\psi}^{\mathrm{x}}$ is invertible in n^{x} for ϑ fixed; granted this, (14) defines a sorption isotherm of the form $n^{\mathrm{x}} = \mathcal{I}(n, \vartheta)$. We also provide a simple derivation of the classical Langmuir [26] sorption isotherm.

The general interfacial equations that arise on using the constitutive equations developed in Sec. VII in the balances (3b), (3c), (4), and (5a) are presented in Sec. XI. Those equations are complicated and, for that reason, in Sec. XII we develop approximate equations based on (i) the assumption that the behavior of the system remains close to a flat equilibrium state and (ii) a scaling under which various dissipative processes are negligible. The reduced versions of the molecular balance, energy balance, standard momentum balance, and normal configurational momentum balance are

$$\mathring{n}^{\mathrm{x}} - n^{\mathrm{x}}(KV - \mathrm{div}_{\mathcal{S}}\mathbf{u}_{\mathrm{tan}}) = \mathrm{div}_{\mathcal{S}}\{m_s \ \mathrm{grad}_{\mathcal{S}} \ \mu\} - \{m \ \mathrm{grad} \ \mu\} \cdot \mathrm{n}$$
$$- nV^{\mathrm{mig}}, \tag{15a}$$

$$\vartheta_v\{\mathring{\eta}^{\mathrm{x}} - \eta^{\mathrm{x}}(KV - \mathrm{div}_{\mathcal{S}}\mathbf{u}_{\mathrm{tan}})\} = -\{k \ \mathrm{grad} \ \vartheta\} \cdot \mathrm{n} - \ell V^{\mathrm{mig}}, \tag{15b}$$

$$\sigma K\mathrm{n} + \mathrm{grad}_{\mathcal{S}}\sigma + 2 \ \mathrm{div}_{\mathcal{S}}\{\zeta\mathbb{D}_0\} = 2\varrho\nu\mathbf{D}\mathrm{n} - \left\{p - \frac{J^2}{\varrho_v}\right\}\mathrm{n}, \tag{15c}$$

$$\beta V^{\mathrm{mig}} = -\ell\left\{\frac{\vartheta}{\vartheta_v} - 1\right\} - \left\{p - \frac{J^2}{\varrho_v}\right\} - \psi_0\left\{\frac{n}{n_0} - 1\right\} + \frac{1}{2}\varrho|\mathbf{u}|^2, \tag{15d}$$

where m is the bulk surfactant mobility, ℓ is the latent heat of evaporation, and ψ_0 and n_0 is the bulk densities of the free energy and surfactant molecules at flat equilibrium. A comparison of (1) and (15d) shows that our simplfied normal configurational momentum balance provides a slight generalization of the Hertz-Knudsen-Langmuir equation. If we set $\psi_0 = 0$ and assume that the terms $-J^2/\varrho_v$ and $\frac{1}{2}\varrho|\mathbf{u}|^2$ are negligible, then (15d) reduces to

$$\beta V^{\mathrm{mig}} = -\ell\left\{\frac{\vartheta}{\vartheta_v} - 1\right\} - p. \tag{16}$$

Bearing in mind that p is measured relative to the pressure of the vapor, (16) coincides with an equation considered by Wayner [27]. If, in addition to the foregoing assumptions, we require that $\vartheta_v = \vartheta_s$, then [20] becomes an equation used in place of the Hertz-Knudsen-Langmuir equation by Moosman and Homsey [28] and Ajaev and Homsey [29]. Pressure effects aside, (15d) shows that the vapor recoil effect embodied by the term $-J^2/\varrho_v$ in the standard momentum balance (15c) may exert a direct influence on evaporation and condensation. (The early experiments of Hickman [30,31] idenitifed the importance of vapor recoil in the stability of liquid-vapor interfaces. Stability analyses incorporating the vapor recoil term in the standard momentum balance while using the Hertz-Knudsen-Langmuir equation are provided by Palmer [32] and Burelback, Bankoff and Davis [10].) Also evident in (15d) are influences of the bulk molecular density n and the bulk kinetic energy density $\frac{1}{2}\varrho|\mathbf{u}|^2$.

The reduced version of normal combined momentum balance

$$\beta V^{\mathrm{mig}} = \omega^{\mathrm{x}} K - \ell \left\{ \frac{\vartheta}{\vartheta_v} - 1 \right\} - \psi_0 \left\{ \frac{n}{n_0} - 1 \right\} + \tfrac{1}{2} \varrho |\mathbf{u}|^2 \tag{17}$$

provides an alternative to (15d) in which the term $p - J^2/\varrho_v$ associated with pressure and vapor recoil is replaced by the term $\omega^{\mathrm{x}} K$ involving the product of the interfacial grand canonical potential, per unit area, with the total curvature. If we formally set $\psi_0 = 0$ and neglect kinetic energy, then [21] reduces to the kinetic Gibbs-Thomson equation

$$\ell \theta = \omega^{\mathrm{x}} K - \beta V^{\mathrm{mig}}, \quad \theta = \frac{\vartheta - \vartheta_v}{\vartheta_v}, \tag{18}$$

utilized by Voronkov [33] to study solidification. [See also Gurtin [34], who uses configurational forces to derive (18) and its anisotropic generalization.] The theory therefore demonstrates that, in lieu of effects associated with pressure and vapor recoil, processes of evaporation and condensation may be influenced by the curvature of the interface.

The paper concludes with a comparison, in Sec. XIII, of the reduced Eqs. (15) with the equations utilized by Danov *et al.* [9].

II. THEORY IN BULK

Throughout this section $\mathcal{P}(t)$ denotes an arbitrarily chosen bulk region that convects with the solution and $\mathbf{m}(\mathbf{x}, t)$ denotes the outward unit normal to $\partial\mathcal{P}(t)$.

A. Kinematics

We write $\mathbf{u}(\mathbf{x}, t)$ for the velocity and

$$\mathbf{L} = \operatorname{grad} \mathbf{u}, \quad \mathbf{D} = \tfrac{1}{2}(\mathbf{L} + \mathbf{L}^{\mathsf{T}}), \quad \text{and} \quad \mathbf{W} = \tfrac{1}{2}(\mathbf{L} - \mathbf{L}^{\mathsf{T}}) \tag{19}$$

for the *velocity gradient*, *rate of stretch*, and *rate of spin*. We assume that the solution is incompressible, so that

$$\operatorname{div} \mathbf{u} = \operatorname{tr} \mathbf{D} = 0. \tag{20}$$

We use a superposed dot to denote the *material time derivative*; e.g., for a scalar field $\Phi(\mathbf{x}, t)$,

$$\dot{\Phi} = \frac{\partial \Phi}{\partial t} + (\operatorname{grad} \Phi) \cdot \mathbf{u}. \tag{21}$$

Then, for $\mathcal{P}(t)$ for a region that convects with the solution and any field $\Phi(\mathbf{x}, t)$,

$$\frac{d}{dt} \int_{\mathcal{P}(t)} \Phi \, dv = \int_{\mathcal{P}(t)} \dot{\Phi} \, dv. \tag{22}$$

B. Balance of surfactant molecules

We write $n(\mathbf{x}, t)$ and $\mathbf{j}(\mathbf{x}, t)$ for the *molecular density* and *molecular flux* of surfactant in the solution. The balance of surfactant molecules then requires that, for any region $\mathcal{P}(t)$ that convects with the solution,

$$\frac{d}{dt} \int_{\mathcal{P}(t)} n \, dv = - \int_{\partial\mathcal{P}(t)} \mathbf{j} \cdot \mathbf{m} \, da \tag{23}$$

or, equivalently, by (22) and the divergence theorem, that the local law

$$\dot{n} = - \operatorname{div} \mathbf{j} \tag{24}$$

holds in the solution.

C. Standard balances for linear and angular momentum

We write ϱ for the (constant) *mass density* and $\mathbf{T}(\mathbf{x}, t)$ for the *Cauchy stress*. The balances of linear and angular momentum then require that, for any region $\mathcal{P}(t)$ that convects with the solution,

$$\frac{d}{dt} \int_{\mathcal{P}(t)} \varrho \mathbf{u} \, dv = \int_{\partial\mathcal{P}(t)} \mathbf{T}\mathbf{m} \, da \tag{25}$$

and

$$\frac{d}{dt} \int_{\mathcal{P}(t)} (\mathbf{x} - \mathbf{0}) \times \varrho \mathbf{u} \, dv = \int_{\partial\mathcal{P}(t)} (\mathbf{x} - \mathbf{0}) \times \mathbf{T}\mathbf{m} \, da \tag{26}$$

or, equivalently, by [25] and the divergence theorem, that the local laws

$$\varrho \dot{\mathbf{u}} = \operatorname{div} \mathbf{T}, \tag{27a}$$

$$\mathbf{T} = \mathbf{T}^{\mathsf{T}} \tag{27b}$$

hold in the solution.

The incompressibility of the solution requires that the Cauchy stress $\mathbf{T}$ admit a decomposition

$$\mathbf{T} = - p\mathbf{1} + \mathbf{S} \tag{28}$$

into a constitutively *indeterminate pressure* $p(\mathbf{x}, t)$ and a symmetric, traceless *extra stress* $\mathbf{S}(\mathbf{x}, t)$ available for constitutive prescription.

D. Digression: The chemical potential

We view the chemical potential as a *primitive quantity* that enters the theory through the manner in which it appears in the basic law expressing balance of energy. This contrasts sharply with what is most often done in the literature, where chemical potentials are either defined as derivatives of free energy with respect to molecular densities or are introduced variationally as Lagrange multipliers corresponding to constraint expressing the conservation of mass. To the contrary, we use a framework in which the balance of energy is basic and take the view that that balance should account properly for energy carried with the flow of molecules through the material [35,36]. To characterize the energy carried into regions by molecular transport, we introduce a *chemical potential* $\mu(\mathbf{x}, t)$; specifically, the flux of surfactant molecules, as represented by $\mathbf{j}$, is presumed to carry with it a flux of energy described by $\mu\mathbf{j}$; thus,

$$-\int_{\partial P(t)} \mu \mathbf{j} \cdot \mathbf{m}\, da \qquad (29)$$

represents the net rate at which energy is carried into $\mathcal{P}$ by the diffusive flow of surfactant molecules across $\partial\mathcal{P}$.

E. Balance of energy: Growth of entropy

We write $\varepsilon(\mathbf{x},t)$ and $\eta(\mathbf{x},t)$ for the *internal energy density* and *entropy density*, $\mu(\mathbf{x},t)$ for the *chemical potential* of the surfactant (measured relative to the chemical potential of the solvent), $\mathbf{q}(\mathbf{x},t)$ for the *heat flux*, and $\vartheta(\mathbf{x},t)$ for the (absolute) *temperature*. The first and second laws of thermodynamics—namely, *balance of energy* and *growth of entropy*—require that, for any region $\mathcal{P}(t)$ that convects with the solution,

$$\frac{d}{dt}\int_{\mathcal{P}(t)}\left\{\varepsilon + \frac{1}{2}\varrho|\mathbf{u}|^2\right\}dv$$

$$= \int_{\partial P(t)} \mathbf{Tm}\cdot\mathbf{u}\,da - \int_{\partial P(t)} \mu\mathbf{j}\cdot\mathbf{m}\,da - \int_{\partial P(t)} \mathbf{q}\cdot\mathbf{m}\,da$$

$$(30)$$

and

$$\frac{d}{dt}\int_{\mathcal{P}(t)} \eta\,dv \geqslant -\int_{\partial P(t)} \frac{\mathbf{q}}{\vartheta}\cdot\mathbf{m}\,da \qquad (31)$$

or, equivalently, by (20) and the divergence theorem, (22), (27), and (28), that the local laws

$$\dot{\varepsilon} = \mathbf{S}:\mathbf{D} + \mu\dot{n} - \mathbf{j}\cdot\operatorname{grad}\mu - \operatorname{div}\mathbf{q} \qquad (32)$$

and

$$\dot{\eta} \geqslant -\operatorname{div}\frac{\mathbf{q}}{\vartheta} \qquad (33)$$

hold in the solution.

If we define the *free-energy density* $\psi(\mathbf{x},t)$, measured relative to the free-energy density of the vapor, via

$$\psi = \varepsilon - \vartheta\eta, \qquad (34)$$

then, subtracting (33) from (32), we arrive at the *local free-energy inequality*

$$\dot{\psi} + \eta\dot{\vartheta} - \mu\dot{n} - \mathbf{S}:\mathbf{D} + \mathbf{j}\cdot\operatorname{grad}\mu + \frac{1}{\vartheta}\mathbf{q}\cdot\operatorname{grad}\vartheta \leqslant 0.$$

$$(35)$$

F. Constitutive equations

As constitutive equations for the solution, we take the classical state relations

$$\psi = \hat{\psi}(n,\vartheta), \qquad (36a)$$

$$\mu = \frac{\partial\hat{\psi}(n,\vartheta)}{\partial n}, \qquad (36b)$$

$$\eta = -\frac{\partial\hat{\psi}(n,\vartheta)}{\partial\vartheta}, \qquad (36c)$$

the Newtonian viscous flow relation

$$\mathbf{S} = 2\varrho\,\nu(n,\vartheta)\mathbf{D}, \qquad (37)$$

the Fick-Soret law

$$\mathbf{j} = -M(n,\vartheta)\operatorname{grad}\mu - M_s(n,\vartheta)\operatorname{grad}\vartheta, \qquad (38)$$

and the Fourier-Dufour law

$$\mathbf{q} = -L_d(n,\vartheta)\operatorname{grad}\mu - L(n,\vartheta)\operatorname{grad}\vartheta. \qquad (39)$$

Here, the kinematic viscosity ν, surfactant mobility M, Soret coefficient M_s, Dufour coefficient L_d, and thermal conductivity L obey

$$\nu \geqslant 0, \quad M \geqslant 0, \quad L \geqslant 0, \quad \text{and} \quad ML \geqslant \tfrac{1}{4}(M_s + L_d)^2. \qquad (40)$$

Granted (40), the constitutive relations (36)–(39) are consistent with the free-energy inequality (35).

Also important in what follows is the *grand canonical potential density* defined by

$$\omega = \varepsilon - \vartheta\eta - n\mu = \psi - n\mu \qquad (41)$$

and described by the constitutive equation

$$\omega = \hat{\omega}(n,\vartheta) = \hat{\psi}(n,\vartheta) - n\frac{\partial\hat{\psi}(n,\vartheta)}{\partial n}. \qquad (42)$$

Somewhat more conventional alternatives to (38) and (39) arise on using (36b) to express $\operatorname{grad}\mu$ in terms of the gradients of $\operatorname{grad}\vartheta$ and $\operatorname{grad}n$.

III. CONFIGURATIONAL MECHANICS AND THERMODYNAMICS IN BULK

We now modify the discussion of Anderson *et al.* [8], which recasts in a spatial setting Gurtin's [21,22] approach to configurational forces, to account for solute diffusion.

A. Balance of configurational momentum

We consider a configurational momentum balance involving three fields: a *specific configurational momentum* $\mathbf{p}(\mathbf{x},t)$, a *configurational stress* $\mathbf{C}(\mathbf{x},t)$, and an *internal configurational force density* $\mathbf{f}(\mathbf{x},t)$. The balance of configurational momentum then requires that, for any region $\mathcal{P}(t)$ that convects with the solution,

$$\frac{d}{dt}\int_{\mathcal{P}(t)} \varrho\mathbf{p}\,dv = \int_{\partial P(t)} \mathbf{Cm}\,da + \int_{\mathcal{P}(t)} \mathbf{f}\,dv \qquad (43)$$

or, equivalently, by [25] and the divergence theorem, that the local law

$$\varrho\dot{\mathbf{p}} = \operatorname{div}\mathbf{C} + \mathbf{f} \qquad (44)$$

hold in the solution.

B. Migrating control volumes: Observed and relative velocities

To characterize the way that configurational forces perform work, a means of capturing the kinematics associated with the transfer of material is needed. We accomplish this with the aid of *control volumes* $\mathcal{R}(t)$ that migrate relative to the solution and thereby result in the transfer of matter to— and the removal of material from—$\mathcal{R}(t)$ at $\partial\mathcal{R}(t)$. Here it is essential that regions $\mathcal{P}(t)$ convecting with the solution not be confused with control volumes $\mathcal{R}(t)$ that migrate relative to the solution.

Unless specified to the contrary, $\mathcal{R}(t)$ is a *migrating control volume* with $V_{\partial\mathcal{R}}(\mathbf{x},t)$ the (scalar) *normal velocity* of $\partial\mathcal{R}(t)$ in the direction of the outward unit normal $\mathbf{m}(\mathbf{x},t)$. To describe power expenditures associated with the migration of $\mathcal{R}(t)$, we introduce a *velocity field* $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$ for $\partial\mathcal{R}(t)$. Compatibility then requires that $\mathbf{v}_{\partial\mathcal{R}}$ have $V_{\partial\mathcal{R}}$ as its normal component,

$$\mathbf{v}_{\partial\mathcal{R}} \cdot \mathbf{m} = V_{\partial\mathcal{R}}, \qquad (45)$$

but $\mathbf{v}_{\partial\mathcal{R}}$ is otherwise arbitrary.

Non-normal velocity fields, while not intrinsic, are important. For example, given an arbitrary time-dependent parametrization $\mathbf{x} = \hat{\mathbf{x}}(\xi_1,\xi_2,t)$ of $\partial\mathcal{R}(t)$, the field defined by $\mathbf{v}_{\partial\mathcal{R}}(\hat{\mathbf{x}}(\xi_1,\xi_2,t),t) = \partial\hat{\mathbf{x}}(\xi_1,\xi_2,t)/\partial t$ [holding (ξ_1,ξ_2) fixed] is a velocity field for $\partial\mathcal{R}(t)$, but $\mathbf{v}_{\partial\mathcal{R}}(\mathbf{x},t)$ is generally non-normal. We refer to the normal velocity $V_{\partial\mathcal{R}}$ and any choice of the velocity field $\mathbf{v}_{\partial\mathcal{R}}$ for $\partial\mathcal{R}$ as *observed velocities* for $\partial\mathcal{R}$, since they represent velocity fields that characterize the motion of $\mathcal{R}$ through space, independent of the motion of the solution. While it is important that we allow for the use of non-normal velocity fields, we require the following hypothesis: (A) *that the theory itself not depend on the particular observed velocity field used to describe a given migrating control volume*. We refer to the hypothesis (A) as *intrinsicality*. Intrinsicality is reminiscent of, but different from, the general requirement that physical theories be independent of the observer.

It is also possible to characterize the motion of $\mathcal{R}$ *relative to the solution*; in this case we use the *migrational velocities*

$$\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}} = \mathbf{v}_{\partial\mathcal{R}} - \mathbf{u} \quad \text{and} \quad V_{\partial\mathcal{R}}^{\mathrm{mig}} = V_{\partial\mathcal{R}} - \mathbf{u} \cdot \mathbf{m}. \qquad (46)$$

C. Basic laws for a migrating control volume

Since div $\mathbf{u}=0$, we may use (21) and $(46)_2$ and the divergence theorem to conclude that

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \Phi \, dv = \int_{\mathcal{R}(t)} \frac{\partial\Phi}{\partial t} dv + \int_{\partial\mathcal{R}(t)} \Phi V_{\partial\mathcal{R}} \, da$$

$$= \int_{\mathcal{R}(t)} \{\dot{\Phi} - \mathbf{u} \cdot \mathrm{grad}\, \Phi\} dv$$

$$+ \int_{\partial\mathcal{R}(t)} \Phi\{V_{\partial\mathcal{R}}^{\mathrm{mig}} + \mathbf{u} \cdot \mathbf{m}\} da$$

$$= \int_{\mathcal{R}(t)} \dot{\Phi} \, dv + \int_{\partial\mathcal{R}(t)} \Phi V_{\partial\mathcal{R}}^{\mathrm{mig}} \, da. \qquad (47)$$

By integrating the local laws $(27)_1$, (24), (32), (33), and (44) over $\mathcal{R}(t)$ and using (47) and the divergence theorem, we obtain versions of those laws valid for a migrating control volume:

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \varrho\mathbf{u} \, dv = \int_{\partial\mathcal{R}(t)} \{\mathbf{Tm} + \varrho\mathbf{u}V_{\partial\mathcal{R}}^{\mathrm{mig}}\} da, \qquad (48\mathrm{a})$$

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \varrho\mathbf{p} \, dv = \int_{\partial\mathcal{R}(t)} \{\mathbf{Cm} + \varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}\} da + \int_{\mathcal{R}(t)} \mathbf{f} \, dv, \qquad (48\mathrm{b})$$

$$\frac{d}{dt}\int_{\mathcal{R}(t)} n \, dv = -\int_{\partial\mathcal{R}(t)} \{\mathbf{j} \cdot \mathbf{m} - nV_{\partial\mathcal{R}}^{\mathrm{mig}}\} da, \qquad (48\mathrm{c})$$

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \left\{\varepsilon + \frac{1}{2}\varrho|\mathbf{u}|^2\right\} dv = \int_{\partial\mathcal{R}(t)} \left\{\mathbf{Tm} \cdot \mathbf{u} - \mu\mathbf{j} \cdot \mathbf{m} - \mathbf{q} \cdot \mathbf{m}\right.$$
$$\left. + \left\{\varepsilon + \frac{1}{2}\varrho|\mathbf{u}|^2\right\}V_{\partial\mathcal{R}}^{\mathrm{mig}}\right\} da, \qquad (48\mathrm{d})$$

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \eta \, dv \geq -\int_{\partial\mathcal{R}(t)} \frac{\mathbf{q} \cdot \mathbf{m} - \vartheta\eta V_{\partial\mathcal{R}}^{\mathrm{mig}}}{\vartheta} da. \qquad (48\mathrm{e})$$

In view of (46), the first two equations of (48) suggest that $\mathbf{Tm}+\varrho\mathbf{u}V_{\partial\mathcal{R}}^{\mathrm{mig}}=\{\mathbf{T}+\varrho\mathbf{u}\otimes\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}\}\mathbf{m}$ and $\mathbf{Cm}+\varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}=\{\mathbf{C}+\varrho\mathbf{p}\otimes\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}\}\mathbf{m}$ be viewed as *effective tractions*. Similarly, Eqs. (48c) and (48e) suggest that $\mathbf{j}-n\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}$ and $\{\mathbf{q}-\vartheta\eta\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}\}/\vartheta$ be viewed as *effective fluxes of surfactant molecules and entropy*. While correct, the interpretation of $-\mathbf{T}^{\mathsf{T}}\mathbf{u}+\mu\mathbf{j}+\mathbf{q}-\{\varepsilon+\frac{1}{2}\varrho|\mathbf{u}|^2\}\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}$ as an *effective energy flux* is of limited value.

The energy balance (48d) accounts only *implicitly* for the power expended by configurational forces. We next consider an alternative version of that balance in which cofigurational power expenditures are accounted for *explicitly*.

D. Configurational form of the first law

Following Gurtin [21,22] and Anderson *et al.* [8], a version of energy balance for a migrating control volume $\mathcal{R}(t)$ that accounts explicitly for configurational power expenditures is

$$\frac{d}{dt}\int_{\mathcal{R}(t)} \left\{\varepsilon + \frac{1}{2}\varrho|\mathbf{u}|^2\right\} dv$$

$$= \underbrace{\int_{\partial\mathcal{R}(t)} \{(\mathbf{Tm} + \varrho\mathbf{u}V_{\partial\mathcal{R}}^{\mathrm{mig}}) \cdot \mathbf{v}_{\partial\mathcal{R}} + (\mathbf{Cm} + \varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}) \cdot \mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}\} da}_{W(\mathcal{R}(t))}$$

$$\underbrace{-\int_{\partial\mathcal{R}(t)} \mu\{\mathbf{j} \cdot \mathbf{m} - nV_{\partial\mathcal{R}}^{\mathrm{mig}}\} da}_{E(\mathcal{R}(t))} \underbrace{- \int_{\partial\mathcal{R}(t)} \{\mathbf{q} \cdot \mathbf{m} - \vartheta\eta V_{\partial\mathcal{R}}^{\mathrm{mig}}\} da}_{Q(\mathcal{R}(t))}. \qquad (49)$$

Before establishing the precise way in which (49) is equiva-

lent to the standard form (48d), we discuss the physical ideas underlying (49).

The abstract structure of (49) treats a migrating control volume as a "thermodynamic entity" in which the inflow of energy is subsumed by an expenditure of power—accounting for both standard and configurational forces—and effective flows of energy associated with surfactant and heat transport.

The physical hypothesis underlying the chosen form for the power expenditure $W(\mathcal{R})$ is the presumption that configurational forces expend power in consort with transfers of material. In particular, *we view* $\mathbf{Cm} + \varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}$ *as a force, per unit area, associated with the transfer of material across* $\partial\mathcal{R}$; since the migrational velocity $\mathbf{v}_{\partial\mathcal{R}} - \mathbf{u}$ represents the velocity with which *material is transferred across* $\partial\mathcal{R}$, we take $\mathbf{v}_{\partial\mathcal{R}} - \mathbf{u}$ to be an appropriate power-conjugate velocity for $\mathbf{Cm} + \varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}$ and, therefore, assume that the migration of $\mathcal{R}$ is accompanied by the power expenditure

$$\int_{\partial\mathcal{R}(t)} \{\mathbf{Cm} + \varrho\mathbf{p}V_{\partial\mathcal{R}}^{\mathrm{mig}}\} \cdot (\mathbf{v}_{\partial\mathcal{R}} - \mathbf{u})da. \qquad (50)$$

In deciding on the appropriate expenditure by extended standard traction, it is important to emphasize that material is continually being transferred across $\partial\mathcal{R}$ as a result of its migration through the solution; hence, $\partial\mathcal{R}(t)$ *has no intrinsic material description*. We therefore take the observed velocity $\mathbf{v}_{\partial\mathcal{R}}$ of $\partial\mathcal{R}$, rather than the material velocity $\mathbf{u}$, as the appropriate conjugate velocity for $\mathbf{Tm} + \varrho\mathbf{u}V_{\partial\mathcal{R}}^{\mathrm{mig}}$ and write the standard power expenditure in the form

$$\int_{\partial\mathcal{R}(t)} \{\mathbf{Tm} + \varrho\mathbf{u}V_{\partial\mathcal{R}}^{\mathrm{mig}}\} \cdot \mathbf{v}_{\partial\mathcal{R}} \, da. \qquad (51)$$

Finally, the body force $\mathbf{f}$, being internal, is viewed as acting *within* the control volume $\partial\mathcal{R}$; as such, $\mathbf{f}$ cannot affect the *external* power expenditure $W(\mathcal{R})$.

The integral $E(\mathcal{R})$ represents the effective energy flow induced by the flow of surfactant molecules across $\partial\mathcal{R}$. The chosen form of $E(\mathcal{R})$ is completely consistent with the reasoning leading to the conventional term (29) entering the energy balance for a region $\mathcal{P}$ convecting with the solution: granted the interpretation of $\mathbf{j} \cdot \mathbf{m} - nV_{\partial\mathcal{R}}^{\mathrm{mig}}$ as the effective flux of surfactant molecules on $\partial\mathcal{R}$, $\mu\{\mathbf{j} \cdot \mathbf{m} - nV_{\partial\mathcal{R}}^{\mathrm{mig}}\}$ is the associated energy flux and we are led to consider

$$E(\mathcal{R}(t)) = -\int_{\partial\mathcal{R}(t)} \mu\{\mathbf{j} \cdot \mathbf{m} - nV_{\partial\mathcal{R}}^{\mathrm{mig}}\}da \qquad (52)$$

as the appropriate choice for the effective energy flow across $\partial\mathcal{R}$.

The integral $Q(\mathcal{R})$ represents the effective heat flow across $\partial\mathcal{R}$. The chosen form of $Q(\mathcal{R})$ is completely consistent with the relation between heat flux and entropy flux underlying the conventional statements (30) and (31) of the first two laws. Specifically, granted the interpretation of $\{\mathbf{q} - \vartheta\eta\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}\}/\vartheta$ as the effective flux of entropy on $\partial\mathcal{R}$, we require that, on $\partial\mathcal{R}$,

$$\text{entropy flow per unit area} = \frac{\text{heat flow per unit area}}{\vartheta},$$

then we are led to consider

$$Q(\mathcal{R}(t)) = -\int_{\partial\mathcal{R}(t)} \{\mathbf{q} \cdot \mathbf{m} - \vartheta\eta V_{\partial\mathcal{R}}^{\mathrm{mig}}\}da \qquad (53)$$

as the appropriate choice for the effective heat flow across $\partial\mathcal{R}$.

E. Equivalence of the standard and configurational forms of the first law: The Eshelby relation as a consequence of intrinsicality

The basic laws (48) for a migrating control volume involve only the intrinsic normal migrational velocity $V_{\partial\mathcal{R}}^{\mathrm{mig}}$ and, thus, satisy the intrinsicality hypothesis (A). The power expenditure $W(\mathcal{R})$ entering the configurational statement (49) of the first law involves, however, the vectorial migrational velocity $\mathbf{v}_{\partial\mathcal{R}}^{\mathrm{mig}}$ and, therefore, is not necessarily intrinsic. In Appendix A, we establish the following.

Equivalency theorem: *The first law in the configurational forms* (49), *subject to the intrinsicality hypothesis* (A), *is equivalent to this laws in the standard form* (48d), *supplemented by the* Eshelby relation

$$\mathbf{C} = \left\{\psi - \mu n - \tfrac{1}{2}\varrho|\mathbf{u}|^2\right\}\mathbf{1} - \mathbf{T} \qquad (54)$$

and the configurational-momentum relation

$$\mathbf{p} = -\mathbf{u}. \qquad (55)$$

Before proceeding, we note that, by (41), the Eshelby relation (54) admits an alternative form

$$\mathbf{C} = \left\{\omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2\right\}\mathbf{1} - \mathbf{T}, \qquad (56)$$

involving the grand canonical potential density ω.

F. Role of the bulk configurational momentum balance in the theory

Roughly speaking, the configurational system—that is, the configurational stress $\mathbf{C}$, momentum $\mathbf{p} = -\mathbf{u}$, and internal force density $\mathbf{f}$—is related to the integrity of the body's material structure and expends power in concert with the transfer of material and in the motion of defects. For a solution free of bulk defects, one therefore expects that the bulk configurational momentum balance should be irrelevant to the theory. Consistent with this expectation, we view $\mathbf{f}$ as determined via the configurational momentum balance. In view of the linear momentum balance (27a) and the Eshelby relation (56), it follows that $\varrho\dot{\mathbf{u}} - \mathrm{div}\,\mathbf{C} = -\mathrm{grad}\{\omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2\}$ (independent of constitution). The configurational momentum balance (44) therefore implies that $\mathbf{f} = -\mathrm{grad}\{\omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2\}$ and, granted this and the relations (54) and (55), the configurational force balance is a direct consequence of the standard force balance. On the other hand, as we shall see, the configurational bal-

ance on the interface separating the solution and the vapor is an independent balance, not derivable from standard interfacial results.[1]

IV. INTERFACIAL KINEMATICS

We assume that the interface separating the solution and vapor is a smoothly evolving surface $\mathcal{S}(t)$ oriented by a *unit normal field* $\mathrm{n}(\mathbf{x},t)$ directed into the region occupied by the vapor. We write $V(\mathbf{x},t)$ for the (scalar) *normal velocity* of $\mathcal{S}(t)$.

Instead of working in a reference frame that moves with the interface, which might be valuable for the analysis of certain specific problems, we find it advantageous to use an intrinsic coordinate-free formulation. In particular, this approach allows us to state and examine the consequences of invariance requirements that allow us to determine a representation for the interfacial configurational stress.

A. Interfacial fields

An *interfacial field* is a smooth field defined on $\mathcal{S}(t)$ for all time t. An interfacial vector field $\mathrm{g}(\mathbf{x},t)$ is *tangential* if

$$\mathrm{g} \cdot \mathrm{n} = 0. \tag{57}$$

For an interfacial tensor field $\mathbb{G}(\mathbf{x},t)$ we require that[2]

$$\mathbb{G}\mathrm{n} = \mathbf{0}; \tag{58}$$

if, in addition,

$$\mathbb{G}^{\mathsf{T}}\mathrm{n} = \mathbf{0}, \tag{59}$$

so that $\mathbb{G}$ maps tangent vectors to tangent vectors, we then say that $\mathbb{G}$ is *fully tangential*. An example of a fully tangential interfacial tensor field is the *projection*

$$\mathbb{P} = \mathbf{1} - \mathrm{n} \otimes \mathrm{n} \tag{60}$$

onto $\mathcal{S}$. Each interfacial tensor field $\mathbb{G}$ admits a decomposition of the form

$$\mathbb{G} = \mathbb{G}_{\mathrm{tan}} + \mathrm{n} \otimes \mathrm{g}, \tag{61}$$

in which $\mathbb{G}_{\mathrm{tan}} = \mathbb{P}\mathbb{G}$ is fully tangential and $\mathrm{g} = \mathbb{G}^{\mathsf{T}}\mathrm{n}$ is *tangential*. The verification of the decomposition (61) is straightforward: simply expand $\mathbb{P}\mathbb{G}$ using (60).

B. Interfacial gradient: Interfacial divergence theorem

The *interfacial gradient* $\mathrm{grad}_{\mathcal{S}}$ is defined by the chain rule; that is, for $\varphi(\mathbf{x},t)$ an interfacial scalar field, $\mathrm{g}(\mathbf{x},t)$ an interfacial vector field, and $\mathrm{z}(\lambda)$ an arbitrary curve on $\mathcal{S}$,

$$\frac{d}{d\lambda}\varphi(\mathrm{z}(\lambda),t) = [\mathrm{grad}_{\mathcal{S}}\varphi(\mathrm{z}(\lambda),t)] \cdot \frac{d\mathrm{z}}{d\lambda}$$

and

$$\frac{d}{d\lambda}\mathrm{g}(\mathrm{z}(\lambda),t) = [\mathrm{grad}_{\mathcal{S}}\mathrm{g}(\mathrm{z}(\lambda),t)]\frac{d\mathrm{z}}{d\lambda}.$$

Since $d\mathbf{z}/d\lambda$ is tangent to $\mathcal{S}$, this defines $\mathrm{grad}_{\mathcal{S}}\varphi$ and $\mathrm{grad}_{\mathcal{S}}\mathrm{g}$ only on vectors tangent to $\mathcal{S}$, but in accordance with (57) and (58), we extend $\mathrm{grad}_{\mathcal{S}}\varphi$ and $\mathrm{grad}_{\mathcal{S}}\mathrm{g}$ by requiring that $(\mathrm{grad}_{\mathcal{S}}\varphi) \cdot \mathrm{n} = 0$ and $(\mathrm{grad}_{\mathcal{S}}\mathrm{g})\mathrm{n} = \mathbf{0}$. Thus $\mathrm{grad}_{\mathcal{S}}\varphi$ is a tangential vector field, while $\mathrm{grad}_{\mathcal{S}}\mathrm{g}$ is an interfacial tensor field. The *interfacial divergence* of g is then defined by

$$\mathrm{div}_{\mathcal{S}}\mathrm{g} = \mathrm{tr}(\mathrm{grad}_{\mathcal{S}}\mathrm{g}) \tag{62}$$

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

$$\mathrm{k} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{G} = \mathrm{div}_{\mathcal{S}}(\mathbb{G}^{\mathsf{T}}\mathrm{k}) - \mathbb{G}{:}\mathrm{grad}_{\mathcal{S}}\mathrm{k} \tag{63}$$

for all interfacial vector fields k.

A smooth interfacial field can always be extended smoothly to a (three-dimensional) neighborhood of any given point $\mathbf{x}$ of $\mathcal{S}(t)$. Such local extensions can be used to express $\mathrm{grad}_{\mathcal{S}}$ in terms of the bulk gradient operator. For example,

$$\mathrm{grad}_{\mathcal{S}}\varphi = \mathbb{P}\mathrm{grad}_{\mathcal{S}} \quad \text{and} \quad \mathrm{grad}_{\mathcal{S}}\mathrm{g} = (\mathrm{grad}\,\mathrm{g})\mathbb{P}, \tag{64}$$

so that, for the particular vector field $\mathrm{g}(\mathbf{x}) = \mathbf{x}$,

$$\mathrm{grad}_{\mathcal{S}}\mathrm{g} = \mathbb{P}. \tag{65}$$

Let g and k be surface vector fields with g *tangential*, and let $\mathbb{G}$ be an interfacial tensor field. Then the *interfacial divergence theorem* asserts that, for any subsurface $\mathcal{A}$ of $\mathcal{S}$,

$$\int_{\partial\mathcal{A}} \mathrm{g} \cdot \mathrm{m}\, ds = \int_{\mathcal{A}} \mathrm{div}_{\mathcal{S}}\mathrm{g}\, da, \tag{66a}$$

$$\int_{\partial\mathcal{A}} \mathbb{G}\mathrm{m}\, ds = \int_{\mathcal{A}} \mathrm{div}_{\mathcal{S}}\mathbb{G}\, da, \tag{66b}$$

$$\int_{\partial\mathcal{A}} \mathbb{G}\mathrm{m} \cdot \mathrm{k}\, ds = \int_{\mathcal{A}} \{\mathrm{k} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{G} + \mathbb{G}{:}\mathrm{grad}_{\mathcal{S}}\mathrm{k}\}da, \tag{66c}$$

where m denotes the unit normal to $\partial\mathcal{A}$. Granted (63), (66b), and (66c) are simple corollaries of (66a): to obtain (66b) from (66a), choose $\mathrm{g} = \mathbb{G}^{\mathsf{T}}\mathrm{a}$ with $\mathbb{G}$ a superficial tensor field and $\mathrm{a} \neq \mathbf{0}$ constant; to obtain (66c) from (66a), choose $\mathrm{g} = \mathbb{G}^{\mathsf{T}}\mathrm{k}$ with $\mathbb{G}$ an interfacial tensor field and k a (not necessarily tangential) interfacial vector field.

C. Interfacial curvature tensor:
Total curvature—scalar normal velocity

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

$$\mathbb{K} = -\mathrm{grad}_{\mathcal{S}}\mathrm{n} \tag{67}$$

is fully tangential and symmetric, and

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[1]Cf. the materials science literature, where one often finds interfacial configurational balances determined via a minimum principle, assuming equilibrium, and then used as missing interface conditions for dynamical problems.

[2]An interfacial tensor field would generally be defined at each $\mathbf{x}$ on $\mathcal{S}(t)$ as a linear transformation of the tangent space at $\mathbf{x}$ into $\mathbb{R}^3$; the requirement (58) allows us to consider $\mathbb{G}(\mathbf{x},t)$ at each point $\mathbf{x}$ on $\mathcal{S}(t)$ as a linear transformation of $\mathbb{R}^3$ into $\mathbb{R}^3$.

$$K = \text{tr}\mathbb{K} = -\text{div}_{\mathcal{S}}\text{n} \qquad (68)$$

is the *total curvature* (i.e., twice the mean curvature). Then, by (60), we have the identity

$$\text{div}_{\mathcal{S}}\mathbb{P} = K\text{n}. \qquad (69)$$

Since $\mathbb{G}^{\mathsf{T}}\text{n} = \mathbf{0}$ for any fully tangential tensor field $\mathbb{G}$, choosing $\text{h} = \text{n}$ and $\mathbb{G}$ fully tangential in (63) and (67) yields the useful identity

$$\text{n} \cdot \text{div}_{\mathcal{S}}\mathbb{G} = \mathbb{G}:\mathbb{K} \quad \text{for } \mathbb{G} \text{ fully tangential.} \qquad (70)$$

Recalling that $V(\mathbf{x},t)$ denotes the (scalar) *normal velocity* of $\mathcal{S}$, we then have the useful identities

$$\text{grad}_{\mathcal{S}}(V\text{n}) = \text{n} \otimes \text{grad}_{\mathcal{S}}V - V\mathbb{K},$$

$$\text{div}_{\mathcal{S}}(V\text{n}) = -KV. \qquad (71)$$

D. Interfacial limit of the bulk velocity: Interfacial velocity gradient

We write $\mathbf{u}_{\text{tan}}(\mathbf{x},t)$ for the tangential component of the interfacial limit of the bulk velocity, as defined by

$$\mathbf{u}_{\text{tan}} = \mathbb{P}\mathbf{u}. \qquad (72)$$

Then, the interfacial limit of $\mathbf{u}$ can be expressed as

$$\mathbf{u} = \mathbf{u}_{\text{tan}} + (\mathbf{u} \cdot \text{n})\text{n} \qquad (73)$$

and, by (67), has interfacial gradient

$$\text{grad}_{\mathcal{S}}\mathbf{u} = \text{grad}_{\mathcal{S}}\mathbf{u}_{\text{tan}} - (\mathbf{u} \cdot \text{n})\mathbb{K} + \text{n} \otimes \text{grad}_{\mathcal{S}}(\mathbf{u} \cdot \text{n}) \quad (74)$$

and interfacial divergence

$$\text{div}_{\mathcal{S}}\mathbf{u} = \text{div}_{\mathcal{S}}\mathbf{u}_{\text{tan}} - (\mathbf{u} \cdot \text{n})K. \qquad (75)$$

Additionally, we may define the *interfacial velocity gradient*, *interfacial rate of stretch*, and *interfacial rate of spin* by

$$\mathbb{L} = \text{grad}_{\mathcal{S}}\mathbf{u} = \mathbf{L}\mathbb{P} = (\mathbf{D} + \mathbf{W})\mathbb{P}, \qquad (76a)$$

$$\mathbb{D} = \tfrac{1}{2}(\mathbb{P}\mathbf{L} + \mathbf{L}^{\mathsf{T}}\mathbb{P}) = \mathbb{P}\mathbf{D}\mathbb{P}, \qquad (76b)$$

$$\mathbb{W} = \tfrac{1}{2}(\mathbb{P}\mathbf{L} - \mathbf{L}^{\mathsf{T}}\mathbb{P}) = \mathbb{P}\mathbf{W}\mathbb{P}, \qquad (76c)$$

where it is understood that $\mathbf{L}$, $\mathbf{D}$, and $\mathbf{W}$ are evaluated on $\mathcal{S}$. The tensors $\mathbb{D}$ and $\mathbb{W}$ are fully tangential.

E. Interfacial velocity fields

We let $\text{v}(\mathbf{x},t)$ denote a *velocity field for $\mathcal{S}$*—that is, a velocity field describing the evolution of the interface. The normal component of v must then satisfy

$$V = \text{v} \cdot \text{n}, \qquad (77)$$

but the tangential component of v—namely, $\mathbb{P}\text{v}$—which is not intrinsic, *may be arbitrarily chosen*. The fields

$$\text{v}^{\text{mig}} = \text{v} - \mathbf{u}, \qquad (78a)$$

$$V^{\text{mig}} = V - \mathbf{u} \cdot \text{n}, \qquad (78b)$$

represent *migrational velocites of $\mathcal{S}$ relative to the bulk solution.*

Consider an arbitrary migrating subsurface $\mathcal{A}(t)$ of $\mathcal{S}(t)$. To describe the migration of $\mathcal{A}(t)$, we introduce a field $\text{v}_{\partial\mathcal{A}}(\mathbf{x},t)$ defined over $\partial\mathcal{A}(t)$ for all t. Compatibility then requires that

$$\text{v}_{\partial\mathcal{A}} \cdot \text{n} = V, \qquad (79a)$$

$$\text{v}_{\partial\mathcal{A}} \cdot \text{m} = V_{\partial\mathcal{A}}, \qquad (79b)$$

where $V_{\partial\mathcal{A}}$, which is intrinsic, is the scalar normal velocity of $\partial\mathcal{A}$ in the direction of its normal m.

The motion of $\partial\mathcal{A}$ relative to the solution is described by the *migrational velocity* $\text{v}_{\partial\mathcal{A}} - \mathbf{u}$. Further,

$$V_{\partial\mathcal{A}}^{\text{mig}} = V_{\partial\mathcal{A}} - \mathbf{u}_{\text{tan}} \cdot \text{m} \qquad (80)$$

represents the *normal migrational velocity of $\partial\mathcal{A}$.*

Let $\text{w}_{\partial\mathcal{A}}(\mathbf{x},t)$ be defined by the decomposition

$$\text{v}_{\partial\mathcal{A}} = \text{v} + \text{w}_{\partial\mathcal{A}}. \qquad (81)$$

Then, by (77) and (79), $\text{w}_{\partial\mathcal{A}} \cdot \text{n} = \text{v}_{\partial\mathcal{A}} \cdot \text{n} - \text{v} \cdot \text{n} = V - V = 0$ and $\text{w}_{\partial\mathcal{A}}$ is *tangential.*

The component of $\text{v}_{\partial\mathcal{A}}$ tangential to $\partial\mathcal{A}$ is not intrinsic and *may be arbitrarily chosen*. We require that the theory not depend on the velocity field $\text{v}_{\partial\mathcal{A}}$ chosen to characterize the migration of $\partial\mathcal{A}$, and therefore that the theory be invariant under transformations of $\text{v}_{\partial\mathcal{A}}$ of the form

$$\text{v}_{\partial\mathcal{A}} \rightarrow \text{v}_{\partial\mathcal{A}} + \mathbf{t}, \quad \mathbf{t} \text{ tangent to } \partial\mathcal{A}. \qquad (82)$$

F. Migrationally normal velocity field for $\mathcal{S}$

We continue to write $V(\mathbf{x},t)$ for the scalar normal velocity of $\mathcal{S}(t)$. In addition, we let $\text{v}(\mathbf{x},t)$ denote a (arbitrary) velocity field for $\mathcal{S}(t)$. In discussing the formulation of integral balance laws for the interface $\mathcal{S}$ what is needed is not the normal velocity V of $\mathcal{S}$, but, instead, a velocity that characterizes, intrinsically, the migration of that surface. We therefore seek a velocity field $\mathbf{v}$ for $\mathcal{S}$ that renders the migrational velocity $\mathbf{v} - \mathbf{u}$ normal. With this in mind, note that

$$\text{v} - \mathbf{u} = \text{v} - (\mathbf{u} \cdot \text{n})\text{n} - \mathbf{u}_{\text{tan}} = (V - \mathbf{u} \cdot \text{n})\text{n} + (\mathbf{v}_{\text{tan}} - \mathbf{u}_{\text{tan}}),$$

so that, choosing $\text{v}_{\text{tan}} = \mathbf{u}_{\text{tan}}$, we arrive at a choice of velocity field v for $\mathcal{S}$ that renders its migrational velocities $\text{v} - \mathbf{u}^{\pm}$ normal and hence intrinsic:

$$\text{v} - \mathbf{u} = (V - \mathbf{u} \cdot \text{n})\text{n}. \qquad (83)$$

The resulting velocity field v, called the *migrationally normal velocity field* for $\mathcal{S}$, has the specific form

$$\text{v} = V\text{n} + \mathbf{u}_{\text{tan}} \qquad (84)$$

and is important *because it is normal when computed relative to the bulk solution.*

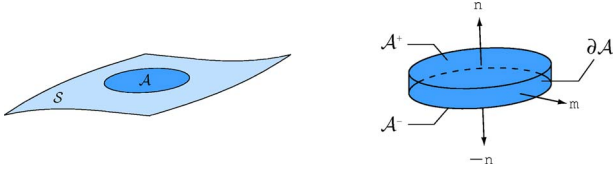Finally, granted (84), the relations (80), (81), and (83) imply that

FIG. 1. (Color online) Schematic of a migrating subsurface $\mathcal{A}(t)$ of the interface $\mathcal{S}$ showing an enlarged view of the associated surface pillbox.

$$\mathbb{w}_{\partial\mathcal{A}} \cdot \mathbb{m} = (\mathbb{v}_{\partial\mathcal{A}} - \mathbf{u}) \cdot \mathbb{m} - \overbrace{(\mathbb{v} - \mathbf{u}) \cdot \mathbb{m}}^{=0} = V_{\partial\mathcal{A}}^{\mathrm{mig}}. \quad (85)$$

G. Migrationally normal time derivative following the interface: Transport theorem for interfacial fields

Let $\varphi(\mathbf{x},t)$ be an interfacial field and $\mathbb{v}$ the migrationally normal velocity field (84). Given any time t_0 and any point $\mathbf{x}_0$ on $\mathcal{S}(t_0)$, let $\mathbb{z}(t)$ denote the unique solution of

$$\frac{d\mathbb{z}(t)}{dt} = \mathbb{v}(\mathbb{z}(t),t), \quad \mathbb{z}(t_0) = \mathbf{x}_0,$$

and define

$$\mathring{\varphi}(\mathbf{x}_0,t_0) = \left. \frac{d\varphi(\mathbb{z}(t),t)}{dt} \right|_{t=t_0}. \quad (86)$$

The interfacial field $\mathring{\varphi}$ defined in this manner is referred to as the *migrationally normal time derivative of φ following $\mathcal{S}$.*

The velocities V^{mig} and $V_{\partial\mathcal{A}}^{\mathrm{mig}}$ defined in (78) and (85) represent respective migrational velocities of $\mathcal{S}$ and $\partial\mathcal{A}$ relative to the bulk solution. Similarly, the migrationally normal time derivative $\mathring{\varphi}$ following $\mathcal{S}$ utilizes, as a velocity field $\mathbb{v}$ for $\mathcal{S}$, one that renders *normal* the migrational velocity $\mathbb{v} - \mathbf{u}$ relative to the bulk solution.

Important to what follows is the following theorem.

Interfacial transport theorem [23]: For φ a smooth surface scalar field and $\mathring{\varphi}$ its migrationally normal time derivative following $\mathcal{S}$,

$$\frac{d}{dt} \int_{\mathcal{A}(t)} \varphi \, da = \int_{\mathcal{A}(t)} \{\mathring{\varphi} + \varphi \mathrm{div}_{\mathcal{S}} \mathbf{u}_{\mathrm{tan}} - \varphi K V\} da$$

$$+ \int_{\partial\mathcal{A}(t)} \varphi V_{\partial\mathcal{A}}^{\mathrm{mig}} \, ds. \quad (87)$$

H. Migrating pillboxes

Consider an arbitrary migrating subsurface $\mathcal{A}(t)$ of $\mathcal{S}(t)$. The *migrating interfacial-pillbox* determined by $\mathcal{A}$ is a control volume of infinitesimal thickness consisting of (Fig. 1): (i) a surface $\mathcal{A}^+(t)$, with unit normal $\mathbb{n}(\mathbf{x},t)$, lying in the vapor; (ii) a surface $\mathcal{A}^-(t)$, with unit normal $-\mathbb{n}(\mathbf{x},t)$, lying in the solution; (iii) a lateral bounding surface $\partial\mathcal{A}(t)$ with outward unit normal $\mathbb{m}(\mathbf{x},t)$.

In what follows we formulate basic laws for the interface using an arbitrary migrating interfacial pillbox.

V. MECHANICAL BALANCES AT THE INTERFACE

A. Balance of mass: No-slip condition

Let ϱ_v and $\mathbf{u}_v$, respectively, denote the mass density and velocity of the vapor at the interface, so that, bearing in mind (78), the respective migrational velocities of $\mathcal{S}$ relative to the bulk solution and vapor are given by

$$V^{\mathrm{mig}} = V - \mathbf{u} \cdot \mathbb{n}, \quad (88a)$$

$$V_v^{\mathrm{mig}} = V - \mathbf{u}_v \cdot \mathbb{n}. \quad (88b)$$

The net mass flow into any migrating interfacial pillbox $\mathcal{A}(t)$ is given by $\int_{\mathcal{A}}(\varrho_v V_v^{\mathrm{mig}} - \varrho V^{\mathrm{mig}})da$ and *balance of mass* requires that this net mass flow vanish; hence,

$$\varrho V^{\mathrm{mig}} = \varrho_v V_v^{\mathrm{mig}} = -J. \quad (89)$$

The field J represents the *mass flow* across $\mathcal{S}$ in the direction of $\mathbb{n}$.

It is clear from (89) that, because of the discrepancy in solution and vapor densities, we must have $\mathbf{u}_v \cdot \mathbb{n} \neq \mathbf{u} \cdot \mathbb{n}$. On the other hand, we assume that *the tangential components of the solution and vapor velocities at the interface coincide*:

$$\mathbb{P}\mathbf{u} = \mathbb{P}\mathbf{u}_v \quad (\mathrm{no-slip\ condition}); \quad (90)$$

equivalently,

$$\mathbf{u}_v - \mathbf{u} = (\mathbf{u}_v \cdot \mathbb{n} - \mathbf{u} \cdot \mathbb{n})\mathbb{n}. \quad (91)$$

B. Balance of surfactant molecules at the interface

We endow the interface with an *interfacial molecular density* $n^{\mathrm{x}}(\mathbf{x},t)$ and an *interfacial molecular flux* $\mathbb{j}(\mathbf{x},t)$. We write n and $\mathbf{j}$ for the interfacial limits of the bulk molecular density and flux. Let $\mathcal{A}(t)$ be an arbitrary migrating interfacial pillbox. Surface diffusion then results in a flow $\mathbb{j} \cdot \mathbb{m}$ of surfactant molecules across $\partial\mathcal{A}$, while bulk diffusion results in a flow $\mathbf{j} \cdot \mathbb{n}$ of surfactant molecules to $\mathcal{A}$ from the solution. The migration of $\partial\mathcal{A}$ within $\mathcal{S}$ results in a flow $n^{\mathrm{x}} V_{\partial\mathcal{A}}^{\mathrm{mig}}$ of surfactant molecules across $\partial\mathcal{A}$, while the migration of $\mathcal{S}$ results in a flow $-nV^{\mathrm{mig}}$ of surfactant molecules into $\mathcal{A}$ across $\mathcal{A}^-$.

In view of the foregoing discussion, the balance of surfactant molecules requires that, for $\mathcal{A}(t)$ any migrating interfacial pillbox,

$$\frac{d}{dt} \int_{\partial\mathcal{A}} n^{\mathrm{x}} \, da = -\int_{\partial\mathcal{A}(t)} \{\mathbb{j} \cdot \mathbb{m} - n^{\mathrm{x}} V_{\partial\mathcal{A}}^{\mathrm{mig}}\} ds$$

$$+ \int_{\mathcal{A}(t)} \{\mathbf{j} \cdot \mathbb{n} - nV^{\mathrm{mig}}\} da \quad (92)$$

or, equivalently, using the interfacial divergence theorem (66a) and the transport theorem (87), that the local law

$$\mathring{n}^{\mathrm{x}} - n^{\mathrm{x}}(KV - \mathrm{div}_{\mathcal{S}}\mathbf{u}_{\mathrm{tan}}) = -\mathrm{div}_{\mathcal{S}}\mathbb{j} + \mathbf{j} \cdot \mathbb{n} - nV^{\mathrm{mig}} \quad (93)$$

hold on the interface. As Cermelli, Fried, and Gurtin [23] note, (93) is equivalent to a balance obtained by Mavrovouniotis and Brenner [37] (see also Mavrovouniotis [38] and Edwards, Brenner, and Wassan [39]).

C. Momentum flows

1. Standard flows

Given any migrating interfacial pillbox $\mathcal{A}(t)$, there are linear momentum flows $-\varrho \mathbf{u} V^{\mathrm{mig}}$ and $\varrho_v \mathbf{u}_v V_v^{\mathrm{mig}}$ into $\mathcal{A}$ across $\mathcal{A}^-$ and $\mathcal{A}^+$, so that, by (89) and (91), the flows of linear and angular momentum into $\mathcal{A}$ are given by

$$-\int_{\mathcal{A}(t)} J(\mathbf{u}_v \cdot \mathbf{n} - \mathbf{u} \cdot \mathbf{n})\mathbf{n}\, da \tag{94}$$

and

$$-\int_{\mathcal{A}(t)} J(\mathbf{x} - \mathbf{0}) \times (\mathbf{u}_v \cdot \mathbf{n} - \mathbf{u} \cdot \mathbf{n})\mathbf{n}\, da. \tag{95}$$

On the other hand,

$$\mathbf{u}_v \cdot \mathbf{n} - \mathbf{u} \cdot \mathbf{n} = \frac{J(1-\delta)}{\varrho_v}, \tag{96a}$$

$$\delta = \frac{\varrho_v}{\varrho}, \tag{96b}$$

and the standard *momentum flows* (94) and (95) become

$$-\int_{\mathcal{A}(t)} \frac{J^2(1-\delta)}{\varrho_v}\mathbf{n}\, da \tag{97}$$

and

$$-\int_{\mathcal{A}(t)} (\mathbf{x} - \mathbf{0}) \times \left\{ \frac{J^2(1-\delta)}{\varrho_v}\mathbf{n} \right\} da. \tag{98}$$

2. Configurational flow

By (55), $\mathbf{p} = -\mathbf{u}$, and assuming the same holds for the specific configurational momentum of the vapor, so that $\mathbf{p}_v = -\mathbf{u}_v$, the argument leading to (97) yields

$$\int_{\mathcal{A}(t)} \frac{J^2(1-\delta)}{\varrho_v}\mathbf{n}\, da \tag{99}$$

for the configurational momentum flow into the pillbox $\mathcal{A}$.

3. Vapor approximation

We neglect configurational stress in the vapor. We suppose that counterparts of the bulk constitutive Eqs. (36) and the bulk Eshelby relation (54) hold also in the vapor. Then, consistent with our neglect of configurational stress, *we neglect standard stress and kinetic energy in the vapor*,[3] and, what is cogent to what follows, we require the following hypothesis: (B) that the *bulk and interfacial free energy densities of the solution be reckoned relative to free energy density of the vapor.*

Further, the mass density of the vapor is much smaller than that of the solution. Thus, bearing in mind that $\delta = \varrho_v / \varrho$, we henceforth assume that

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[3]But a partial accounting of inertial effects is retained in the momentum flows (101).

$$\delta = 0. \tag{100}$$

An important consequence of (100) is that the standard momentum flows (97) and (98) become

$$-\int_{\mathcal{A}(t)} \frac{J^2}{\varrho_v}\mathbf{n}\, da, \tag{101a}$$

$$-\int_{\mathcal{A}(t)} (\mathbf{x} - \mathbf{0}) \times \left\{ \frac{J^2}{\varrho_v}\mathbf{n} \right\} da, \tag{101b}$$

while the configurational momentum flow (99) becomes

$$\int_{\mathcal{A}(t)} \frac{J^2}{\varrho_v}\mathbf{n}\, da. \tag{102}$$

D. Standard balances of linear and angular momentum: Momentum balances

We endow the interface with *Cauchy interfacial stress* $\mathbb{T}(\mathbf{x}, t)$, but neglect interfacial distributions of linear momentum. We write $\mathbf{T}$ for the interfacial limit of the bulk stress. Let $\mathcal{A}$ be an arbitrary migrating interfacial pillbox. The portion of $\mathcal{S}$ exterior to $\mathcal{A}$ then exerts a standard traction $\mathbb{T}\mathbf{m}$ across $\partial\mathcal{A}$, while the solution exerts a traction $-\mathbf{T}\mathbf{n}$ on $\mathcal{A}^-$. Since we neglect vapor stress, these represent the only standard forces on $\mathcal{A}$.

In view of (101), the balances of linear and angular momentum require that, for $\mathcal{A}(t)$ any migrating interfacial pillbox,

$$\int_{\partial\mathcal{A}(t)} \mathbb{T}\mathbf{m}\, ds = \int_{\mathcal{A}(t)} \left\{ \mathbf{T}\mathbf{n} + \frac{J^2}{\varrho_v}\mathbf{n} \right\} da \tag{103}$$

and

$$\int_{\partial\mathcal{A}(t)} (\mathbf{x} - \mathbf{0}) \times \mathbb{T}\mathbf{m}\, ds = \int_{\mathcal{A}(t)} (\mathbf{x} - 0) \times \left\{ \mathbf{T}\mathbf{n} + \frac{J^2}{\varrho_v}\mathbf{n} \right\} da \tag{104}$$

or, equivalently, using the interfacial divergence theorem, that the local laws

$$\mathrm{div}_{\mathcal{S}}\mathbb{T} = \mathbf{T}\mathbf{n} + \frac{J^2}{\varrho_v}\mathbf{n}, \tag{105a}$$

$$\mathbb{T} = \mathbb{T}^{\mathsf{T}} \tag{105b}$$

hold on the interface. These local laws appear also in the work of Mavrovouniotis and Brenner [37] (see also Mavrovouniotis [38] and Edwards, Brenner, and Wassan [39]).

Since $\mathbb{T}$ is an interfacial tensor field, it follows from (105) that

$$\mathbb{T}^{\mathsf{T}}\mathbf{n} = \mathbf{0}, \tag{106}$$

and the Cauchy interfacial stress $\mathbb{T}$ is *fully tangential*. Thus (70) implies that $\mathbf{n} \cdot \mathrm{div}_{\mathcal{S}}\mathbb{T} = \mathbb{T}:\mathbb{K}$ and the component of the linear momentum balance (105a) in the direction $\mathbf{n}$ normal to the interface takes the form

$$\mathbb{T}:\mathbb{K} = \mathrm{n} \cdot \mathbf{T}\mathrm{n} + \frac{J^2}{\varrho_v} \qquad (107)$$

of a generalized Young-Laplace relation.

E. Balance of configurational momentum

We endow the interface with a *configurational interfacial stress* $\mathbb{C}(\mathbf{x},t)$ and an *internal configurational force density* $\mathrm{f}(\mathbf{x},t)$, measured per unit area. Consistent with our neglect of interfacial distributions of linear momentum, we neglect interfacial distributions of configurational momentum. Let $\mathcal{A}$ be an arbitrary migrating interfacial pillbox. The portion of $\mathcal{S}$ exterior to $\mathcal{A}$ then exerts a configurational traction $\mathbb{C}\mathrm{m}$ across $\partial\mathcal{A}$, while the solution exerts a configurational traction $-\mathbf{C}\mathrm{n}$.

Bearing in mind (101b), balance of configurational momentum requires that, for $\mathcal{A}(t)$ any migrating interfacial-pillbox,

$$\int_{\partial\mathcal{A}(t)} \mathbb{C}\mathrm{m}\,ds + \int_{\mathcal{A}(t)} \left\{ \mathrm{f} - \mathbf{C}\mathrm{n} + \frac{J^2}{\varrho_v}\mathrm{n} \right\} da = \mathbf{0} \qquad (108)$$

or, equivalently, appealing to the interfacial diverence thorem (66b), that

$$\mathrm{div}_{\mathcal{S}}\mathbb{C} + \mathrm{f} = \mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v}\mathrm{n} \qquad (109)$$

hold on the interface.

In terms of the decomposition

$$\mathbb{C} = \mathbb{C}_{\mathrm{tan}} + \mathrm{n} \otimes \mathrm{c}. \qquad (110)$$

[cf. (61)], $\mathbb{C}_{\mathrm{tan}}$ represents configurational forces that act tangential to $\mathcal{S}$, while $\mathrm{n}\otimes\mathrm{c}$ (or, more simply, the *interfacial configurational shear* c) represents shearing forces that act normal to $\mathcal{S}$.

We let

$$f = \mathrm{f} \cdot \mathrm{n} \qquad (111)$$

denote the *normal* part of the internal configurational force. Thus, on applying (61) to $\mathbb{C}$ and using (67), (70), and (110),

$$\mathrm{div}_{\mathcal{S}}\mathbb{C} = \mathrm{div}_{\mathcal{S}}\mathbb{C}_{\mathrm{tan}} + \mathrm{div}_{\mathcal{S}}(\mathrm{n} \otimes \mathrm{c})$$
$$= (\mathbb{C}_{\mathrm{tan}}:\mathbb{K} + \mathrm{div}_{\mathcal{S}}\mathrm{c})\mathrm{n} + \mathbb{P}\mathrm{div}_{\mathcal{S}}\mathbb{C}_{\mathrm{tan}} - \mathbb{K}\mathrm{c} \qquad (112)$$

and it follows that the interfacial configurational balance (109) may be decomposed into a *normal configurational momentum balance*

$$\mathbb{C}_{\mathrm{tan}}:\mathbb{K} + \mathrm{div}_{\mathcal{S}}\mathrm{c} + f = \mathrm{n} \cdot \mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v} \qquad (113)$$

and a tangential balance

$$\mathbb{P}\mathrm{f} = -\mathbb{P}\mathrm{div}_{\mathcal{S}}\mathbb{C}_{\mathrm{tan}} + \mathbb{K}\mathrm{c} + \mathbb{P}\left\{ \mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v}\mathrm{n} \right\}, \qquad (114)$$

which is irrelevant to what follows [cf. the discussions following (119) and (133)].

VI. POWER

To express the power expended by the tractions, we proceed as in Sec. III D and mimic the reasoning leading to the expression $W(\mathcal{R}(t))$ (cf. Sec. III D) for the power expenditure on a control volume migrating through the solution. The configurational and standard tractions $\mathbb{C}\mathrm{m}$ and $\mathbb{T}\mathrm{m}$ are distributed over the boundary $\partial\mathcal{A}$ of the pillbox. As in our discussion of the bulk phases, we take the migrational velocity $\mathrm{v}_{\partial\mathcal{A}} - \mathbf{u}$ of $\partial\mathcal{A}$ to be the appropriate power conjugate velocity for $\mathbb{C}\mathrm{m}$. For $\mathbb{T}\mathrm{m}$, we reason by analogy to our treatment of the power expended by the standard traction on a migrating control volume and take as power conjugate the observed velocity $\mathrm{v}_{\partial\mathcal{A}}$ of $\partial\mathcal{A}$. We therefore write the power expended by the standard and configurational *interfacial* stresses $\mathbb{C}$ and $\mathbb{T}$—on $\mathcal{A}$ across $\partial\mathcal{A}$—in the form

$$w(\mathcal{A}) = \int_{\partial\mathcal{A}(t)} \{\mathbb{T}\mathrm{m} \cdot \mathrm{v}_{\partial\mathcal{A}} + \mathbb{C}\mathrm{m} \cdot (\mathrm{v}_{\partial\mathcal{A}} - \mathbf{u})\}ds. \qquad (115)$$

The *effective* configurational and standard tractions $-(\mathbf{C}\mathrm{n} + \varrho\mathbf{p}V^{\mathrm{mig}})$ and $-(\mathbf{T}\mathrm{n} + \varrho\mathbf{u}V^{\mathrm{mig}})$ are treated exactly as in Sec. III D: as power conjugate for the former we take the velocity $\mathrm{v}^{\mathrm{mig}} = \mathrm{v} - \mathbf{u}$ of $\mathcal{S}$ relative to the underlying material; as power conjugate for the latter we take the observed velocity v of $\mathcal{S}$. The external power expended on $\mathcal{A}(t)$ then has the form

$$W^{\mathrm{x}}(\mathcal{A}(t)) = w(\mathcal{A}) - \int_{\mathcal{A}(t)} \left(\mathbf{T}\mathrm{n} + \frac{J^2}{\varrho_v}\mathrm{n} \right) \cdot \mathrm{v}\,da + \int_{\mathcal{A}(t)} \left(\mathbf{C}\mathrm{n} - \frac{J^2}{\varrho_v}\mathrm{n} \right) \cdot \mathrm{v}^{\mathrm{mig}}\,da. \qquad (116)$$

As for the power $W(\mathcal{R})$ acting on a migrating control volume (cf. Sec. III D), we require that the power $W^{\mathrm{x}}(\mathcal{A}(t))$ be consistent with the intrinsicality hypothesis (A). As shown in Appendix B, this implies a interfacial *pre-Eshelby relation*

$$\mathbb{C} = \varphi\mathbb{P} - \mathbb{T} + \mathrm{n} \otimes \mathrm{c}. \qquad (117)$$

We recall [cf. (106)] that $\mathbb{T}$ is fully tangential. Further, because both $\mathbb{P}$ and $\mathbb{T}$ are fully tangential and symmetric, so also is the tangential component $\mathbb{C}_{\mathrm{tan}} = \varphi\mathbb{P} - \mathbb{T}$ of $\mathbb{C}$:

$$\mathbb{C}_{\mathrm{tan}} = \mathbb{C}_{\mathrm{tan}}^{\mathbf{T}}. \qquad (118)$$

Furthermore, just as the bulk pre-Eshelby relation (A4) yields an intrinsic expression for the power $W(\mathcal{R}(t))$ expended on a migrating control volume $\mathcal{R}(t)$, we show in Appendix B that, as a consequence of the interfacial pre-Eshelby relation and requiring that the velocity field v for $\mathcal{S}$ be migrationally normal, the power (116) expended on $\mathcal{A}$ admits the intrinsic form

$$W^x(\mathcal{A}(t)) = \int_{\partial\mathcal{A}(t)} \varphi V_{\partial\mathcal{A}}^{\mathrm{mig}}\, ds - \int_{\mathcal{A}(t)} \varphi(KV - \mathrm{div}_S\mathbf{u}_{\mathrm{tan}})\, da$$

$$+ \int_{\mathcal{A}(t)} \{\mathbb{C}_{\mathrm{tan}}{:}\mathbb{D} + fV^{\mathrm{mig}} - \mathbb{c}\cdot\mathrm{grad}_S V^{\mathrm{mig}}\}\, da.$$

$$(119)$$

From (119) that there is no expenditure of power associated with tangential motion of the interface S (which is to be expected, since only the normal motion of S is intrinsic). Consistent with a constraint of this type, we leave as indeterminate the tangential component $\mathbb{P}f$ of the internal configurational force density f. This assumption renders the tangential balance (114) irrelevant and allows us to restrict attention to the normal configurational force balance (113). This will be the case throughout what follows; for that reason, we shall henceforth leave unmentioned the tangential component of the configurational momentum balance.

VII. FIRST TWO LAWS AT THE INTERFACE

A. Basic hypothesis

As a basic hypothesis for the interface between the solution and the vapor we assume the following hypothesis: (C) *that the bulk, the surfactant chemical potential μ and temperature ϑ are smooth up to the interface S, and the interfacial limits of μ and ϑ are equal to the surfactant chemical potential and temperature on S.* Importantly, this hypothesis allows for discontinuities between the interfacial limits of the chemical potential and the temperature of the solution and the corresponding interfacial limits in the vapor.

We assume further the following hypothesis: (D) *that the flow of surfactant molecules to the vapor is negligible. The temperature ϑ_v of the vapor is constant; we admit the possibility that $\vartheta \neq \vartheta_v$.*

B. Balance of energy and the entropy imbalance for the interface

We endow the interface with *interfacial internal-energy density* $\varepsilon^x(\mathbf{x},t)$, *interfacial entropy density* $\eta^x(\mathbf{x},t)$, and *interfacial heat flux* $\mathbb{h}(\mathbf{x},t)$. However, consistent with our neglect of surface distributions of linear momentum, we neglect interfacial distributions of kinetic energy. We write $\psi^x(\mathbf{x},t)$ for the interfacial *free-energy density*, as given by

$$\psi^x = \varepsilon^x - \vartheta\eta^x. \qquad (120)$$

Guided by the statements (49) and (48e) of energy balance and entropy growth for a migrating control volume $\mathcal{R}(t)$, we express the first two laws for a migrating pillbox $\mathcal{A}(t)$ in the forms

$$\frac{d}{dt}\int_{\mathcal{A}(t)} \varepsilon^x\, da$$

$$= W^x(\mathcal{A}(t)) - \underbrace{\int_{\partial\mathcal{A}(t)} \mu\{\mathbb{j}\cdot\mathbb{m} - n^x V_{\partial\mathcal{A}}^{\mathrm{mig}}\}\, ds + \int_{\mathcal{A}(t)} \mu\{\mathbb{j}\cdot\mathbb{n} - nV^{\mathrm{mig}}\}\, da}_{E^x(\mathcal{A}(t))}$$

$$- \underbrace{\int_{\partial\mathcal{A}(t)} \{\mathbb{h}\cdot\mathbb{m} - \vartheta\eta^x V_{\partial\mathcal{A}}^{\mathrm{mig}}\}\, ds + \int_{\mathcal{A}(t)} \{\mathbf{q}\cdot\mathbb{n} - \vartheta\eta V^{\mathrm{mig}} + q\}\, da}_{Q^x(\mathcal{A}(t))},$$

$$(121)$$

and

$$\frac{d}{dt}\int_{\mathcal{A}(t)} \eta^x da \geq \underbrace{-\int_{\partial\mathcal{A}(t)} \frac{\mathbb{h}\cdot\mathbb{n} - \vartheta\eta^x V_{\partial\mathcal{A}}^{\mathrm{mig}}}{\vartheta}\, ds + \int_{\mathcal{A}(t)} \left\{\frac{\mathbf{q}\cdot\mathbb{n} - \vartheta\eta V^{\mathrm{mig}}}{\vartheta} + \frac{q}{\vartheta_v}\right\} da}_{H^x(\mathcal{A}(t))},$$

$$(122)$$

where the power $W^x(\mathcal{A}(t))$ expended on $\mathcal{A}(t)$ is given by (115) or its intrinsic equivalent (119), while $E^x(\mathcal{A}(t))$, $Q^x(\mathcal{A}(t))$, and $H^x(\mathcal{A}(t))$ represent *flows of energy, heat, and entropy* into $\mathcal{A}$ that account for the migrational flows $\mu n^x V_{\partial\mathcal{A}}^{\mathrm{mig}}$, $\vartheta\eta^x V_{\partial\mathcal{A}}^{\mathrm{mig}}$, and $\eta^x V_{\partial\mathcal{A}}^{\mathrm{mig}}$ and also for the flows q and q/ϑ_v of heat and entropy from the solution to the vapor.

The transport theorem (87) implies that

$$\frac{d}{dt}\int_{\mathcal{A}(t)} \varepsilon^x\, da = \int_{\mathcal{A}(t)} \{\dot{\varepsilon}^x + \varepsilon^x\mathrm{div}_S\mathbf{u}_{\mathrm{tan}} - \varepsilon^x KV\}\, da$$

$$+ \int_{\partial\mathcal{A}(t)} \varepsilon^x V_{\partial\mathcal{A}}^{\mathrm{mig}}\, ds. \qquad (123)$$

Because of (119), the interfacial energy balance (121) subject to (123) therefore contains a term

$$\int_{\partial\mathcal{A}} \{\varphi - \varepsilon^x + \vartheta\eta^x + \mu n^x\}V_{\partial\mathcal{A}}^{\mathrm{mig}}\, ds \qquad (124)$$

on its right side, there being no other term containing $V_{\partial\mathcal{A}}^{\mathrm{mig}}$. Since the migrating subsurface $\mathcal{A}(t)$ is arbitrary, we may at any given time vary $V_{\partial\mathcal{A}}$ and (hence) $V_{\partial\mathcal{A}}^{\mathrm{mig}} = V_{\partial\mathcal{A}} - \mathbf{u}\cdot\mathbb{m}$ arbitrarily without changing any of the remaining fields involved in the balance (121) as supplemented by (119) and (123). For this augmented balance to be valid, for all choices of the migrating subsurface $\mathcal{A}(t)$, we must therefore have

$$\varphi = \varepsilon^x - \vartheta\eta^x - \mu n^x = \psi^x - \mu n^x. \qquad (125)$$

Thus, (117) takes the form of a *interfacial Eshelby relation*

$$\mathbb{C} = (\psi^x - \mu n^x)\mathbb{P} - \mathbb{T} + \mathbb{n}\otimes\mathbb{c}, \qquad (126)$$

which bears comparison to the bulk Eshelby relation (54). The Eshelby relation may also be written in the form

$$C = \omega^x P - T + n \otimes c, \qquad (127)$$

with

$$\omega^x = \psi^x - n^x \mu \qquad (128)$$

a *grand canonical potential* for the interface.

Next, using (126) in the intrinsic form (119) for the power expended on $\mathcal{A}(t)$, we find that (121) can be expressed as

$$\frac{d}{dt} \int_{\mathcal{A}(t)} \varepsilon^x \, da = \int_{\partial\mathcal{A}(t)} \varepsilon^x V_{\partial\mathcal{A}}^{mig} \, ds + \int_{\mathcal{A}(t)} (\psi^x - \mu n^x)\{\text{div}_S \mathbf{u}_{tan}$$

$$- KV\}da - \int_{\mathcal{A}(t)} \{C_{tan}:D + fV^{mig}$$

$$- c \cdot \text{grad}_S V^{mig}\}da + \int_{\mathcal{A}(t)} \mu\{\mathbf{j} \cdot n - nV^{mig}\}da$$

$$+ \int_{\mathcal{A}(t)} \{\mathbf{q} \cdot n - \vartheta\eta V^{mig} + q\}da$$

$$- \int_{\partial\mathcal{A}(t)} \{\mu\mathbf{j} + h\} \cdot m \, ds. \qquad (129)$$

Further, applying the interfacial divergence theorem (66a) to the final term in (129) and invoking the molecular balance (93), we obtain

$$\frac{d}{dt} \int_{\mathcal{A}(t)} \varepsilon^x \, da = \int_{\partial\mathcal{A}(t)} \varepsilon^x V_{\partial\mathcal{A}}^{mig} \, ds + \int_{\mathcal{A}(t)} \{\psi^x(\text{div}_S \mathbf{u}_{tan} - KV)$$

$$+ \mu\mathring{n}^x - \mathbf{j} \cdot \text{grad}_S \mu\}da - \int_{\mathcal{A}(t)} \{C_{tan}:D + fV^{mig}$$

$$- c \cdot \text{grad}_S V^{mig} + \text{div}_S h - \mathbf{q} \cdot n + \vartheta\eta V^{mig}$$

$$- q\}da \qquad (130)$$

or, equivalently, by using the interfacial divergence theorem (66a), the transport theorem (87), and the molecular balance (93), that the local law

$$\mathring{\varepsilon}^x - \vartheta\eta^x(KV - \text{div}_S \mathbf{u}_{tan}) = \mu\mathring{n}^x - \mathbf{j} \cdot \text{grad}_S \mu - C_{tan} \cdot D - fV^{mig}$$

$$+ c \cdot \text{grad}_S V^{mig} - \text{div}_S h + \mathbf{q} \cdot n$$

$$- \vartheta\eta V^{mig} + q \qquad (131)$$

holds on the interface.

Similarly, appealing to the interfacial divergence theorem (66a) and the transport theorem (87) and (122) localizes to yield the local law

$$\vartheta\mathring{\eta}^x \geq \vartheta\eta^x(KV - \text{div}_S \mathbf{u}_{tan}) - \text{div}_S \frac{h}{\vartheta} + \mathbf{q} \cdot n - \vartheta\eta V^{mig} + \frac{\vartheta}{\vartheta_v}q$$

$$(132)$$

for the interface.

Subtracting (132) from (131) and using (120) and (125), we arrive at the *interfacial dissipation inequality*

$$\mathring{\psi}^x + \eta^x \mathring{\vartheta} - \mu\mathring{n}^x + C_{tan}:D + fV^{mig} - c \cdot \text{grad}_S V^{mig} + \mathbf{j} \cdot \text{grad}_S \mu$$

$$+ \frac{1}{\vartheta}h \cdot \text{grad}_S \vartheta + \left\{\frac{\vartheta}{\vartheta_v} - 1\right\}q \leq 0. \qquad (133)$$

This inequality is basic to our discussion of constitutive equations. Since the *tangential* part Pf of the configurational force density f does not enter (133), we consider Pf as indeterminate, a consideration consistent with the discussion following (119).

VIII. STANDARD AND NORMAL CONFIGURATIONAL MOMENTUM BALANCES REVISITED

A. Standard momentum balance

Recalling (106) and, thus, that the Cauchy interfacial stress T is fully tangential, the decomposition (110) and the interfacial Eshelby relation (126) imply that $T = \omega^x P - C_{tan}$. Thus, using (69),

$$\text{div}_S T = \omega^x Kn + \text{grad}_S \omega^x - \text{div}_S C_{tan}, \qquad (134)$$

and we may rewrite the standard momentum balance (105a) in the form

$$\omega^x Kn + \text{grad}_S \omega^x - \text{div}_S C_{tan} = Tn + \frac{J^2}{\varrho_v}n. \qquad (135)$$

B. Normal configurational momentum balance

Using the bulk Eshelby relation (56) in (113), we find that the the normal configurational momentum balance can be expressed as

$$C_{tan}:\mathbb{K} + \text{div}_S c + f = \omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2 - n \cdot Tn - \frac{J^2}{\varrho_v}. \qquad (136)$$

C. Normal combined momentum balance

The interfacial Eshelby relation (126) couples the Cauchy and configurational stresses T and C. That coupling allows us to obtain an equation that usefully combines the normal components of the standard and configurational momentum balances for the interface. To obtain that equation, we add (107)–(113) and use (55) to yield the relation

$$(C_{tan} + T):\mathbb{K} + \text{div}_S c + f = n \cdot (\mathbf{C} + \mathbf{T})n, \qquad (137)$$

which when supplemented by the bulk and interfacial Eshelby relations (56) and (126) has the form

$$\omega^x K + \text{div}_S c + f = \omega - \tfrac{1}{2}\varrho|\mathbf{u}|^2. \qquad (138)$$

D. Complete set of momentum balances

A complete set of momentum balances for the interface consists of (i) the standard momentum balance in the form (135) and (ii) *either* the normal configurational momentum balance in the form (136) *or* the normal combined momentum balance (138).

IX. CONSTITUTIVE EQUATIONS FOR THE INTERFACE

A. Equations of state

Guided by our treatment of the bulk phases, we suppose that the free-energy density, chemical potential, and entropy density of the interface are determined by state relations

$$\psi^x = \hat{\psi}^x(n^x, \vartheta), \tag{139a}$$

$$\mu = \hat{\mu}^x(n^x, \vartheta) = \frac{\partial \hat{\psi}^x(n^x, \vartheta)}{\partial n^x}, \tag{139b}$$

$$\eta^x = \hat{\eta}^x(n^x, \vartheta) = -\frac{\partial \hat{\psi}^x(n^x, \vartheta)}{\partial \vartheta}. \tag{139c}$$

By (139), differentiating the identity $\varepsilon^x = \psi^x + \vartheta \eta^x$ yields the *Gibbs relation*

$$\mathring{\varepsilon}^x = \mu \mathring{n}^x + \vartheta \mathring{\eta}^x. \tag{140}$$

B. Dissipative constitutive relations

Granted (139), (133) takes the form of a *reduced dissipation inequality*

$$- \mathbb{C}_{\tan} : \mathbb{D} + \mathbb{c} \cdot \mathrm{grad}_S V^{\mathrm{mig}} - f V^{\mathrm{mig}} - \mathbb{j} \cdot \mathrm{grad}_S \mu + \frac{1}{\vartheta} \mathbb{h} \cdot \mathrm{grad}_S \vartheta$$

$$- q \left\{ \frac{\vartheta}{\vartheta_v} - 1 \right\} \geq 0, \tag{141}$$

which we use to develop a constitutive theory compatible with the second law. For simplicity, we consider constitutive equations in which the classical dissipative mechanisms associated with surfactant transport, momentum transport, and heat transport are decoupled from the dissipative mechanisms associated with the migration of the interface relative to the solution. In particular, we assume that the interfacial fluxes $\mathbb{j}$ and $\mathbb{h}$ of surfactant molecules and heat are given by counterparts

$$\mathbb{j} = - m(n^x, \vartheta) \mathrm{grad}_S \mu + m_s(n^x, \vartheta) \mathrm{grad}_S \vartheta, \tag{142a}$$

$$\mathbb{h} = - l_d(n^x, \vartheta) \mathrm{grad}_S \mu + l(n^x, \vartheta) \mathrm{grad}_S \vartheta, \tag{142b}$$

of the linear, isotropic bulk Fick-Soret and Fourier-Dufour laws (38) and (39). Here, the *interfacial surfactant mobility* m, *interfacial Soret coefficient* m_s, *interfacial Dufour coefficient* l_d, and *interfacial thermal conductivity* l obey $m \geq 0$, $l \geq 0$, and $ml \geq \frac{1}{4}(m_s + l_d)^2$; cf. (40). In addition, we consider uncoupled, linear, isotropic relations between $\mathbb{C}_{\tan}$ and $\mathbb{D}$, $\mathbb{c}$ and $\mathrm{grad}_S V^{\mathrm{mig}}$, f and V^{mig}, and q and $(\vartheta - \vartheta_v)$, with moduli signed to ensure satisfaction of the dissipation inequality (141).[4] Specifically, we consider (i) a relation

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[4]More generally, mixed terms that couple the various dissipative mechanisms entering (141) are possible; such terms, whose inclusion involves only cosmetic changes, are, for convenience, neglected.

$$\mathbb{C}_{\tan} = - \kappa(n^x, \vartheta)(\mathrm{tr}\mathbb{D})\mathbb{P} - 2\zeta(n^x, \vartheta)\mathbb{D} \tag{143}$$

between the tangential configurational stress and the stretch rate, with *dilatational viscosity* $\kappa(n^x, \vartheta) + \zeta(n^x, \vartheta) \geq 0$ and *shear viscosity* $\zeta(n^x, \vartheta) \geq 0$; (ii) a relation

$$\mathbb{c} = \alpha(n^x, \vartheta) \mathrm{grad}_S V^{\mathrm{mig}} \tag{144}$$

between the configurational shear and the gradient of the migrational velocity, with *rotational viscosity* $\alpha(n^x, \vartheta) \geq 0$; (iii) a *kinetic* relation

$$f = - \beta(n^x, \vartheta) V^{\mathrm{mig}}, \tag{145}$$

with *kinetic coefficient* $\beta(n^x, \vartheta) \geq 0$; and (iv) a *vapor heat-flow* relation

$$q = - \lambda(n^x, \vartheta)(\vartheta - \vartheta_v), \tag{146}$$

with *heat transfer coefficient* $\lambda(n^x, \vartheta) \geq 0$. To render the resulting interface conditions more transparent, we suppress the argument (n^x, ϑ) when discussing the moduli m, m_s, l_d, l, κ, ζ, α, β, and λ.

Constitutive relation for $\mathbb{T}$

By (139), the grand canonical potential density $\omega^x = \psi^x - n^x \mu$ [cf. (128)] of the interface obeys the constitutive relation

$$\omega^x = \hat{\omega}^x(n^x, \vartheta) = \hat{\psi}^x(n^x, \vartheta) - n^x \frac{\partial \hat{\psi}^x(n^x, \vartheta)}{\partial n^x}. \tag{147}$$

Thus a consequence of the relation (143) for the tangential component $\mathbb{C}_{\tan}$ of the interfacial configurational stress, supplemented by (117) and (125), is a constitutive equation

$$\mathbb{T} = \{\omega^x + (\kappa + \zeta)\mathrm{tr}\mathbb{D}\}\mathbb{P} + 2\zeta\mathbb{D}_0 \tag{148}$$

for the Cauchy interfacial stress, where

$$\mathbb{D}_0 = \mathbb{D} - \frac{1}{2}(\mathrm{tr}\mathbb{D})\mathbb{P} \tag{149}$$

is the *deviatoric stretch rate*. Further, (153) implies that the *interfacial tension*

$$\sigma = \frac{1}{2}\mathrm{tr}\mathbb{T} \tag{150}$$

has the form

$$\sigma = \omega^x + \{\kappa + \zeta\}\mathrm{tr}\mathbb{D} \tag{151}$$

and therefore consists of an equilibrium contribution coincident with the grand canonical potential density and dissipative contribution associated with the rate of dilation of $\mathcal{S}$.

Note that, since tr $\mathbf{D} = \mathbf{0}$, it follows from (76) that

$$\mathrm{tr}\mathbb{D} = \mathrm{tr}(\mathbb{P}\mathbf{D}\mathbb{P}) = - \mathbb{n} \cdot \mathbf{D}\mathbb{n}. \tag{152}$$

Thus, by (148) and (151),

$$\mathbb{T} = \sigma\mathbb{P} + 2\zeta\mathbb{D}_0, \tag{153}$$

with

$$\sigma = \omega^x - (\kappa + \zeta)\mathbb{n} \cdot \mathbf{D}\mathbb{n}. \tag{154}$$

X. SORPTION ISOTHERMS

A. General sorption isotherm

In view of the hypothesis (C), the bulk and surface constitutive relations (36b) and (139b) yield a condition [40,41]

$$\mu = \frac{\partial\hat{\psi}(n,\vartheta)}{\partial n} = \frac{\partial\hat{\psi}^x(n^x,\vartheta)}{\partial n^x}. \tag{155}$$

For each fixed value of ϑ, (155) relates the surface limit of the bulk molecular density n to the surface molecular density n^x and, therefore, defines a *sorption isotherm*. When the function $\partial^2\hat{\psi}^x/\partial n^x\partial n^x$ is strictly positive, $\partial\hat{\psi}^x(n^x,\vartheta)/\partial n^x$ is invertible in n^x for fixed ϑ; in this case we may express the sorption isotherm (155) in the explicit form

$$n^x = \mathcal{I}(n,\vartheta). \tag{156}$$

B. Langmuir sorption isotherm

The specific forms for the response functions $\hat{\psi}$ and $\hat{\psi}^x$ determining the bulk and superficial free-energy densities dictate the nature of the sorption isotherms. In particular, granted the classical choices [40]

$$\hat{\psi}(n,\vartheta) = \psi_0(\vartheta) + n\mu_0(\vartheta) + k_B n\vartheta\left\{\ln\left(\frac{n}{n_0(\vartheta)}\right) - 1\right\}, \tag{157}$$

where $\mu_0(\vartheta)$ and $n_0(\vartheta)$ denote reference values of the bulk chemical potential and the bulk molecular density at temperature ϑ, and

$$\hat{\psi}^x(n^x,\vartheta) = \psi_0^x(\vartheta) + n^x\mu_0^x(\vartheta) + k_B\vartheta\left\{n^x\ln\left(\frac{n^x}{n_{sat}^x(\vartheta)}\right) + [n_{sat}^x(\vartheta) - n^x]\ln\left(1 - \frac{n^x}{n_{sat}^x(\vartheta)}\right)\right\}, \tag{158}$$

where $\mu_0^x(\vartheta)$ denotes a reference value of the interfacial chemical potential at temperature ϑ and $n_{sat}^x(\vartheta)$ denotes the saturation value of the interfacial molecular density at temperature ϑ, for $\hat{\psi}$ and $\hat{\psi}^x$ [both of which are consistent with the hypothesis (B) stipulating that the free-energy densities be reckoned relative to the free-energy density of the vapor]; (155) then requires that

$$\mu_0(\vartheta) + k_B\vartheta\ln\left\{\frac{n}{n_0(\vartheta)}\right\} = \mu_0^x(\vartheta) + k_B\vartheta\ln\left\{\frac{n^x}{n_{sat}^x(\vartheta) - n^x}\right\}. \tag{159}$$

On defining

$$N(\vartheta) = n_0(\vartheta)\exp\left\{\frac{\mu_0^x(\vartheta) - \mu_0(\vartheta)}{k_B\vartheta}\right\}, \tag{160}$$

(159) therefore yields, as a special version of (156), the classical *Langmuir sorption isotherm* [23]

$$\frac{n^x}{n_{sat}^x(\vartheta)} = \frac{n}{N(\vartheta) + n}. \tag{161}$$

For the particular choice (158) of $\hat{\psi}^x$, the response function $\hat{\omega}^x$ determining the grand canonical potential density ω^x—or, equivalently, the equilibrium contribution to the surface tension [cf. (154)]—has the specific form $\hat{\omega}^x(n^x,\vartheta) = \psi_0^x(\vartheta) + k_B\vartheta n_{sat}^x(\vartheta)\ln[1 - n^x/n_{sat}^x(\vartheta)]$, which is the Frumkin [43] equation of state.

XI. GENERAL EVOLUTION EQUATIONS FOR THE INTERFACE

Apart from the appropriate kinematical equations, the equations for the interface consist of the *sorption isotherm condition*

$$\mu = \frac{\partial\hat{\psi}(n,\vartheta)}{\partial n} = \frac{\partial\hat{\psi}^x(n^x,\vartheta)}{\partial n^x} \tag{162}$$

and the balances (93), (131), (135), and (136) for surfactant molecules, energy, standard linear momentum, and normal configurational momentum, and energy, augmented by the constitutive relations (139) and (143)–(146) for the surface. Bearing in mind the decomposition (28) of **T** and the constitutive relations (37)–(39) for **S**, **j**, and **q**, the resulting conditions are *molecular balance*

$$\mathring{n}^x - n^x(KV - \text{div}_S\mathbf{u}_{tan}) = \text{div}_S\{m\text{grad}_S\mu + m_s\text{grad}_S\vartheta\} - \{M\text{grad}\mu + M_s\text{grad}\vartheta\}\cdot n - nV^{mig}, \tag{163}$$

energy balance

$$\vartheta\{\mathring{\eta}^x - \eta^x(KV - \text{div}_S\mathbf{u}_{tan})\} = \text{div}_S\{l_d\text{grad}\mu + l\text{grad}\vartheta\} - \{L_d\text{grad}\mu + L\text{grad}\vartheta\}\cdot n - \vartheta\eta V^{mig} - \lambda(\vartheta - \vartheta_v) + \mathcal{D}_0, \tag{164}$$

standard momentum balance

$$\sigma K n + \text{grad}_S\sigma + 2\text{div}_S\{\zeta\mathbb{D}_0\} = 2\varrho\nu\mathbf{D}n - \left\{p - \frac{J^2}{\varrho_v}\right\}n, \tag{165}$$

and either *normal configurational momentum balance*

$$\beta V^{mig} = -\left\{\omega - \frac{1}{2}\varrho|\mathbf{u}|^2 + p - \frac{J^2}{\varrho_v}\right\} + \{2\varrho\nu + (\kappa + \zeta)K\}n\cdot\mathbf{D}n - 2\zeta\mathbb{D}_0:\mathbb{K} + \text{div}_S\{\alpha\text{grad}_S V^{mig}\} \tag{166}$$

or *normal combined momentum balance*

$$\beta V^{mig} = \omega^x K + \text{div}_S\{\alpha\text{grad}_S V^{mig}\} - \omega + \frac{1}{2}\varrho|\mathbf{u}|^2. \tag{167}$$

These equations are derived as follows: (163) follows from (38), (93), and (142); (164) follows from (39), (131), and (140); (165) follows from (135), (143), and (154); (166) follows from (136) and (143)–(145); (167) follows from (138), (144), and (145).

The balances (164) and (165) should be supplemented by the bulk and surface constitutive equations for entropy

$$\eta = -\frac{\partial \hat{\psi}(n, \vartheta)}{\partial \vartheta}, \qquad \eta^{\mathrm{x}} = -\frac{\partial \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial \vartheta}; \qquad (168)$$

the bulk and surface constitutive equations for grand canonical potential

$$\omega = \hat{\psi}(n, \vartheta) - n\frac{\partial \hat{\psi}(n, \vartheta)}{\partial n}, \qquad (169\mathrm{a})$$

$$\omega^{\mathrm{x}} = \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta) - n^{\mathrm{x}}\frac{\partial \hat{\psi}^{\mathrm{x}}(n^{\mathrm{x}}, \vartheta)}{\partial n^{\mathrm{x}}}; \qquad (169\mathrm{b})$$

the surface-tension relation

$$\sigma = \omega^{\mathrm{x}} - (\kappa + \zeta)\mathrm{n} \cdot \mathbf{D}\mathrm{n}; \qquad (170)$$

and the expression

$$\mathcal{D}_0 = (\kappa + \zeta)(\mathrm{n} \cdot \mathbf{D}\mathrm{n})^2 + 2\zeta|\mathbb{D}_0|^2 + \alpha|\mathrm{grad}_S V^{\mathrm{mig}}|^2 + \beta(V^{\mathrm{mig}})^2$$
$$+ m_S|\mathrm{grad}_S\mu|^2 \qquad (171)$$

for the *nonthermal dissipation density*.

XII. APPROXIMATE CONDITIONS AT THE INTERFACE

A. Flat-equilibrium conditions

If we assume that all velocities, bulk thermal and diffusive fluxes, and time derivatives vanish, then the basic equations (163)–(166) reduce to

$$\omega = \omega^{\mathrm{x}} K, \qquad \omega^{\mathrm{x}} K\mathrm{n} + \mathrm{grad}_S\omega^{\mathrm{x}} = -p\mathrm{n}, \qquad (172\mathrm{a})$$

$$\mathrm{div}_S\{m_S\mathrm{grad}_S\mu\} = 0, \qquad \lambda(\vartheta - \vartheta_v) = 0. \qquad (172\mathrm{b})$$

A solution of these equations in which the interface is flat ($K = 0$) and all of the basic fields uniform on the interface, so that $\mu = \mathrm{const}$, and $\omega^{\mathrm{x}} = \mathrm{const}$, has

$$\omega = 0, \qquad p = 0, \qquad \vartheta = \vartheta_v, \qquad (173)$$

and may be referred to as describing a *flat equilibrium*. The condition $\omega = 0$ is the familiar assertion that, *in a flat equilibrium, the value of the grand canonical potential ω on the surface of the solution must coincide with that of the vapor*, here normalized to be zero [42]. Similarly, the condition $p = 0$ is the assertion that, *in a flat equilibrium, the value of the pressure p on the surface of the solution must coincide with that of the vapor*, here also normalized to be zero. The final condition $\vartheta = \vartheta_v$ is the assertion that, *in a flat equilibrium, the value of the temperature ϑ on the surface of the solution must coincide with that of the vapor*.

B. Bulk thermodynamic quantities close to a flat equilibrium

If we assume, for the moment, that the system is in a flat-equilibrium state, then we may conclude from the paragraph containing (173) that, in particular,

$$\omega = 0, \qquad n = n_0, \qquad \vartheta = \vartheta_v, \qquad (174)$$

with n_0 the equilibrium value of the surfactant molecular density in bulk. Then, using a subscripted zero to denote field-values at this equilibrium,

$$\omega_0 = \psi_0 - n_0\mu_0 = \varepsilon_0 - \vartheta_v\eta_0 - n_0\mu_0 = 0, \qquad (175)$$

where, by (36),

$$\psi_0 = \hat{\psi}(n_0, \theta_v), \qquad (176\mathrm{a})$$

$$\mu_0 = \left. \frac{\partial \hat{\psi}(n, \vartheta)}{\partial n} \right|_{(n, \vartheta)=(n_0, \theta_v)}, \qquad (176\mathrm{b})$$

$$\eta_0 = -\left. \frac{\partial \hat{\psi}(n, \vartheta)}{\partial \vartheta} \right|_{(n, \vartheta)=(n_0, \theta_v)}. \qquad (176\mathrm{c})$$

Now, if the system remains close to flat equilibrium, we then have that

$$\delta = \left| \frac{n}{n_0} - 1 \right| + \left| \frac{\vartheta}{\vartheta_v} - 1 \right| \ll 1. \qquad (177)$$

We now expand the bulk grand canonical potential ω near equilibrium. Then we may use (175) and (176) to conclude that

$$\omega = \mu_0(n - n_0) - \eta_0(\vartheta - \vartheta_v) + O(\delta^2)$$
$$= \psi_0\left\{ \frac{n}{n_0} - 1 \right\} + \ell\left\{ \frac{\vartheta}{\vartheta_v} - 1 \right\} + O(\delta^2), \qquad (178)$$

where ℓ defined via

$$\ell = -\vartheta_v\eta_0 \qquad (179)$$

is the *latent heat of evaporation*. Similarly,

$$\eta = \eta_0 + O(\delta), \qquad \vartheta\eta = \vartheta_v\eta_0 + O(\delta) = -\ell + O(\delta). \qquad (180)$$

C. Scaling of dissipative quantities

Introducing characteristic length and time scales l_* and t_* and characteristic values μ_* and ϑ_* of the chemical potential μ and the temperature ϑ, we assume that the material moduli ϱ, ν, M, M_{s}, L_{d}, L, m, m_s, l_{d}, l, κ, ζ, α, β, m_S, and λ are consistent with the relations

$$\frac{M_{\mathrm{s}}\vartheta_*}{M\mu_*} \ll 1, \qquad (181\mathrm{a})$$

$$\frac{L_{\mathrm{d}}\mu_*}{L\vartheta_*} \ll 1, \qquad (181\mathrm{b})$$

$$\frac{m_{\mathrm{s}}\vartheta_*}{Ml_*\mu_*} \ll 1, \qquad (181\mathrm{c})$$

$$\frac{l_{\mathrm{d}}\mu_*}{Ll_*\vartheta_*} \ll 1, \qquad (181\mathrm{d})$$

$$\frac{\varrho\nu}{\beta l_*} \ll 1, \tag{181e}$$

$$\frac{\zeta}{\beta l_*^2} \ll 1, \tag{181f}$$

$$\frac{\kappa + \zeta}{\beta l_*^2} \ll 1, \tag{181g}$$

$$\frac{\alpha}{\beta l_*^2} \ll 1, \tag{181h}$$

$$\frac{l}{Ll_*} \ll 1, \tag{181i}$$

$$\frac{\beta l_*^3}{L\vartheta_* t_*^2} \ll 1, \tag{181j}$$

$$\frac{\lambda l_*}{L} \ll 1. \tag{181k}$$

While (181a)–(181d) stipulate that the coupling effects embodied by the bulk and interfacial Soret and Dufour coefficients are negligible, (181e)–(181g) stipulate that dissipative effects associated with viscous stresses in the bulk and on the surface are dominated by that associated with the exchange of solvent between solution and vapor, (181h) stipulates that the dissipative effect associated with spatial variations in the migrational velocity of the interface are dominated by that associated with the exchange of solvent between solution and vapor, (181i) stipulates that the transport of heat within the interface is dominated by the exchange of heat between the solution and the vapor, and (181j) and (181k) stipulate that the dissipative effects associated with the exchanges of solvent and heat between solution and vapor are negligible in comparison to that associated with the transport of heat in bulk.

D. Simplified interfacial evolution equations

Performing an obvious scaling based on the characteristic values of length, time, chemical potential, and temperature introduced above (with l_*/t_* assumed to provide a characteristic velocity), invoking the scaling assumptions (181), and neglecting terms of $O(\delta)$ in (164) and of $O(\delta^2)$ in (166), we find that the interfacial balances (163)–(166) reduce to

$$\mathring{n}^{\mathbf{x}} - n^{\mathbf{x}}(KV - \mathrm{div}_{\mathcal{S}}\,\mathbf{u}_{\mathrm{tan}}) = \mathrm{div}_{\mathcal{S}}\{m\,\mathrm{grad}_{\mathcal{S}}\,\mu\} - \{M\,\mathrm{grad}\,\mu\}\cdot\mathrm{n}$$
$$- nV^{\mathrm{mig}}, \tag{182a}$$

$$\vartheta_v\{\mathring{\eta}^{\mathbf{x}} - \eta^{\mathbf{x}}(KV - \mathrm{div}_{\mathcal{S}}\,\mathbf{u}_{\mathrm{tan}})\} = -\{L\,\mathrm{grad}\,\vartheta\}\cdot\mathrm{n} + \ell V^{\mathrm{mig}}, \tag{182b}$$

$$\sigma K\mathrm{n} + \mathrm{grad}_{\mathcal{S}}\,\sigma + 2\,\mathrm{div}_{\mathcal{S}}\{\zeta\mathbb{D}_0\} = 2\varrho\,\nu\mathbf{D}\mathrm{n} - \left\{p - \frac{J^2}{\varrho_v}\right\}\mathrm{n}, \tag{182c}$$

$$\beta V^{\mathrm{mig}} = -\ell\left\{\frac{\vartheta}{\vartheta_v} - 1\right\} - \left\{p - \frac{J^2}{\varrho_v}\right\} - \psi_0\left\{\frac{n}{n_0} - 1\right\} + \tfrac{1}{2}\varrho|\mathbf{u}|^2, \tag{182d}$$

while, with terms of $O(\delta^2)$ neglected, the alternative (167) and (166) reduces to

$$\beta V^{\mathrm{mig}} = \omega^{\mathbf{x}}K - \ell\left\{\frac{\vartheta}{\vartheta_v} - 1\right\} - \psi_0\left\{\frac{n}{n_0} - 1\right\} + \tfrac{1}{2}\varrho|\mathbf{u}|^2. \tag{183}$$

XIII. COMPARISON

We now compare the above approximate equations for the interface with the equations used by Danov *et al.* [9]. All comparisons are made using our notation: in particular, $\mathbf{u}$, $\mathbf{u}_{\mathrm{tan}}$, n, $n^{\mathbf{x}}$, ϑ, and ϑ_v correspond, respectively, to $\mathbf{v}$, $\mathbf{v}_s$, c, Γ, T, and T_e of Danov *et al.* [9].

A. Molecular balance

Danov *et al.* [9] work with concentrations instead of molecular densities. We ignore this trivial distinction and instead simply interpret the concentrations of Danov *et al.* [9] as molecular densities. Employing our notation, the molecular balance of Danov *et al.* [9] reads[5]

$$\frac{\partial n^{\mathbf{x}}}{\partial t} + \mathrm{div}_{\mathcal{S}}\{n^{\mathbf{x}}\mathbf{u}_{\mathrm{tan}}\} = \mathrm{div}_{\mathcal{S}}\{D^{\mathcal{S}}\,\mathrm{grad}_{\mathcal{S}}\,n^{\mathbf{x}}\} - \{D\,\mathrm{grad}\,n\}\cdot\mathrm{n}$$
$$- nV^{\mathrm{mig}}, \tag{184}$$

where D and $D^{\mathcal{S}}$ denote bulk and interfacial molecular diffusivities. When compared to (182a), this equation shows obvious differences in the forms of its rate terms and diffusive fluxes.

Whereas the flux terms in (182a) involve the surface gradient $\mathrm{grad}_{\mathcal{S}}\,\mu$ of the chemical potential on the interface and the limit, from the solution, of the gradient $\mathrm{grad}\,\mu$ of the chemical potential in bulk, those in (184) involve the surface gradient $\mathrm{grad}\,n^{\mathrm{x}}$ of the surface molecular density and the limit from the solution, of the gradient $\mathrm{grad}\,n$ of the molecular density in bulk. These differences are easily reconciled by assuming that the cross terms associated with the mixed partial derivatives that result on computing the surface and bulk gradients of the state relations (139b) and (36b) are negligible in a suitable sense. With such assumptions, the right side of (182a) reduces to that of (184). To illustrate this point, we focus on the surface molecular flux $\mathbf{j} = -m_{\mathcal{S}}\,\mathrm{grad}_{\mathcal{S}}\,\mu$. By the state relation (139b),

$$\mathrm{grad}_{\mathcal{S}}\,\mu = \mathrm{grad}_{\mathcal{S}}\left\{\frac{\partial\hat{\psi}^{\mathbf{x}}(n^{\mathbf{x}},\vartheta)}{\partial n^{\mathbf{x}}}\right\}$$
$$= \frac{\partial^2\hat{\psi}^{\mathbf{x}}(n^{\mathbf{x}},\vartheta)}{\partial(n^{\mathbf{x}})^2}\,\mathrm{grad}_{\mathcal{S}}\,n^{\mathbf{x}} + \frac{\partial^2\hat{\psi}^{\mathbf{x}}(n^{\mathbf{x}},\vartheta)}{\partial n^{\mathbf{x}}\partial\vartheta}\,\mathrm{grad}_{\mathcal{S}}\,\vartheta. \tag{185}$$

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[5]Cf. Eq. (3b) of Danov *et al.* [9].

Thus, on defining the surface molecular diffusivity D^S and Soret diffusivity coefficient D_s^S via

$$D^S(n^{\mathbf{x}}, \vartheta) = m(n^{\mathbf{x}}, \vartheta) \frac{\partial^2 \hat{\psi}^{\mathbf{x}}(n^{\mathbf{x}}, \vartheta)}{\partial(n^{\mathbf{x}})^2}, \qquad (186a)$$

$$D_s^S(n^{\mathbf{x}}, \vartheta) = m(n^{\mathbf{x}}, \vartheta) \frac{\partial^2 \hat{\psi}^{\mathbf{x}}(n^{\mathbf{x}}, \vartheta)}{\partial n^{\mathbf{x}} \partial \vartheta}, \qquad (186b)$$

and assuming, analogous to (181a), that $D_s^S \vartheta_* / D^S \mu_* \ll 1$, where μ_* and θ_* are the characteristic values of chemical potential and temperature introduced in connection with the relations (181), it follows that

$$\mathbf{j} = - m_S \operatorname{grad}_S \mu \rightarrow - D^S \operatorname{grad}_S n^{\mathbf{x}}. \qquad (187)$$

A completely analogous argument starting with (36b) yields $m \operatorname{grad} \mu \rightarrow D \operatorname{grad} n$, with the bulk molecular diffusivity D defined by $D(n, \vartheta) = m(n, \vartheta)[\partial^2 \hat{\psi}(n, \vartheta)/\partial n^2]$. What is important here is that the diffusivities D and D^S should not be assigned independently of the state relations defining the chemical potential in bulk and on the interface. In particular, as is shown in (155), the chosen expressions for ψ and $\psi^{\mathbf{x}}$ determine the sorption isotherm. The forms of the sorption isotherm and the molecular diffusivities are therefore thermodynamically linked, albeit with some freedom allowed through the chosen forms for molecular mobilities in bulk and on the surface.

The more significant difference between (182a) and (184) concerns their rate terms. Consider the partial derivative $\partial n^{\mathbf{x}}/\partial t$ on the left side of (184). For a surface field such as $n^{\mathbf{x}}$, the difference quotient

$$\frac{n^{\mathbf{x}}(\mathbf{x}, t + \tau) - n^{\mathbf{x}}(\mathbf{x}, t)}{\tau} \qquad (188)$$

is generally undefined because, even for sufficiently small τ, there is no assurance that $\mathbf{x}$ lies on $\mathcal{S}(t + \tau)$ when $\mathbf{x}$ lies on $\mathcal{S}(t)$. Without explanation, conventional partial derivatives like $\partial n^{\mathbf{x}}/\partial t$ are therefore meaningless. If, as discussed by Cermelli, Fried, and Gurtin [23], one uses the normally constant extension of $n^{\mathbf{x}}$ to define the partial time derivative, then

$$\frac{\partial n^{\mathbf{x}}}{\partial t} = \mathring{n}^{\mathbf{x}} - \mathbf{u}_{\tan} \cdot \operatorname{grad}_S n^{\mathbf{x}} \qquad (189)$$

and, since $n^{\mathbf{x}} \operatorname{div}_S \mathbf{u}_{\tan} + \mathbf{u}_{\tan} \cdot \operatorname{grad}_S n^{\mathbf{x}} = \operatorname{div}_S \{n^{\mathbf{x}} \mathbf{u}_{\tan}\}$, the left side of (182a) can be expressed as

$$\frac{\partial n^{\mathbf{x}}}{\partial t} + \operatorname{div}_S \{n^{\mathbf{x}} \mathbf{u}_{\tan}\} - n^{\mathbf{x}} K V. \qquad (190)$$

In conclusion, granted suitable assumptions concerning the cross terms associated with the mixed partial derivatives that result on computing the surface and bulk gradients of the state relations (139b) and (36b) and that the partial time derivative is defined via the normally constant extension [so that (189) holds], the molecular balance (182a) of our theory becomes

$$\frac{\partial n^{\mathbf{x}}}{\partial t} + \operatorname{div}_S \{n^{\mathbf{x}} \mathbf{u}_{\tan}\} - n^{\mathbf{x}} K V = \operatorname{div}_S \{D^S \operatorname{grad}_S n^{\mathbf{x}}\}$$
$$- \{D \operatorname{grad} n\} \cdot \mathbf{n} - n V^{\mathrm{mig}}, \qquad (191)$$

which differs from the molecular balance (184) of Danov *et al.* [9] only by an additional term $-n^{\mathbf{x}} K V$ on its left side. Due to the factor of the total curvature, we expect that this term may influence the stability of the interface. In particular, this term is likely to be very important in the evaporation or condensation of a droplet.

B. Energy balance

Employing our notation, the energy balance of Danov *et al.* [9] reads[6]

$$L J = \{\lambda \operatorname{grad} \vartheta\} \cdot \mathbf{n}, \qquad (192)$$

where L and λ are related to our quantities ϱ, ℓ, and k by

$$L = \frac{\ell}{\varrho} \quad \text{and} \quad \lambda = k. \qquad (193)$$

The obvious difference between (182b) and (192) is the absence of rate terms in the latter. To reconcile this difference, let $\eta_*^{\mathbf{x}}$ denote a characteristic value of the entropy density $\eta^{\mathbf{x}}$ on the interface. Granted (89) and (193), the energy balance (182b) then reduces to (192) provided that $\eta_*^{\mathbf{x}} l_* / k t_* \ll 1$, which corresponds to assuming that the time scale associated with the redistribution of the entropy density within the interface is much slower than that associated with thermal transport from the solution to the interface.

C. Standard momentum balance

To account for van der Waals interactions that may affect surfactant films with thicknesses ranging between 10 nm and 20 μm, Danov *et al.* [9] include a disjoining pressure Π in their statement of standard momentum balance on the evaporation surface. With this effect taken into account, (182c) becomes

$$\sigma K \mathbf{n} + \operatorname{grad}_S \sigma + 2 \operatorname{div}_S \{\zeta \mathbb{D}_0\} = 2 \varrho \nu \mathbf{D} \mathbf{n} - \left\{ p + \Pi - \frac{J^2}{\varrho_v} \right\} \mathbf{n}, \qquad (194)$$

which is exactly the form taken by the standard momentum balance of Danov *et al.* [9] in our notation.[7] Hence, setting aside the absence of the disjoining pressure term, the stan-

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[6]Cf. Eq. (3d) of Danov *et al.* [9], who instead of the migrational velocity work with the mass flow across the interface and uses a latent heat $L = \ell/\varrho L$, measured per unit mass. Also, Danov *et al.* [9] use λ instead of k to denote the thermal conductivity of the solution.

[7]Cf. Eq. (3c) of Danov *et al.* [9], who do not measure the pressure of the solution relative to that of the vapor and, therefore, instead of p have $p - p_v$, where p_v denotes the vapor pressure (so that the pressures p and p_v of the solution and the vapor are measured with respect some independent gauge).

dard momentum balance (182) of our theory is identical to that of Danov *et al.* [9].

D. Normal configurational momentum balance

The notions of normal configurational momentum balance or combined momentum balance do not enter the considerations of Danov *et al.* [9]. These authors instead impose the Hertz-Knudsen-Langmuir Eq. (1), expressed as[8]

$$J = J_\vartheta(\vartheta - \vartheta_s), \quad (195)$$

where J_ϑ is related to our quantities ϱ, β, and ℓ via

$$J_\vartheta = \frac{\varrho\ell}{\beta\vartheta_s}. \quad (196)$$

It is not difficult to reduce the normal configurational momentum balance (182d) to an equation of the form (195). Indeed, if we assume that $\psi_0/\ell \ll 1$, $p/\ell \ll 1$, $J^2/\varrho_v\ell \ll 1$, $\varrho l_*^2/\ell t_*^2 \ll 1$, and $\vartheta_v = \vartheta_s$, then (182d) reduces immediately to (1), which, with (89) and (196), coincides with (195). Hence, our theory yields the Hertz-Knudsen-Langmuir equation in the form (195) used by Danov *et al.* [9] provided that the flat equilbrium value of the free-energy density, the pressure, the vapor recoil term, and the kinetic-energy density are all neglible as compared with the latent heat of evaporation.

As noted in Sec. I, (182d) also contains as special cases generalizations of the Hertz-Knudsen-Langmuir equation used by Wayner [27], Moosman and Homsey [28], and Ajaev and Homsey [29]. In particular, Ajaev and Homsey [29] consider the equation[9]

$$KJ = \frac{\vartheta}{\vartheta_s} - 1 + \delta p, \quad (197)$$

and K and δ are related to our quanties ϱ, β, and ℓ via

$$K = \frac{\beta}{\varrho\ell} \quad \text{and} \quad \delta = \frac{1}{\ell}. \quad (198)$$

This equation obviously ensues from (182d) on replacing p by $p - p_v$, taking $(p - p_v)/\ell$ to be of order unity, and assuming that $\psi_0/\ell \ll 1$, $J^2/\varrho_v\ell \ll 1$, $\varrho l_*^2/\ell t_*^2 \ll 1$, and $\vartheta_v = \vartheta_s$.

ACKNOWLEDGMENTS

APPENDIX A: PROOF OF THE EQUIVALENCY THEOREM

Consider the first law in the configurational form (49) and note that the requirement that (49) satisfy the intrinsicality hypothesis (A) is equivalent to the requirement, hypothesis (E), that *the power $W(\mathcal{R}(t))$ be independent of the choice of*

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[8]Cf. Eq. (6) of Danov *et al.* [9].
[9]Cf. Eq. (19) of Ajaev and Homsey [29]. Like Danov *et al.* [9], Ajaev and Homsey [29] work with $p - p_v$ instead of p.

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observed velocity field $\mathbf{v}_{\partial R}$ chosen to characterize the migration of $\mathcal{R}(t)$.

Our first step is to determine the consequences of the invariance requirement (E). Since all observed velocity fields have the same normal component, while the tangential components are arbitrary, (E) is equivalent to the requirement that $W(\mathcal{R}(t))$ be invariant under all transformations of the form

$$\mathbf{v}_{\partial R} \mapsto \mathbf{v}_{\partial R} + \mathbf{t}, \quad (A1)$$

with $\mathbf{t}$ tangential to $\partial\mathcal{R}$, or, equivalently, that

$$\int_{\partial R(t)} \{(\mathbf{T} + \mathbf{C})\mathbf{m} + \varrho(\mathbf{u} + \mathbf{p})V_{\partial R}^{\text{mig}}\} \cdot \mathbf{t}\,da = 0 \quad (A2)$$

for all such transformations. Then, granted (A2), since $\mathcal{R}$ and $\mathbf{t}$ (tangential to $\partial\mathcal{R}$) may be arbitrarily chosen, it follows that

$$\{(\mathbf{T} + \mathbf{C})\mathbf{m} + (\mathbf{u} + \mathbf{p})U\} \cdot \mathbf{t} = 0 \quad (A3)$$

for all $\mathbf{t}$ and $\mathbf{m}$ with $\mathbf{t}$ orthogonal to $\mathbf{m}$ and any scalar U. Since U is arbitrary, we obtain the configurational-momentum relation (55).

Next, bearing in mind (55), it follows from (A3) that, for each $\mathbf{m}$, $(\mathbf{T}+\mathbf{C})\mathbf{m}$ must lie in the direction of $\mathbf{m}$, a restriction satisfied if and only if $\mathbf{T}+\mathbf{C} = \varphi\mathbf{1}$, with φ a scalar field. Invariance therefore yields the *pre-Eshelby relation*

$$\mathbf{C} = \varphi\mathbf{1} - \mathbf{T}. \quad (A4)$$

In view of (A4), the power expended on $\mathcal{R}$ has the form

$$W(\mathcal{R}(t)) = \int_{\partial R(t)} \{\mathbf{Tm} \cdot \mathbf{u} + (\varphi + \varrho|\mathbf{u}|^2)V_{\partial R}^{\text{mig}}\}da, \quad (A5)$$

which is clearly consistent with the intrinisicality hypothesis in the form (E).

Further, by (34), (46), and (A5), the energy balance (49) becomes

$$\frac{d}{dt}\int_{R(t)} \left\{\varepsilon + \frac{1}{2}\varrho|\mathbf{u}|^2\right\}dv = \int_{\partial R(t)} \mathbf{Tm} \cdot \mathbf{u}\,da$$

$$- \int_{\partial R(t)} \mu\mathbf{j} \cdot \mathbf{m}\,da$$

$$- \int_{\partial R(t)} \mathbf{q} \cdot \mathbf{m}\,da + \int_{\partial R(t)} \{\varphi + \varepsilon$$

$$- \psi + \mu n + \varrho|\mathbf{u}|^2\}V_{\partial R}^{\text{mig}}\,da, \quad (A6)$$

a relation that coincides with the standard form (48d) provided we take

$$\varphi = \psi - \mu n - \tfrac{1}{2}\varrho|\mathbf{u}|^2. \quad (A7)$$

Granted (A7), (A4) reduces to the Eshelby relation (54).

Finally, (A7) is also a necessary for (A6) to be satisfied for all migrating control volumes $\mathcal{R}(t)$. Indeed, by (47),

$$\frac{d}{dt}\int_{\mathcal{R}(t)}\{\varepsilon+\tfrac{1}{2}\varrho|\mathbf{u}|^2\}dv=\int_{\mathcal{R}(t)}\overline{\{\varepsilon+\tfrac{1}{2}\varrho|\mathbf{u}|^2\}}\,dv$$

$$+\int_{\mathcal{R}(t)}\{\varepsilon+\tfrac{1}{2}\varrho|\mathbf{u}|^2\}V_{\partial\mathcal{R}}^{\mathrm{mig}}\,da,$$

a relation that when combined with (A6) yields

$$\int_{\mathcal{R}(t)}\overline{\{\varepsilon+\tfrac{1}{2}\varrho|\mathbf{u}|^2\}}dv=\int_{\partial\mathcal{R}(t)}\mathbf{T}\mathbf{m}\cdot\mathbf{u}da$$

$$-\int_{\partial\mathcal{R}(t)}\mu\mathbf{j}\cdot\mathbf{m}da-\int_{\partial\mathcal{R}(t)}\mathbf{q}\cdot\mathbf{m}da$$

$$+\int_{\partial\mathcal{R}(t)}\underbrace{\{\varphi-\psi+\mu n+\tfrac{1}{2}\varrho|\mathbf{u}|^2\}}_{=A}V_{\partial\mathcal{R}}^{\mathrm{mig}}da. \tag{A8}$$

Since the choice of migrating control volume is arbitrary, the normal velocity $V_{\partial\mathcal{R}}$ and (hence) the normal migrational velocity $V_{\partial\mathcal{R}}^{\mathrm{mig}}$ in (A8) may, at any time, be considered an arbitrary scalar field on $\partial\mathcal{R}$ [without disturbing the remaining fields in (A8)]. Hence we must have $A=0$, which is (A7). This completes the proof of the equivalency theorem.

APPENDIX B: MIGRATIONALLY NORMAL EXPRESSION FOR THE POWER EXPENDED ON THE SURFACE

Consider the power (115) expended on $\mathcal{A}(t)$ and note that the requirement that (115) satisfy the intrinsicality hypothesis (#) is equivalent to the following requirement, hypothesis (F): *that the power $w(\mathcal{A})$ be independent of the choice of observed velocity field $\mathrm{v}_{\partial\mathcal{A}}$ chosen to characterize the migration of $\partial\mathcal{A}$.* Necessary and sufficient that (F) be satisfied is that

$$w(\mathcal{A}(t))=\int_{\partial\mathcal{A}(t)}\{\mathbb{T}\mathrm{m}\cdot\mathrm{v}_{\partial\mathcal{A}}+\mathbb{C}\mathrm{m}\cdot(\mathrm{v}_{\partial\mathcal{A}}-\mathbf{u})\}ds \tag{B1}$$

be invariant under all transformations of the form

$$\mathrm{v}_{\partial\mathcal{A}}\mapsto\mathrm{v}_{\partial\mathcal{A}}+\mathrm{t},\quad\mathrm{t}\cdot\mathrm{m}=0, \tag{B2}$$

which, by (81) and the tangential nature of $\mathrm{w}_{\partial\mathcal{A}}$, is necessarily accompanied by the transformation

$$\mathrm{v}_{\partial\mathcal{A}}-\mathbf{u}\mapsto\mathrm{v}_{\partial\mathcal{A}}-\mathbf{u}+\mathrm{t}. \tag{B3}$$

The requirement (F) therefore holds if and only if

$$\int_{\partial\mathcal{A}(t)}(\mathbb{T}+\mathbb{C})\mathrm{m}\cdot\mathrm{t}\,ds=0 \tag{B4}$$

for all subsurfaces $\mathcal{A}$ of $\mathcal{S}$ and all fields t tangential to $\partial\mathcal{A}$. It follows that $\mathbb{T}+\mathbb{C}$ must satisfy $\mathrm{t}\cdot(\mathbb{T}+\mathbb{C})\mathrm{m}=0$ whenever t and m are orthogonal and tangent to $\mathcal{S}$. Thus $(\mathbb{T}+\mathbb{C})\mathrm{m}$ must lie in the direction of m for each m orthogonal to n, which is possible if and only if the *tangential* component $(\mathbb{T}+\mathbb{C})_{\mathrm{tan}}$ of

$\mathbb{T}+\mathbb{C}$ has the form $(\mathbb{T}+\mathbb{C})_{\mathrm{tan}}=\varphi\mathbb{P}$, with φ a surface scalar field. Bearing in mind (61) and (106), invariance therefore implies that the interfacial configurational stress $\mathbb{C}$ must be of the form (117).

Next, by (81), (85), and (117), it follows that

$$w(\mathcal{A}(t))=\int_{\partial\mathcal{A}(t)}\{\varphi V_{\partial\mathcal{A}}^{\mathrm{mig}}+\mathbb{T}\mathrm{m}\cdot\mathrm{v}+\mathbb{C}\mathrm{m}\cdot\mathrm{v}^{\mathrm{mig}}\}ds. \tag{B5}$$

Further, using the surface divergence theorem (66c) and the surface balances (105) and (109) for standard and configurational momenta, we have

$$w(\mathcal{A}(t))=\int_{\partial\mathcal{A}(t)}\varphi V_{\partial\mathcal{A}}^{\mathrm{mig}}\,ds+\int_{\mathcal{A}(t)}\{\mathbb{T}\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}$$

$$+\mathbb{C}\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}^{\mathrm{mig}}\}da+\int_{\mathcal{A}(t)}\left\{\left(\mathbb{T}\mathrm{m}+\frac{J^2}{\varrho_v}\mathrm{n}\right)\cdot\mathrm{v}\right.$$

$$+\left.\left(\mathbb{C}\mathrm{m}-\frac{J^2}{\varrho_v}\mathrm{n}-\mathrm{f}\right)\cdot\mathrm{v}^{\mathrm{mig}}\right\}da, \tag{B6}$$

which allows us to rewrite (116) in the form

$$W^{\mathrm{x}}(\mathcal{A}(t))=\int_{\partial\mathcal{A}(t)}\varphi V_{\partial\mathcal{A}}^{\mathrm{mig}}\,ds+\int_{\mathcal{A}(t)}\{(\mathbb{T}+\mathbb{C})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}$$

$$-\mathbb{C}\!:\!\mathrm{L}-\mathrm{f}\cdot\mathrm{v}^{\mathrm{mig}}\}da. \tag{B7}$$

Toward further simplification of (116), consider the second term on the right side of (B7). By (117),

$$(\mathbb{T}+\mathbb{C})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}=\{(\mathbb{T}+\mathbb{C})_{\mathrm{tan}}+\mathrm{n}\otimes\mathrm{c}\}\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}$$

$$=\varphi\,\mathrm{div}_{\mathcal{S}}\,\mathrm{v}+(\mathrm{n}\otimes\mathrm{c})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}. \tag{B8}$$

Also, by (76), (106), and (117),

$$\mathbb{C}\!:\!\mathrm{L}=\mathbb{C}\!:\!(\mathbb{P}\mathrm{L}+\mathrm{n}\otimes\mathrm{L}^{\mathrm{T}}\mathrm{n})$$

$$=\mathbb{C}_{\mathrm{tan}}\!:\!\mathrm{D}+\mathbb{C}\!:\!\mathbb{W}+\mathbb{C}^{\mathrm{T}}\mathrm{n}\cdot\mathrm{L}^{\mathrm{T}}\mathrm{n}$$

$$=\mathbb{C}_{\mathrm{tan}}\!:\!\mathrm{D}+(\varphi\mathbb{P}-\mathbb{T})\!:\!\mathbb{W}+(\mathrm{c}-\mathbb{T}^{\mathrm{T}}\mathrm{n})\cdot\mathrm{L}^{\mathrm{T}}\mathrm{n}$$

$$=\mathbb{C}_{\mathrm{tan}}\!:\!\mathrm{D}+(\mathrm{n}\otimes\mathrm{c})\!:\!\mathrm{L}$$

$$=\mathbb{C}_{\mathrm{tan}}\!:\!\mathrm{D}+(\mathrm{n}\otimes\mathrm{c})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathbf{u}. \tag{B9}$$

Thus,

$$(\mathbb{T}+\mathbb{C})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}-\mathbb{C}\!:\!\mathrm{L}$$

$$=\varphi\,\mathrm{div}_{\mathcal{S}}\,\mathrm{v}-\mathbb{C}\!:\!\mathrm{D}+(\mathrm{m}\otimes\mathrm{c})\!:\!\mathrm{grad}_{\mathcal{S}}\,\mathrm{v}^{\mathrm{mig}}. \tag{B10}$$

Finally, we require that the velocity field v for $\mathcal{S}$ be migrationally normal. Then, recalling (83)–(85), we have

$$\mathrm{v}=V\mathrm{n}+\mathbf{u}_{\mathrm{tan}},\quad\mathrm{v}^{\mathrm{mig}}=V^{\mathrm{mig}}\mathrm{n},$$

$$\mathrm{div}_{\mathcal{S}}\mathrm{v}=-KV+\mathrm{div}_{\mathcal{S}}\mathbf{u}_{\mathrm{tan}},\quad\mathrm{w}_{\partial\mathcal{A}}\cdot\mathrm{m}=V_{\partial\mathcal{A}}^{\mathrm{mig}}, \tag{B11}$$

which together with (B10) allow us to express the power (115) expended on $\mathcal{A}(t)$ in the intrinsic form (119).

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