PHYSICAL REVIEW E **88**, 022149 (2013)

Dynamics of multiphase systems with complex microstructure. I. Development of the governing equations through nonequilibrium thermodynamics

Leonard M. C. Sagis*
Food Physics Group, Wageningen University, Bomenweg 2, 6703 HD Wageningen, The Netherlands

Hans Christian Öttinger
ETH Zurich, Department of Materials, Polymer Physics, Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

(Received 26 March 2013; revised manuscript received 11 June 2013; published 29 August 2013)

In this paper we present a general model for the dynamic behavior of multiphase systems in which the bulk phases and interfaces have a complex microstructure (for example, immiscible polymer blends with added compatibilizers, or polymer stabilized emulsions with thickening agents dispersed in the continuous phase). The model is developed in the context of the GENERIC framework (general equation for the nonequilibrium reversible irreversible coupling). We incorporate scalar and tensorial structural variables in the set of independent bulk and surface excess variables, and these structural variables allow us to link the highly nonlinear rheological response typically observed in complex multiphase systems, directly to the time evolution of the microstructure of the bulk phases and phase interfaces. We present a general form of the Poisson and dissipative brackets for the chosen set of bulk and surface excess variables, and show that to satisfy the entropy degeneracy property, we need to add several contributions to the moving interface normal transfer term, involving the tensorial bulk and interfacial structural variables. We present the full set of balance equations, constitutive equations, and boundary conditions for the calculation of the time evolution of the bulk and interfacial variables, and this general set of equations can be used to develop specific models for a wide range of complex multiphase systems.

DOI: 10.1103/PhysRevE.88.022149 PACS number(s): 05.70.Ln, 05.70.Np, 47.10.ab, 47.55.N−

I. INTRODUCTION

Immiscible polymer blends with added compatibilizers, dispersions of anisotropic particles in the two-phase coexistence regime, and polymer or particle stabilized oil-in-water emulsions with thickening agents added to the aqueous phase are typical examples of multiphase systems in which both the bulk phases and interfaces have a complex microstructure. These complex systems tend to have highly nonlinear responses to deformations, even when departures from equilibrium are relatively small [1]. Deformations induce changes in the microstructure of the bulk phases and interfaces, and as a result, the bulk and surface rheological properties depend strongly on the degree of deformation. Since these systems tend to have high surface to volume ratios, the surface rheological properties have a significant effect on the overall dynamics, and need to be accounted for when constructing models for the dynamics of these systems [1]. Currently there are very few models available describing nonlinear stress deformation behavior of interfaces [1–8], and those that exist are generally valid only for small departures from equilibrium [1,4,6,8].

The GENERIC framework (general equation for the nonequilibrium reversible irreversible coupling) is an ideal tool to develop continuum models for the dynamics of complex multiphase systems. This framework derives all time evolution equations and boundary conditions of a system from a single equation [9–11], which contains all reversible and irreversible contributions to the overall dynamics of a system. An important advantage of the GENERIC framework compared to other nonequilibrium thermodynamic frameworks is that it is relatively straightforward to construct nonlinear constitutive equations for the fluxes in a system, which are valid also far from equilibrium [9–11].

Recently, the GENERIC framework was extended to simple multiphase systems, with inviscid interfaces, in the context of bubble growth by exsolution of a volatile component from a solution [12]. Sagis extended this formalism to systems with simple viscous interfaces [13], and multiphase systems with viscoelastic interfaces with a complex microstructure [14]. In the latter study the effect of the microstructure on macroscopic dynamics was incorporated by including bulk and surface excess structural variables in the set of independent system variables. The microstructure of the bulk phase was incorporated through a single scalar density $\bar{\Gamma}$ and a single tensorial density $\bar{\mathbf{C}}$ [14]. The scalar density can be a local colloidal particle density, a local polymer segment density, or a local degree of stretching of segments (multiplied by the segment density). The tensorial density can for example describe the orientation of anisotropic colloidal particles or polymer segments. The effect of the microstructure of the interface on macroscopic dynamics was incorporated through a surface scalar excess density $\bar{\Gamma}^s$ and a tangential surface tensor density $\bar{\mathbf{C}}^s$ [14]. Examples of the former are the surface excess density of adsorbed colloidal particles or adsorbed polymer segments. The latter may represent the (in-plane) orientation of adsorbed anisotropic particles, or (in-plane) orientation of adsorbed polymer segments.

In this paper we will present a number of important improvements of the model presented by Sagis [14], which significantly extends the type of practical multiphase systems we can describe with this model. For the sake of simplicity, the tensorial surface variable in [14] was restricted to the class of tangential surface tensors [2], i.e., tensors of the form $\mathbf{K} = K_{\alpha\beta}\mathbf{a}^{\alpha}\mathbf{a}^{\beta}$, where $\mathbf{a}^{\alpha}$ ($\alpha = 1,2$), are the tangential

---

*leonard.sagis@wur.nl

dual basis vectors for the interface [2]. The first modification we introduce here is to eliminate this restriction, and allow these tensors to be general surface tensors (with components perpendicular to the interface). When anisotropic particles or polymers are adsorbed at an interface at low concentrations their orientations tend to remain parallel to the interface, and the orientation can be described adequately with a tangential surface tensor field. But at high concentrations the long axis of colloidal particles may also be oriented perpendicular to the interface. Similarly, when polymers adsorb at high concentrations, parts of the chain may form loops and dangling ends, and segments in those parts have an orientation which is no longer purely parallel to the interface. Tangential surface tensors are then no longer sufficient to describe the orientation, and we must assume that the surface tensorial structural variables belong to the class of general surface tensors. With respect to a basis formed by the tangential surface dual basis vectors, and the unit normal vector $\boldsymbol{\xi}$, these tensors take the form

$$\mathbf{K} = K_{\alpha\beta}\mathbf{a}^{\alpha}\mathbf{a}^{\beta} + K_{\alpha\xi}\mathbf{a}^{\alpha}\boldsymbol{\xi} + K_{\xi\alpha}\boldsymbol{\xi}\mathbf{a}^{\alpha} + K_{\xi\xi}\boldsymbol{\xi}\boldsymbol{\xi}. \tag{1}$$

Removing the restriction to tangential surface tensor may seem a rather trivial extension of the model. But we will show that allowing the surface tensorial variables to belong to the class of general surface tensors requires us to introduce several additional contributions to the GENERIC to satisfy conservation of momentum and the entropy degeneracy property. These contributions are all part of a term referred to as the moving interface normal transfer term, or MINT term, introduced by Öttinger *et al.* [12] in their study of inviscid interfaces. For interfaces with a complex microstructure the MINT bracket contains several additional terms, and the meaning of these terms will be discussed.

Another substantial improvement over the model presented in [14] involves a modification of the dissipative bracket, in particular the parts describing the transfer of mass, momentum, energy, and the structural variables, between the bulk phases and interfaces. In [14] the transfer of the scalar and tensorial densities is described by two separate terms. In the version presented here we have introduced a coupling between the transfer of these two variables. When anisotropic particles are adsorbing at an interface, this adsorption is likely to be affected by the orientation of the particles in the immediate neighborhood of the interface. Before a particle can adsorb it may have to rotate into a preferred orientation (for example, completely parallel to the interface in a low density scenario, or completely perpendicular to the interface, when surface loadings are high). So the scalar structural variable (in this case a particle density) is affected by the tensorial variable, and vice versa. The coupling introduced in our new model allows for such an interaction between transfer of the structural variables from bulk to interface.

Apart from these extensions, the new model also fixes two minor inconsistencies in the model presented in [14]. In the latter model the surface tensorial variable was chosen to be a tensorial density. However the contributions to the Poisson bracket describing the reversible processes associated with this variable are more appropriate for a tensor, rather than a tensor density. For tensor densities these contributions may not satisfy the Jacobi identity [11], which means that the time evolution equations for the tensor obtained from this formulation may not satisfy time-structure invariance. To fix this problem the new model introduces the tensorial variables as true tensors, and not tensor densities. We have also modified the terms describing the effect of the microstructure on the hydrostatic pressure. The form chosen in [14] is appropriate for single phase systems [11], but for multiphase systems it may also violate the Jacobi identity. The form introduced in Sec. III of this paper does satisfy this identity, and guarantees time-structure invariance of the resulting time evolution equations.

This paper is structured as follows: in Sec. II we discuss the specific details of our model. We introduce the set of independent system variables, and present the expressions for the Hamiltonian and total entropy of our multiphase system. In Sec. III we present the specific forms of the Poisson bracket and MINT term, and in Sec. IV we discuss the dissipative bracket for the given set of system variables. In Sec. V we discuss the degeneracy requirement for the entropy, and the restrictions this requirement puts on the microstructural contributions to the hydrostatic pressure and surface tension. In Sec. VI we extract the time evolution equations for the set of system variables from the GENERIC.

II. PROBLEM STATEMENT

The system we aim to describe is a multiphase system in which both the bulk phases and the interfaces are a mixture of low molecular weight components (dissolved on a molecular level), and macro- or supramolecular structures, such as rodlike or ellipsoidal colloidal particles, or (liquid crystalline) polymers. We will assume that the set of independent bulk and surface excess variables describing the dynamics of the system is given by

$$\begin{gathered}\{\rho, \mathbf{m}, \bar{U}^{*}, \rho_{(1)}, \ldots, \rho_{(N-1)}, \bar{\Gamma}, \mathbf{C}, \rho^{s}, \mathbf{m}^{s}, \bar{U}^{s*},\\ \rho^{s}_{(1)}, \ldots, \rho^{s}_{(N-1)}, \bar{\Gamma}^{s}, \mathbf{C}^{s}\}.\end{gathered} \tag{2}$$

Here ρ is the density in the bulk phase, $\mathbf{m}$ is the bulk momentum density, equal to $\rho\mathbf{v}$, $\mathbf{v}$ is the bulk velocity field, $\bar{U}^{*}$ is the internal energy per unit volume of the bulk phase, and $\rho_{(J)}$ is the density of species J ($J = 1, \ldots, N-1$) in the bulk. In the remainder of this paper we will assume that $\bar{U}^{*}$ can be split in a nonconfigurational contribution $\bar{U}$, and a configurational contribution $\bar{U}_c$. The variable ρ^{s} represents the surface mass density (kg/m^2), $\mathbf{m}^{s} = \rho^{s}\mathbf{v}^{s}$ is the surface momentum density, $\mathbf{v}^{s}$ is the surface velocity field, $\bar{U}^{s*}$ is the internal energy per unit area of the interface, and $\rho^{s}_{(J)}$ is the surface density of species J in the interface. Similar to the splitting of the bulk internal energy, we will assume that $\bar{U}^{s*} = \bar{U}^{s} + \bar{U}^{s}_{c}$, where $\bar{U}^{s}$ and $\bar{U}^{s}_{c}$ are, respectively, the nonconfigurational and configurational contributions to the surface internal energy per unit area. $\bar{\Gamma}$ is a scalar density describing the microstructure of the bulk phases (for example, a local segment density, or a local particle density), and $\mathbf{C}$ is a symmetric second order tensor (for example a segment or particle orientation tensor). The microstructure of the interfaces is described by a scalar density $\bar{\Gamma}^{s}$ and a symmetric surface tensor $\mathbf{C}^{s}$. Note that all system variables are densities, except for $\mathbf{C}$ and $\mathbf{C}^{s}$. In case the microstructure is more appropriately described by a tensor density, $\bar{\mathbf{C}}$, we can simply choose $\mathbf{C} = \bar{\mathbf{C}}/\rho$. For the sake of

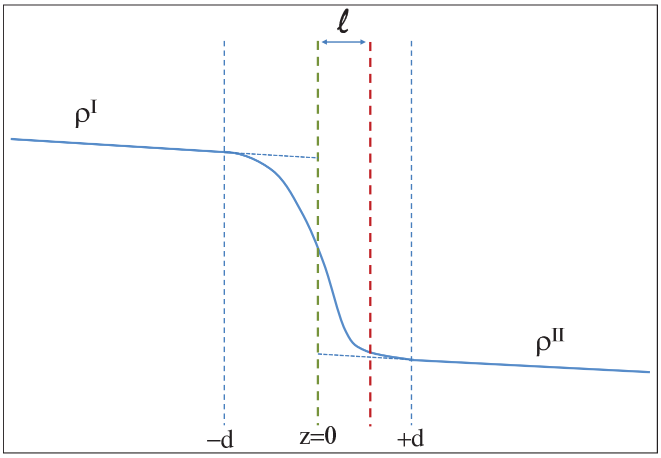

FIG. 1. (Color online) Density profile in the immediate neighborhood of a phase interface. The dividing surface is initially located at $z = 0$ and then displaced over a distance ℓ.

simplicity we have assumed that the microstructure of the bulk phases and the interfaces can both be described by a single scalar and a single tensorial structural variable. The generalization to systems described by multiple scalars or tensors is straightforward.

Note that in (2) we have chosen the number of surface variables to be equal to the number of bulk variables. Applying Gibbs' phase rule the state of the interface appears to be overspecified by one variable for our chosen set of interfacial variables. Moreover there is a certain degree of ambiguity associated with some of the interfacial variables we have chosen, in the sense that they are very sensitive to the choice for the location of the dividing surface (which we have so far not specified). Surface excess variables, like the surface mass density ρ^s, arise naturally in the description of multiphase materials when interfacial regions are modeled as two-dimensional dividing surfaces, placed sensibly within the interfacial region. Bulk properties are extrapolated up to the dividing surface, and the difference between the actual continuously changing fields and the extrapolated ones is accounted for by associating an excess property with the dividing surface. This is illustrated in Fig. 1 for the density profile across the interface of a single component system. The surface excess density ρ^s for such a system can be expressed as

$$\rho^s = \int_{-d}^{0} (\rho - \rho^{\mathrm{I}})dz + \int_{0}^{d} (\rho - \rho^{\mathrm{II}})dz. \tag{3}$$

From its definition we see that this density is very sensitive to the exact location of the dividing surface. If we displace the location of the dividing surface by a small distance ℓ (Fig. 1), we find a new value for the surface density, related to the old value by

$$\rho^{s\prime} = \rho^s + \ell(\rho^{\mathrm{I}} - \rho^{\mathrm{II}}). \tag{4}$$

We can even choose a location of the dividing surface for which ρ^s vanishes completely. A similar ambiguity is also observed for the surface momentum density:

$$\mathbf{m}^{s\prime} = \mathbf{m}^s + \ell(\mathbf{m}^{\mathrm{I}} - \mathbf{m}^{\mathrm{II}}). \tag{5}$$

For static single component systems the location of the dividing surface is typically fixed by setting $\rho^s = 0$, and this choice reduces the set of interfacial variables by 1, and Gibbs' phase rule is then satisfied. In this particular gauge $\mathbf{m}^s = \mathbf{0}$, and from (4) and (5) we find that the surface velocity $\mathbf{v}^s$ can be expressed as

$$\mathbf{v}^s = \frac{\mathbf{m}^{s\prime}}{\rho^{s\prime}} = \frac{\rho^{\mathrm{I}}\mathbf{v}^{\mathrm{I}} - \rho^{\mathrm{II}}\mathbf{v}^{\mathrm{II}}}{\rho^{I} - \rho^{\mathrm{II}}}, \tag{6}$$

which is independent of the particular choice for the location of the interface. In a similar manner we can also construct unambiguous variables from the other surface excess variables defined in (2).

For multicomponent systems the choice of the dividing surface is more subtle. When components are surface active and preferentially accumulate at the interface, their densities may no longer be ambiguous (in the sense that they cannot be made to vanish by an appropriate choice of the location of the dividing surface). For such systems we choose a gauge for the location of the dividing surface typically by choosing $\rho^s = \rho^s_\infty$ (where ρ^s_∞ is chosen such that all surface excess densities are positive), rather than choosing $\rho^s = 0$, since the latter choice introduces negative surface mass densities. Alternatively, we can choose one of the component densities $\rho^s_{(J)}$ to be equal to 0. For static systems either choice again reduces the set of interfacial variables by 1, and Gibbs' phase rule is satisfied.

For evolving interfaces we can choose a gauge only for the reference configuration, either by choosing $\rho^s(t_r) = 0$, $\rho^s(t_r) = \rho^s_\infty$, or $\rho^s_{(J)}(t_r) = 0$ at some reference time t_r. For $t > t_r$ we must allow for ρ^s and the component surface densities to change by in-plane convection and exchange with the bulk phase, so we must retain the full set of surface excess variables.

In our discussion of the Poisson and dissipative brackets in the next sections we will leave the exact location of the interface unspecified, and we will use the set of surface variables defined in (2), in spite of the fact that in some systems part of these variables may be ambiguous. This set produces simpler versions of the brackets. At the end of the development we can always transform the evolution equations obtained for ambiguous variables to equations for their associated unambiguous variables. So rather than using gauge invariance as a constraint on the brackets we enforce it *a posteriori* on the balance equations and boundary conditions that result from these brackets.

In the GENERIC framework the dynamic behavior of a multiphase system is described by a single equation of the form [12]

$$\frac{dA}{dt} = \{A,E\} + [A,S] + \{A,E\}^{\mathrm{mint}}, \tag{7}$$

where A is an observable of the system, $\{A,B\}$ is the Poisson bracket of the system, $[A,B]$ is the dissipative bracket, $\{A,B\}^{\mathrm{mint}}$ is the moving interface normal transfer (MINT) term, E is the Hamiltonian of the system, and S is the total entropy. The Poisson bracket describes the reversible contributions to the dynamics of the system. Its specific form is determined by the set of system variables, and it is restricted by the following conditions:

$$\{A,B\} = -\{B,A\}, \tag{8}$$

$$\{A,\{B,C\}\} + \{C,\{A,B\}\} + \{B,\{C,A\}\} = 0. \tag{9}$$

We see that the Poisson bracket is antisymmetric, and must satisfy the Jacobi identity (9). The dissipative bracket describes the irreversible contributions to the dynamics of the system, and must satisfy the conditions

$$[A,B] = [B,A], \tag{10}$$

$$[A,A] \geqslant 0, \tag{11}$$

which implies that this bracket is a symmetric positive semidefinite bracket. The MINT term in (7) ensures structural compatibility of the GENERIC with the chain rule of functional calculus when moving interfaces are present in the system.

Both the bulk phases and the interfaces of the system are assumed to have a complex microstructure, and this microstructure generates contributions to both the Hamiltonian and the total entropy of the system. We will assume that the Hamiltonian and total entropy can be expressed as

$$\begin{aligned} E = &\int_R \left[\frac{\mathbf{m}^2}{2\rho} + \bar{U} + \bar{U}_c(\rho,\bar{\Gamma}^s,\mathbf{C}^s)\right] dV \\ &+ \int_\Sigma \left[\frac{(\mathbf{m}^s)^2}{2\rho^s} + \bar{U}^s + \bar{U}_c^s(\rho^s,\bar{\Gamma}^s,\mathbf{C}^s)\right] dA, \end{aligned} \tag{12}$$

$$\begin{aligned} S = &\int_R [\bar{S}(\rho,\bar{U},\rho_{(1)},\ldots,\rho_{(N-1)}) + \bar{S}_c(\rho,\bar{\Gamma},\mathbf{C})] dV \\ &+ \int_\Sigma [\bar{S}^s(\rho^s,\bar{U}^s,\rho^s_{(1)},\ldots,\rho^s_{(N-1)}) + \bar{S}_c^s(\rho^s,\bar{\Gamma}^s,\mathbf{C}^s)] dA. \end{aligned} \tag{13}$$

Here $\bar{S}_c$ is the configurational contribution to the entropy per unit volume of the bulk phase, and $\bar{S}_c^s$ denotes the configurational contribution to the surface entropy per unit area. In these expressions R denotes the union of all bulk phase domains, Σ is the domain of the (internal) interfaces, dV denotes an integration over volume, and dA indicates a surface integration. The first term in the bulk integral of (12) describes the contribution of the kinetic energy density to the local energy per unit volume in the bulk phase, and likewise, the first term in the surface integral describes the contribution of the surface kinetic energy density to the local surface energy per unit area. In the remainder of this paper we will assume that the configurational contributions to the entropy satisfy

$$\bar{S}_c(\rho,\bar{\Gamma},\mathbf{C}) = \rho \hat{S}_c(\hat{\Gamma},\mathbf{C}), \tag{14}$$

$$\bar{S}_c^s(\rho^s,\bar{\Gamma}^s,\mathbf{C}^s) = \rho^s \hat{S}_c^s(\hat{\Gamma}^s,\mathbf{C}^s), \tag{15}$$

where $\hat{S}_c$ represents the configurational entropy per unit mass of the bulk phases, and $\hat{S}_c^s$ is the surface configurational entropy per unit mass of the interfaces. The scalar $\hat{\Gamma}$ equals $\bar{\Gamma}/\rho$, and $\hat{\Gamma}^s$ equals $\bar{\Gamma}^s/\rho^s$.

We will assume that the separation in terms of bulk and interfacial contributions introduced in (12) and (13) can also be applied to the observable A in Eq. (7), which implies that this observable can by written as

$$A = \int_R a\, dV + \int_\Sigma a^s dA, \tag{16}$$

where a denotes the density of A in the bulk phase, and a^s is the surface density of A in the interface.

III. POISSON BRACKET AND MINT TERM

In this section we discuss the specific form of the Poisson bracket $\{A,B\}$, and the moving interface normal transfer term, $\{A,B\}^{\text{mint}}$, for the set of system variables introduced in (2). For convenience we split the Poisson bracket in two parts, according to

$$\{A,B\} = \{A,B\}^b + \{A,B\}^s, \tag{17}$$

where $\{A,B\}^b$ contains the contributions to the Poisson bracket from the bulk variables, and $\{A,B\}^s$ contains the contributions from the surface excess variables. The moving interface normal transfer term contains contributions from both bulk and interfacial variables. The contributions from the bulk phase variables to the Poisson bracket are given by [11]

$$\begin{aligned} \{A,B\}^b = &-\int_R \rho\left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\frac{\partial b}{\partial \rho} - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\frac{\partial a}{\partial \rho}\right) dV - \int_R \mathbf{m}\cdot\left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\frac{\partial b}{\partial \mathbf{m}} - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\frac{\partial a}{\partial \mathbf{m}}\right) dV \\ &- \int_R \bar{U}\left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\frac{\partial b}{\partial \bar{U}} - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\frac{\partial a}{\partial \bar{U}}\right) dV - \sum_{J=1}^{N-1}\int_R \rho_{(J)}\left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\frac{\partial b}{\partial \rho_{(J)}} - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\frac{\partial a}{\partial \rho_{(J)}}\right) dV \\ &- \int_R \left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\left[P'\frac{\partial b}{\partial \bar{U}}\right] - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\left[P'\frac{\partial a}{\partial \bar{U}}\right]\right) dV - \int_R \left\{\frac{\partial a}{\partial \mathbf{m}}\cdot\left[\nabla\cdot\left(\mathbf{\Pi}'\frac{\partial b}{\partial \bar{U}}\right)\right] - \frac{\partial b}{\partial \mathbf{m}}\cdot\left[\nabla\cdot\left(\mathbf{\Pi}'\frac{\partial a}{\partial \bar{U}}\right)\right]\right\} dV \\ &+ \int_R \mathbf{C} : \left[\nabla\cdot\left(\frac{\partial a}{\partial \mathbf{C}}\frac{\partial b}{\partial \mathbf{m}} - \frac{\partial b}{\partial \mathbf{C}}\frac{\partial a}{\partial \mathbf{m}}\right)\right] dV + \int_R \left\{\frac{\partial a}{\partial \mathbf{C}} : \left[\mathbf{C}\cdot\left(\nabla\frac{\partial b}{\partial \mathbf{m}}\right)^T\right] - \frac{\partial b}{\partial \mathbf{C}} : \left[\mathbf{C}\cdot\left(\nabla\frac{\partial a}{\partial \mathbf{m}}\right)^T\right]\right\} dV \\ &+ \int_R \left\{\frac{\partial a}{\partial \mathbf{C}} : \left[\left(\nabla\frac{\partial b}{\partial \mathbf{m}}\right)\cdot\mathbf{C}\right] - \frac{\partial b}{\partial \mathbf{C}} : \left[\left(\nabla\frac{\partial a}{\partial \mathbf{m}}\right)\cdot\mathbf{C}\right]\right\} dV - \int_R \bar{\Gamma}\left(\frac{\partial a}{\partial \mathbf{m}}\cdot\nabla\frac{\partial b}{\partial \bar{\Gamma}} - \frac{\partial b}{\partial \mathbf{m}}\cdot\nabla\frac{\partial a}{\partial \bar{\Gamma}}\right) dV \\ &+ \int_R \mathbf{G} : \left(\frac{\partial a}{\partial \bar{\Gamma}}\nabla\frac{\partial b}{\partial \mathbf{m}} - \frac{\partial b}{\partial \bar{\Gamma}}\nabla\frac{\partial a}{\partial \mathbf{m}}\right) dV, \end{aligned} \tag{18}$$

where the scalar P' and the second order tensor $\mathbf{\Pi}'$ are contributions to the hydrostatic pressure tensor. We will establish the specific form of these parameters in Sec. V, when discussing the degeneracy properties of the entropy of the system. The tensor $\mathbf{G}$ is a second order tensor, describing the coupling between the scalar structural variable and the gradient of the velocity field, and $\mathbf{\nabla}$ denotes the three-dimensional gradient operator. The first four integrals in this expression generate the convective terms for the overall mass density, the momentum density, the internal energy density, and the the species mass density $\rho_{(J)}$ in, respectively, the overall differential mass balance, the differential momentum balance, the differential energy balance, and the differential species mass balance for species J. The fifth and sixth integrals introduce contributions of the hydrostatic pressure tensor in the differential momentum balance and differential energy balance. Integrals seven through nine generate the convective terms for the bulk tensorial variable, and the specific form chosen here ensures that the time derivative in the evolution equation for this tensor will be of an upper-convected nature. Finally, the last two integrals introduce the convective terms for the scalar density $\bar{\Gamma}$ in the time-evolution equation for this variable. The most general form of the tensor $\mathbf{G}$ is given by

$$\mathbf{G} = g_1\mathbf{C} + g_2\mathbf{I} + g_3\mathbf{C}^{-1}, \tag{19}$$

where $g_i = g_i(\bar{\Gamma}, I_1, I_2, I_3)$, are coefficients which depend on $\bar{\Gamma}$, and the three invariants of $\mathbf{C}$, I_i $(i = 1,2,3)$. The specific form of these functions is restricted by the Jacobi identity (9).

The contributions of the interfacial variables to the Poisson bracket are given by

$$\begin{aligned}
\{A,B\}^s = &-\int_\Sigma \rho^s\left(\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial b^s}{\partial \rho^s} - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial a^s}{\partial \rho^s}\right)dA - \int_\Sigma \mathbf{m}^s\cdot\left(\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial b^s}{\partial \mathbf{m}^s} - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial a^s}{\partial \mathbf{m}^s}\right)dA\\
&-\int_\Sigma \bar{U}^s\left(\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial b^s}{\partial \bar{U}^s} - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial a^s}{\partial \bar{U}^s}\right)dA - \sum_{J=1}^{N-1}\int_\Sigma \rho^s_{(J)}\left(\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial b^s}{\partial \rho^s_{(J)}} - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial a^s}{\partial \rho^s_{(J)}}\right)dA\\
&+\int_\Sigma\left[\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\left(\gamma'\frac{\partial b^s}{\partial \bar{U}^s}\right) - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\left(\gamma'\frac{\partial a^s}{\partial \bar{U}^s}\right)\right]dA - \int_\Sigma\left\{\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\left[\mathbf{\nabla}_s\cdot\left(\mathbf{\Pi}^{s\prime}\frac{\partial b^s}{\partial \bar{U}^s}\right)\right]\right.\\
&\left.-\frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\left[\mathbf{\nabla}_s\cdot\left(\mathbf{\Pi}^{s\prime}\frac{\partial a^s}{\partial \bar{U}^s}\right)\right]\right\}dA + \int_\Sigma \mathbf{C}^s:\left[\mathbf{\nabla}_s\cdot\left(\frac{\partial a^s}{\partial \mathbf{C}^s}\frac{\partial b^s}{\partial \mathbf{m}^s} - \frac{\partial b^s}{\partial \mathbf{C}^s}\frac{\partial a^s}{\partial \mathbf{m}^s}\right)\right]dA\\
&+\int_\Sigma\left\{\frac{\partial a^s}{\partial \mathbf{C}^s}:\left[\mathbf{C}^s\cdot\left(\mathbf{\nabla}_s\frac{\partial b^s}{\partial \mathbf{m}^s}\right)^T\right] - \frac{\partial b^s}{\partial \mathbf{C}^s}:\left[\mathbf{C}^s\cdot\left(\mathbf{\nabla}_s\frac{\partial a^s}{\partial \mathbf{m}^s}\right)^T\right]\right\}dA + \int_\Sigma\left\{\frac{\partial a^s}{\partial \mathbf{C}^s}:\left[\left(\mathbf{\nabla}_s\frac{\partial b^s}{\partial \mathbf{m}^s}\right)\cdot\mathbf{C}^s\right]\right.\\
&\left.-\frac{\partial b^s}{\partial \mathbf{C}^s}:\left[\left(\mathbf{\nabla}_s\frac{\partial a^s}{\partial \mathbf{m}^s}\right)\cdot\mathbf{C}^s\right]\right\}dA - \int_\Sigma \bar{\Gamma}^s\left(\frac{\partial a^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial b^s}{\partial \bar{\Gamma}^s} - \frac{\partial b^s}{\partial \mathbf{m}^s}\cdot\mathbf{\nabla}_s\frac{\partial a^s}{\partial \bar{\Gamma}^s}\right)dA\\
&+\int_\Sigma \mathbf{G}^s:\left(\frac{\partial a^s}{\partial \bar{\Gamma}^s}\mathbf{\nabla}_s\frac{\partial b^s}{\partial \mathbf{m}^s} - \frac{\partial b^s}{\partial \bar{\Gamma}^s}\mathbf{\nabla}_s\frac{\partial a^s}{\partial \mathbf{m}^s}\right)dA,
\end{aligned} \tag{20}$$

where γ' and $\mathbf{\Pi}^{s\prime}$ represent contributions to the surface pressure tensor. Again, the specific form of these parameters will be established in Sec. V, when discussing the entropy degeneracy requirement. Note that both these parameters are curvature dependent, and this dependence can be made explicit by introducing Helfrich type expansions [15,16] for both parameters. This would introduce additional parameters characterizing the bending rigidity of the interface, a property that is often relevant in multiphase systems, such as liposomes, phase-separated biopolymers, polymersomes, or Pickering stabilized emulsions [17–23].

The tensor $\mathbf{G}^s$ is a second order surface tensor, describing the coupling with the surface scalar density $\bar{\Gamma}^s$, with the surface gradient of the surface velocity $\mathbf{v}^s$, and $\mathbf{\nabla}_s$ denotes the surface gradient operator. For an arbitrary vector field $\mathbf{h} = h_i\mathbf{e}_i$ defined on the surface (here $\mathbf{e}_i$ are the natural basis vectors), the surface gradient is defined as $\mathbf{\nabla}_s\mathbf{h} = (\partial h_i/\partial y^\alpha)\mathbf{e}_i\mathbf{a}^\alpha$ [2]. Here y^α $(\alpha = 1,2)$ are the surface coordinates [2]. The tensor $\mathbf{G}^s$, in its most general form, is given by

$$\mathbf{G}^s = g_1^s\mathbf{C}^s + g_2^s\mathbf{I} + g_3^s(\mathbf{C}^s)^{-1}, \tag{21}$$

where the coefficients g_i^s, are functions of $\bar{\Gamma}^s$, and the three invariants of $\mathbf{C}^s$. Again, the specific form of these functions is restricted by the Jacobi identity (9).

The physical interpretation of the various contributions from the surface excess variables to the Poisson bracket is analogous to that of the terms involving their corresponding bulk variables. So they generate the convective contributions in the time-evolution equations for the surface variables, and introduce the surface pressure terms in the differential surface energy balance.

The final contribution to the reversible dynamics of the system we need to specify is the MINT term. Öttinger *et al.* showed that this bracket needs to be added to achieve consistency between the thermodynamic evolution equation and the chain rule of functional calculus [12]. Here we assume that this term is given by

$$
\begin{aligned}
\{A,B\}^{\mathrm{mint}} = &-\int_{\Sigma} \left\llbracket \left([\tilde{b}-b]\frac{\partial a^s}{\partial \mathbf{m}^s} - [\tilde{a}-a]\frac{\partial b^s}{\partial \mathbf{m}^s} \right) \cdot \boldsymbol{\xi} \right\rrbracket dA - \int_{\Sigma} 2H \left((\tilde{b}^s - b^s)\frac{\partial a^s}{\partial \mathbf{m}^s} - (\tilde{a}^s - a^s)\frac{\partial b^s}{\partial \mathbf{m}^s} \right) \cdot \boldsymbol{\xi}\, dA \\
&- \int_{\Sigma} \left\llbracket \left(\mathbf{C} : \frac{\partial b}{\partial \mathbf{C}} \right) \frac{\partial a}{\partial \mathbf{m}} \cdot \boldsymbol{\xi} - \left(\mathbf{C} : \frac{\partial a}{\partial \mathbf{C}} \right) \frac{\partial b}{\partial \mathbf{m}} \cdot \boldsymbol{\xi} \right\rrbracket dA \\
&- \int_{\Sigma} 2H \left[\left(\mathbf{C}^s : \frac{\partial b^s}{\partial \mathbf{C}^s} \right) \frac{\partial a^s}{\partial \mathbf{m}^s} \cdot \boldsymbol{\xi} - \left(\mathbf{C}^s : \frac{\partial a^s}{\partial \mathbf{C}^s} \right) \frac{\partial b^s}{\partial \mathbf{m}^s} \cdot \boldsymbol{\xi} \right] dA \\
&- \int_{\Sigma} 4H \left(\frac{\partial a^s}{\partial \mathbf{m}^s} \cdot \left[\mathbf{C}^s \cdot \frac{\partial b^s}{\partial \mathbf{C}^s} \right] - \frac{\partial b^s}{\partial \mathbf{m}^s} \cdot \left[\mathbf{C}^s \cdot \frac{\partial a^s}{\partial \mathbf{C}^s} \right] \right) \cdot \boldsymbol{\xi}\, dA \\
&- \int_{\Sigma} 2H \left(\frac{\partial a^s}{\partial \mathbf{m}^s} \cdot \left[\mathbf{G}^s \frac{\partial b^s}{\partial \bar{\Gamma}^s} \right] - \frac{\partial b^s}{\partial \mathbf{m}^s} \cdot \left[\mathbf{G}^s \frac{\partial a^s}{\partial \bar{\Gamma}^s} \right] \right) \cdot \boldsymbol{\xi}\, dA,
\end{aligned}
\tag{22}
$$

where the modified system variable $\tilde{a}$ is defined by

$$
\tilde{a} = \left(\rho \frac{\partial}{\partial \rho} + \mathbf{m} \cdot \frac{\partial}{\partial \mathbf{m}} + (\bar{U} + P') \frac{\partial}{\partial \bar{U}} + \bar{\Gamma} \frac{\partial}{\partial \bar{\Gamma}} + \sum_{J=1}^{N-1} \rho_{(J)} \frac{\partial}{\partial \rho_{(J)}} \right) a \tag{23}
$$

and $\tilde{a}^s$ equals

$$
\tilde{a}^s = \left(\rho^s \frac{\partial}{\partial \rho^s} + \mathbf{m}^s \cdot \frac{\partial}{\partial \mathbf{m}^s} + (\bar{U}^s - \gamma') \frac{\partial}{\partial \bar{U}^s} + \bar{\Gamma}^s \frac{\partial}{\partial \bar{\Gamma}^s} + \sum_{J=1}^{N-1} \rho^s_{(J)} \frac{\partial}{\partial \rho^s_{(J)}} \right) a^s. \tag{24}
$$

An overview of modified bulk and surface variables is presented in Table I. The parameter H in (22) represents the mean curvature of the interface, and the boldface brackets in the first and third integral in the above expression represent jump terms, defined by

$$
\llbracket \psi \boldsymbol{\xi} \rrbracket \equiv \psi^{\mathrm{I}} \boldsymbol{\xi}^{\mathrm{I}} + \psi^{\mathrm{II}} \boldsymbol{\xi}^{\mathrm{II}}, \tag{25}
$$

where ψ^{M} is the value of an arbitrary observable ψ in bulk phase M ($M = \mathrm{I,II}$), and $\boldsymbol{\xi}^M$ is the unit vector normal to the interface, pointing in the direction of bulk phase M.

The first two integrals in (22) are identical to the contributions introduced by Öttinger *et al.* [12], and as mentioned before, need to be included to obtain consistency between the GENERIC structure and the chain rule of functional calculus. The third and fourth integral are added to ensure that the entropy degeneracy requirement is satisfied (we will have more to say on this in Sec. V). The last two integrals need to be added to ensure that the surface tensorial structural variable is a general surface tensor. Without this contribution we can satisfy the entropy degeneracy requirement only if we assume this tensor is a *tangential* surface tensor, and as already noted in the Introduction, in our model we do not want to limit the structural tensors to this particular class of surface tensors.

Note that the MINT bracket in Eq. (22) is not a proper Poisson bracket, since in a Poisson bracket the observables appear only through derivatives. Therefore we do not expect that this bracket satisfies the Jacobi identity. But in the presence of moving interfaces the structure of the chain rule of functional calculus is incompatible with the Poisson bracket structure, so the introduction of a MINT bracket is unavoidable [12]. Bering [24] discussed modifications of the Poisson structure for systems with a fixed boundary, without excess parameters associated with the boundary. The boundary term he suggests (that actually does satisfy the Jacobi identity) has a distinctly different form than our MINT bracket.

TABLE I. Overview of modified bulk and surface variables, calculated using Eqs. (23) and (24).

a	$\tilde{a}$
ρ	ρ
$\mathbf{m}$	$\mathbf{m}$
$\bar{U}$	$\bar{U} + P'$
$\rho_{(J)}$	$\rho_{(J)}$
$\bar{\Gamma}$	$\bar{\Gamma}$
$\mathbf{C}$	0
$\bar{S}$	$\rho \frac{\partial \bar{S}}{\partial \rho} + \rho \hat{S}_c + (\bar{U} + P') \frac{\partial \bar{S}}{\partial \bar{U}} + \bar{\Gamma} \frac{\partial \bar{S}}{\partial \bar{\Gamma}} + \sum_J \rho_{(J)} \frac{\partial \bar{S}}{\partial \rho_{(J)}}$
$\bar{E}$	$\bar{E} + P' - \bar{U}_c + \rho \frac{\partial \bar{U}_c}{\partial \rho} + \bar{\Gamma} \frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}$
a^s	$\tilde{a}^s$
ρ^s	ρ^s
$\mathbf{m}^s$	$\mathbf{m}^s$
$\bar{U}^s$	$\bar{U}^s - \gamma'$
$\rho^s_{(J)}$	$\rho^s_{(J)}$
$\bar{\Gamma}^s$	$\bar{\Gamma}^s$
$\mathbf{C}^s$	0
$\bar{S}^s$	$\rho^s \frac{\partial \bar{S}^s}{\partial \rho^s} + \rho^s \hat{S}^s_c + (\bar{U}^s - \gamma') \frac{\partial \bar{S}^s}{\partial \bar{U}^s} + \bar{\Gamma}^s \frac{\partial \bar{S}^s}{\partial \bar{\Gamma}^s} + \sum_J \rho^s_{(J)} \frac{\partial \bar{S}^s}{\partial \rho^s_{(J)}}$
$\bar{E}^s$	$\bar{E}^s - \gamma' - \bar{U}^s_c + \rho^s \frac{\partial \bar{U}^s_c}{\partial \rho^s} + \bar{\Gamma}^s \frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}$

IV. DISSIPATIVE BRACKET

Now that we have specified the Poisson bracket and MINT term, we will turn our attention to the dissipative bracket. For the sake of simplicity we will split the dissipative bracket in three contributions, according to

$$
[A,B] = [A,B]^b + [A,B]^s + [A,B]^j\,, \tag{26}
$$

where $[A,B]^b$ contains all contributions to the dissipative processes from the bulk variables, $[A,B]^s$ contains the contributions from the surface excess variables, and $[A,B]^j$ describes the transfer of mass, momentum, energy, and the structural variables between the interface and the adjoining bulk phases. The first term in this expression is given by [11]

$$\begin{aligned}
[A,B]^b = {}& \int_R 2\eta T\left[\overline{\nabla\frac{\partial a}{\partial \mathbf{m}}} - \bar{\mathbf{D}}\frac{\partial a}{\partial \bar{U}}\right]:\left[\overline{\nabla\frac{\partial b}{\partial \mathbf{m}}} - \bar{\mathbf{D}}\frac{\partial b}{\partial \bar{U}}\right]dV + \int_R \eta_b T\left(\nabla\cdot\frac{\partial a}{\partial \mathbf{m}} - \mathrm{tr}\mathbf{D}\frac{\partial a}{\partial \bar{U}}\right)\left(\nabla\cdot\frac{\partial b}{\partial \mathbf{m}} - \mathrm{tr}\mathbf{D}\frac{\partial b}{\partial \bar{U}}\right)dV \\
&+ \int_R \lambda T^2\left(\nabla\frac{\partial a}{\partial \bar{U}}\right)\cdot\left(\nabla\frac{\partial b}{\partial \bar{U}}\right)dV + \sum_{J=1}^{N-1}\sum_{K=1}^{N}\int_R \tilde{D}_{(JK)}\left[\nabla\left(\frac{\partial a}{\partial \rho_{(J)}}\right)\right]\cdot\left[\nabla\left(\frac{\partial b}{\partial \rho_{(K)}}\right)\right]dV \\
&+ \sum_{J=1}^{N-1}\int_R \tilde{\alpha}_{(J)}T^2\left[\nabla\left(\frac{\partial a}{\partial \rho_{(J)}}\right)\cdot\nabla\left(\frac{\partial b}{\partial \bar{U}}\right) + \nabla\left(\frac{\partial b}{\partial \rho_{(J)}}\right)\cdot\nabla\left(\frac{\partial a}{\partial \bar{U}}\right)\right]dV \\
&+ \int_R \left(\frac{\partial a}{\partial \bar{\Gamma}} - \frac{\partial a}{\partial \bar{U}}\frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}\right)R_1\left(\frac{\partial b}{\partial \bar{\Gamma}} - \frac{\partial b}{\partial \bar{U}}\frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}\right)dV + \int_R \left(\frac{\partial a}{\partial \mathbf{C}} - \frac{\partial a}{\partial \bar{U}}\frac{\partial \bar{U}_c}{\partial \mathbf{C}}\right):\mathbf{R}_2:\left(\frac{\partial b}{\partial \mathbf{C}} - \frac{\partial b}{\partial \bar{U}}\frac{\partial \bar{U}_c}{\partial \mathbf{C}}\right)dV \\
&+ \int_R \nabla\left[\frac{\partial a}{\partial \mathbf{C}} - \frac{\partial \bar{U}_c}{\partial \mathbf{C}}\frac{\partial a}{\partial \bar{U}}\right]\vdots\,\mathbf{D}_C\vdots\,\nabla\left[\frac{\partial b}{\partial \mathbf{C}} - \frac{\partial \bar{U}_c}{\partial \mathbf{C}}\frac{\partial b}{\partial \bar{U}}\right]dV + \int_R \nabla\left[\frac{\partial a}{\partial \bar{\Gamma}} - \frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}\frac{\partial a}{\partial \bar{U}}\right]\cdot\mathbf{D}_\Gamma\cdot\nabla\left[\frac{\partial b}{\partial \bar{\Gamma}} - \frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}\frac{\partial b}{\partial \bar{U}}\right]dV.
\end{aligned} \tag{27}$$

Here η is the shear viscosity, η_b is the bulk viscosity, $\bar{\mathbf{D}}$ denotes the traceless part of the rate of deformation tensor $\mathbf{D}$ (equal to $\frac{1}{2}[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]$), T is the bulk temperature, λ is the thermal conductivity, $\tilde{D}_{(JK)}$ denote the components of the $N \times N$ diffusion coefficient matrix of the multicomponent mixture, $\tilde{\alpha}_{(J)}$ is the thermal diffusion coefficient of J, R_1 is a scalar parameter describing relaxation processes for $\bar{\Gamma}$, $\mathbf{R}_2$ is a fourth order tensor field describing relaxation processes for $\mathbf{C}$, $\mathbf{D}_\Gamma$ is a second order tensor, quantifying the diffusion of Γ, and $\mathbf{D}_C$ is a sixth order tensor associated with diffusion processes for $\mathbf{C}$. The bar over the term $\nabla(\partial a/\partial \mathbf{m})$ indicates we are considering only the symmetric traceless part of this tensor.

The first two integrals in this expression introduce the viscous stresses of the continuous phase in the differential momentum balance, and introduce viscous dissipation terms in the differential energy balance. Here we have assumed Newtonian behavior for the continuous phase. The inclusions of these terms will generate an expression for the total extra stress tensor with two contributions: a viscous contribution from the continuous phase, and a contribution from the microstructural elements, dispersed in the continuous phase. When the former are expected to be negligible with respect to microstructural contributions to the stresses, these two integrals can simply be omitted. The third integral in the above expression describes heat conduction, and the fourth introduces a flux term in the differential species mass balance describing diffusion driven by concentration gradients (ordinary diffusion). The fifth integral generates a thermal diffusion flux in the mass balance (the Soret effect, mass diffusion driven by temperature gradients), and an additional thermal flux in the energy balance (the Dufour effect, heat conduction driven by gradients in concentration). Integrals six and seven describe relaxation processes for, respectively, the scalar and tensorial structural variables. Integrals eight and nine introduce diffusive terms in the time evolution equations of the structural variables, relevant only when the applied deformations induce spatial inhomogeneities in the structural fields.

The contributions of the surface variables to the dissipative bracket are assumed to be given by

$$\begin{aligned}
[A,B]^s = {}& \int_\Sigma 2\varepsilon_s T^s\left(\overline{\nabla_s\frac{\partial a^s}{\partial \mathbf{m}^s}} - \bar{\mathbf{D}}^s\frac{\partial a^s}{\partial \bar{U}^s}\right):\left(\overline{\nabla_s\frac{\partial b^s}{\partial \mathbf{m}^s}} - \bar{\mathbf{D}}^s\frac{\partial b^s}{\partial \bar{U}^s}\right)dA \\
&+ \int_\Sigma \varepsilon_d T^s\left(\nabla_s\cdot\frac{\partial a^s}{\partial \mathbf{m}^s} - \mathrm{tr}\mathbf{D}^s\frac{\partial a^s}{\partial \bar{U}^s}\right)\left(\nabla_s\cdot\frac{\partial b^s}{\partial \mathbf{m}^s} - \mathrm{tr}\mathbf{D}^s\frac{\partial b^s}{\partial \bar{U}^s}\right)dA \\
&+ \int_\Sigma \lambda^s(T^s)^2\left(\nabla_s\frac{\partial a^s}{\partial \bar{U}^s}\right)\cdot\left(\nabla_s\frac{\partial b^s}{\partial \bar{U}^s}\right)dA + \sum_{J=1}^{N-1}\sum_{K=1}^{N}\int_\Sigma \tilde{D}^s_{(JK)}\left[\nabla_s\left(\frac{\partial a^s}{\partial \rho^s_{(J)}}\right)\right]\cdot\left[\nabla_s\left(\frac{\partial b^s}{\partial \rho^s_{(K)}}\right)\right]dA \\
&+ \sum_{J=1}^{N-1}\int_\Sigma \tilde{\alpha}^s_{(J)}(T^s)^2\left[\nabla_s\left(\frac{\partial a^s}{\partial \rho^s_{(J)}}\right)\cdot\nabla_s\left(\frac{\partial b^s}{\partial \bar{U}^s}\right) + \nabla_s\left(\frac{\partial b^s}{\partial \rho^s_{(J)}}\right)\cdot\nabla_s\left(\frac{\partial a^s}{\partial \bar{U}^s}\right)\right]dA \\
&+ \int_\Sigma \left(\frac{\partial a^s}{\partial \bar{\Gamma}^s} - \frac{\partial a^s}{\partial \bar{U}^s}\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}\right)R^s_1\left(\frac{\partial b^s}{\partial \bar{\Gamma}^s} - \frac{\partial b^s}{\partial \bar{U}^s}\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}\right)dA
\end{aligned}$$

$$
\begin{aligned}
&+\int_{\Sigma}\left(\frac{\partial a^s}{\partial \mathbf{C}^s}-\frac{\partial a^s}{\partial \bar{U}^s}\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\right):\mathbf{R}^s_2:\left(\frac{\partial b^s}{\partial \mathbf{C}^s}-\frac{\partial b^s}{\partial \bar{U}^s}\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\right)dA\\
&+\int_{\Sigma}\boldsymbol{\nabla}_s\left(\frac{\partial a^s}{\partial \mathbf{C}^s}-\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\frac{\partial a^s}{\partial \bar{U}^s}\right)\vdots\,\mathbf{D}^s_C\vdots\,\boldsymbol{\nabla}_s\left(\frac{\partial b^s}{\partial \mathbf{C}^s}-\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\frac{\partial b^s}{\partial \bar{U}^s}\right)dA\\
&+\int_{\Sigma}\boldsymbol{\nabla}_s\left(\frac{\partial a^s}{\partial \bar{\Gamma}^s}-\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}\frac{\partial a^s}{\partial \bar{U}^s}\right)\cdot\mathbf{D}^s_{\Gamma}\cdot\boldsymbol{\nabla}_s\left(\frac{\partial b^s}{\partial \bar{\Gamma}^s}-\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}\frac{\partial b^s}{\partial \bar{U}^s}\right)dA.
\end{aligned}
\tag{28}
$$

Here ε_s is the surface shear viscosity [1–3], ε_d is the surface dilatational viscosity [1–3], $\tilde{\mathbf{D}}^s$ is the traceless part of the surface rate of deformation tensor $\mathbf{D}^s$, equal to $\frac{1}{2}[\mathbf{P}\cdot(\boldsymbol{\nabla}_s\mathbf{v}^s)+\{(\boldsymbol{\nabla}_s\mathbf{v}^s)^T\}\cdot\mathbf{P}]$ [2], $\mathbf{P}$ is the surface projection tensor [2,3], T^s is the surface temperature, λ^s is the surface thermal conductivity [2,3], $\tilde{D}^s_{(JK)}$ denotes the components of the surface diffusion coefficient matrix [2,3], $\tilde{\alpha}^s_{(J)}$ is the surface thermal diffusion coefficient of J [2,3], R^s_1 is a scalar describing relaxation processes for $\bar{\Gamma}^s$ in the interface, $\mathbf{R}^s_2$ is a fourth order tangential surface tensor field describing relaxation processes for $\mathbf{C}^s$, $\mathbf{D}^s_{\Gamma}$ is a second order tangential tensor tensor, quantifying the diffusion of $\bar{\Gamma}^s$ in the interface, and $\mathbf{D}^s_C$ is a sixth order tangential surface tensor associated with diffusion processes for $\mathbf{C}^s$.

In formulating these contributions we have assumed that, analogous to the bulk stresses, the surfaces stresses can be split in an isotropic contribution from the interfacial continuous phase and an anisotropic contribution from the microstructural elements. The former is assumed to be described by the linear Boussinesq model [25–27]. We have also accounted for the surface equivalents of the Dufour and Soret effects, in the description of the heat and mass fluxes. For both the surface structural variables we have included terms describing relaxation and diffusion of these variables.

The exact nature of the four material parameters associated with the structural variables depends on the microstructure of the interface. If we consider for example an interface stabilized by anisotropic colloidal particles (an example which we will discuss in more detail in Paper II of this sequence of papers [28]), then $\bar{\Gamma}^s$ would be the surface concentration of particles, and $\mathbf{C}^s$ would represent a local average of the orientation of the particles (for example, equal to $\langle\mathbf{n}^s\mathbf{n}^s\rangle$, where $\mathbf{n}^s$ is a unit vector denoting the orientation of the length axis of the particles). If such an interface is deformed by, for example, an arbitrary shear field, particles will orient in the direction of the flow. The flow field may also cause inhomogeneities in the distribution of the particles. When the flow is stopped the microstructure of the interface will relax back to its equilibrium state, a homogeneous isotropic interface with randomly oriented particles. In this process R^s_1 would typically be set to 0, and $\mathbf{D}^s_{\Gamma}$ characterizes the translational diffusion of the colloidal particles. The tensor $\mathbf{R}^s_2$ describes relaxation of the particle orientation by rotational diffusion, and $\mathbf{D}^s_C$ describes the smoothing of spatial gradients in orientation by diffusive processes.

As another example, let us consider an interface stabilized by a mixture of two immiscible surfactants $S1$ and $S2$, and let us assume $S1$ forms deformable circular disklike rafts in a continuous $S2$ phase. So the structure of the interface is basically a two-dimensional emulsion. This problem is relevant for example for raft formation in cell membranes. When such an interface is deformed the circular rafts are deformed to an anisotropic shape and oriented in the direction of flow. When the flow is stopped, the rafts relax back to a circular shape. This problem can be described with a two-dimensional variation of the Doi-Ohta model [29], in which we let $\bar{\Gamma}^s$ be the total amount of contact line per unit area between $S1$ and $S2$, and $\mathbf{C}^s$ is a second order tensor field describing the shape of the rafts. In this model R^s_1 and $\mathbf{R}^s_2$ would then quantify the relaxation process for respectively the total amount of contact line and the shape of the rafts. The two diffusion tensors would describe the smoothing of any spatial gradients of these two variables along the surface.

Note that in this particular example the contact line between the domains of $S1$ and $S2$ may also have excess variables associated with it (for example, a line tension). When additional line excesses are present in the system, and we are interested in the time evolution of these, additional terms involving these line variables will have to be included in the Poisson and dissipative brackets. The framework as we have presented it here can describe only systems with surface excess variables associated with the interfaces.

The measurement of the structural material parameters discussed in the preceding paragraphs is a nontrivial issue, which requires a combination of surface rheological methods and optical methods (two-dimensional rheo-optics [5]). The time evolution of the interfacial microstructure formed by adsorbed colloidal particles can often be studied with microscopic techniques. For smaller species various forms of reflectometry (ligth, neutron, or x ray) may have to be used to explore structural changes [5,30–32].

Finally, we need to specify the contributions to the dissipative bracket describing the transfer of mass, momentum, energy, and structural parameters, between the bulk phases and interfaces. These contributions are given by

$$
\begin{aligned}
[A,B]^j=&\int_{\Sigma}\left[\frac{TT^s}{R_K}\left(\frac{\partial a}{\partial \bar{U}}-\frac{\partial a^s}{\partial \bar{U}^s}\right)\left(\frac{\partial b}{\partial \bar{U}}-\frac{\partial b^s}{\partial \bar{U}^s}\right)\right]dA\\
&+\sum_{M,N=\mathrm{I}}^{\mathrm{II}}\int_{\Sigma}\left(\frac{\partial a^M}{\partial \mathbf{m}^{\mathrm{M}}}-\frac{\partial a^s}{\partial \mathbf{m}^s}-\mathbf{v}^M\frac{\partial a^M}{\partial \bar{U}^M}+\mathbf{v}^s\frac{\partial a^s}{\partial \bar{U}^s}\right)\cdot T^s\boldsymbol{\zeta}^{M,N}\cdot\left(\frac{\partial b^N}{\partial \mathbf{m}^N}-\frac{\partial b^s}{\partial \mathbf{m}^s}-\mathbf{v}^{\mathrm{N}}\frac{\partial b^N}{\partial \bar{U}^N}+\mathbf{v}^s\frac{\partial b^s}{\partial \bar{U}^s}\right)dA
\end{aligned}
$$

$$\begin{aligned}
&+\sum_{J=1}^{N-1}\int_\Sigma \Biggl[\Lambda_{(J)}\biggl(\frac{\partial a}{\partial \rho}-\frac{\partial a^s}{\partial \rho^s}+\frac{\partial a}{\partial \rho_{(J)}}-\frac{\partial a^s}{\partial \rho^s_{(J)}}+\frac{1}{2}\mathbf{v}^2\frac{\partial a}{\partial \bar{U}}-\frac{1}{2}(\mathbf{v}^s)^2\frac{\partial a^s}{\partial \bar{U}^s}\biggr)\biggl(\frac{\partial b}{\partial \rho}-\frac{\partial b^s}{\partial \rho^s}\\
&+\frac{\partial b}{\partial \rho_{(J)}}-\frac{\partial b^s}{\partial \rho^s_{(J)}}+\frac{1}{2}\mathbf{v}^2\frac{\partial b}{\partial \bar{U}}-\frac{1}{2}(\mathbf{v}^s)^2\frac{\partial b^s}{\partial \bar{U}^s}\biggr)\Biggr]dA\\
&+\sum_{J=1}^{N-1}\int_\Sigma \Biggl[\Lambda^T_{(J)}TT^s\biggl\{\biggl(\frac{\partial a}{\partial \bar{U}}-\frac{\partial a^s}{\partial \bar{U}^s}\biggr)\biggl(\frac{\partial b}{\partial \rho}-\frac{\partial b^s}{\partial \rho^s}+\frac{\partial b}{\partial \rho_{(J)}}-\frac{\partial b^s}{\partial \rho^s_{(J)}}+\frac{1}{2}\mathbf{v}^2\frac{\partial b}{\partial \bar{U}}-\frac{1}{2}(\mathbf{v}^s)^2\frac{\partial b^s}{\partial \bar{U}^s}\biggr)\\
&+\biggl(\frac{\partial a}{\partial \rho}-\frac{\partial a^s}{\partial \rho^s}+\frac{\partial a}{\partial \rho_{(J)}}-\frac{\partial a^s}{\partial \rho^s_{(J)}}+\frac{1}{2}\mathbf{v}^2\frac{\partial a}{\partial \bar{U}}-\frac{1}{2}(\mathbf{v}^s)^2\frac{\partial a^s}{\partial \bar{U}^s}\biggr)\biggl(\frac{\partial b}{\partial \bar{U}}-\frac{\partial b^s}{\partial \bar{U}^s}\biggr)\biggr\}\Biggr]dA\\
&+\int_\Sigma\Biggl[\biggl(\mathbf{\Phi}\frac{\partial a}{\partial \bar{\Gamma}}-\mathbf{\Phi}^s\frac{\partial a^s}{\partial \bar{\Gamma}^s}+\frac{\partial a}{\partial \mathbf{C}}-\frac{\partial a^s}{\partial \mathbf{C}^s}-\frac{\partial a}{\partial \bar{U}}\biggl[\mathbf{\Phi}\frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}+\frac{\partial \bar{U}_c}{\partial \mathbf{C}}\biggr]+\frac{\partial a^s}{\partial \bar{U}^s}\biggl[\mathbf{\Phi}^s\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}+\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\biggr]\biggr)\\
&:\mathbf{J}_{\Gamma C}:\biggl(\mathbf{\Phi}\frac{\partial b}{\partial \bar{\Gamma}}-\mathbf{\Phi}^s\frac{\partial b^s}{\partial \bar{\Gamma}^s}+\frac{\partial b}{\partial \mathbf{C}}-\frac{\partial b^s}{\partial \mathbf{C}^s}-\frac{\partial b}{\partial \bar{U}}\biggl[\mathbf{\Phi}\frac{\partial \bar{U}_c}{\partial \bar{\Gamma}}+\frac{\partial \bar{U}_c}{\partial \mathbf{C}}\biggr]+\frac{\partial b^s}{\partial \bar{U}^s}\biggl[\mathbf{\Phi}^s\frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s}+\frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s}\biggr]\biggr)\Biggr]dA.
\end{aligned}\tag{29}$$

Here R_K is the Kapitza coefficient for transfer of energy between bulk phase and interface, and $\boldsymbol{\zeta}^{M,N}$ are the friction tensors for transfer of momentum between bulk phase and interface. In most cases the accumulation of momentum at the interface will be negligible, and the second integral in the above expression can be omitted. But for the sake of completeness, and for better comparison with results derived using other frameworks [2,3], we choose to retain this term here. The parameters $\Lambda_{(J)}$ and $\Lambda^T_{(J)}$ are the transfer coefficients for transfer of species J between bulk phase and interface driven by difference in, respectively, chemical potential and temperature. $\mathbf{J}_{\Gamma C}$ is a fourth order tensor field quantifying the transfer of Γ and $\mathbf{C}$ between bulk phase and interface. In the fifth integral we have introduced a coupling between the transfer of the tensor $\mathbf{C}$ and the scalar density $\bar{\Gamma}$, through the tensors $\mathbf{\Phi}$ and $\mathbf{\Phi}^s$. As discussed in the Introduction, such a coupling would be expected to be important in systems with anisotropic particles or other types of microstructural elements, which first need to adopt a specific orientation with respect to the interface before being adsorbed. Based on dimensional arguments we would expect $\mathbf{\Phi}\sim\bar{\Gamma}\mathbf{C}^{-1}$, and $\mathbf{\Phi}^s\sim\bar{\Gamma}^s(\mathbf{C}^s)^{-1}$.

Now that we have specified all the contributions to the Poisson and dissipative brackets, we can proceed with the extraction of the time-evolution equations for the set of independent system variables. Before we do this we will first take a closer look at the degeneracy properties of the total entropy and momentum.

V. DEGENERACY PROPERTIES

In the preceding we have left the exact definitions of the isotropic pressure P', the isotropic surface tension γ', the anisotropic microstructural contributions to the bulk pressure $\mathbf{\Pi}'$, and the anisotropic microstructural surface pressure $\mathbf{\Pi}^{s\prime}$ unspecified. We can use the entropy degeneracy requirement to fix the specific form of these parameters. The degeneracy requirement for the total entropy is given by

$$\{S,B\}+\{S,B\}^{\text{mint}}=0.\tag{30}$$

Using the expressions for the Poisson brackets defined in Sec. III, we find that to satisfy this identity, P' must take the form

$$P'=T\bar{S}-\bar{U}-\rho T\frac{\partial\bar{S}}{\partial\rho}-\sum_{J=1}^{N-1}\rho_{(J)}T\frac{\partial\bar{S}}{\partial\rho_{(J)}}-\bar{\Gamma}\rho T\frac{\partial\hat{S}_c}{\partial\bar{\Gamma}}\tag{31}$$

and $\mathbf{\Pi}'$ must take the form

$$\mathbf{\Pi}'\equiv\rho T\biggl(2\mathbf{C}\cdot\frac{\partial\hat{S}_c}{\partial\mathbf{C}}+\mathbf{G}\frac{\partial\hat{S}_c}{\partial\bar{\Gamma}}\biggr).\tag{32}$$

We must also require that at the interfaces

$$\mathbf{r}\in\Sigma:[\![\mathbf{\Pi}'(\mathbf{r})\cdot\boldsymbol{\xi}(\mathbf{r})]\!]=0.\tag{33}$$

This condition implies that to satisfy the entropy degeneracy requirement, we must assume that the normal components of $\mathbf{\Pi}'$ (representing the contributions from the microstructural entropy $\hat{S}_c$ to the hydrostatic pressure) are continuous across the interface. With these expressions for P' and $\mathbf{\Pi}'$ the total hydrostatic pressure tensor is simply given by

$$\mathbf{\Pi}=P'\mathbf{I}+\mathbf{\Pi}'.\tag{34}$$

We also find that the surface tension γ' must take the form

$$\begin{aligned}\gamma'=&-T^s\bar{S}^s+\bar{U}^s+\rho^sT^s\frac{\partial\bar{S}^s}{\partial\rho^s}\\&+\sum_{J=1}^{N-1}\rho^s_{(J)}T^s\frac{\partial\bar{S}^s}{\partial\rho^s_{(J)}}+\bar{\Gamma}^s\rho^sT^s\frac{\partial\hat{S}^s_c}{\partial\bar{\Gamma}}\end{aligned}\tag{35}$$

and that the anisotropic contributions to the surface pressure induced by the microstructure, $\mathbf{\Pi}^{s\prime}$, must equal

$$\mathbf{\Pi}^{s\prime}\equiv\rho^sT^s\biggl(2\mathbf{C}^s\cdot\frac{\partial\hat{S}^s_c}{\partial\mathbf{C}^s}+\mathbf{G}^s\frac{\partial\hat{S}^s_c}{\partial\bar{\Gamma}^s}\biggr).\tag{36}$$

The total surface pressure tensor is thus given by

$$\mathbf{\Pi}^s=-\gamma\mathbf{P}+\mathbf{\Pi}^{s\prime}.\tag{37}$$

The total momentum of the system can be expressed as

$$\mathcal{M}=\int_R\mathbf{m}\,dV+\int_\Sigma\mathbf{m}^s dA.\tag{38}$$

The degeneracy requirement for the total momentum is given by

$$\{\mathcal{M},B\} + \{\mathcal{M},B\}^{\mathrm{mint}} = 0, \tag{39}$$

which is satisfied identically, when we assume (31)–(33), (35), and (36).

The degeneracy conditions also give us some additional insight in some of the contributions to the MINT term. If we would eliminate the third integral in (22), then, to satisfy the entropy degeneracy requirement, condition (33) would need to take the form

$$\mathbf{r} \in \Sigma: \quad \left\llbracket \left(\mathbf{C} : \frac{\partial \rho \hat{S}_c}{\partial \mathbf{C}}\right)\boldsymbol{\xi} + \boldsymbol{\Pi}'(\mathbf{r}) \cdot \boldsymbol{\xi}(\mathbf{r}) \right\rrbracket = 0. \tag{40}$$

Whereas (33) has a clear physical interpretation, the additional contribution in (40) does not, and puts an unnecessary restriction on the form of the microstructural contributions to the pressure tensor. By adding the third integral in the MINT bracket, this restriction is removed. The fourth integral in the MINT bracket was added for the same reason: it eliminates a similar term $2H(\mathbf{C} : \frac{\partial \rho \hat{S}_c}{\partial \mathbf{C}})\boldsymbol{\xi}$ from the integral over Σ. The last two contributions are needed to ensure that the tensorial structural variable of the interface belongs to the class of general surface tensors. When these two integrals are omitted, then, to satisfy the entropy degeneracy requirement, apart from (33), we would in addition have to require

$$2H\boldsymbol{\Pi}^{s\prime} \cdot \boldsymbol{\xi} = 0, \tag{41}$$

which means we would have to require that $\mathbf{C}^s$ is a *tangential* surface tensor. As stated in the Introduction, to extend the range of multiphase systems our model can be applied to, we do not wish to impose such a restriction. The last two integrals in the MINT bracket remove the term in (41) from the integral over Σ, ensuring that $\mathbf{C}^s$ remains in the class of general surface tensors.

VI. BALANCE AND CONSTITUTIVE EQUATIONS

In this section we will extract the balance equations for the time evolution of the set of system variables defined in (2), from the GENERIC (7). To extract these balance equations we must first consider the time derivative of the left hand side of (7). The time rate of change of an arbitrary observable A of the system, satisfying (16), equals [2,12]

$$\begin{aligned}\frac{dA}{dt} = {}& \int_R \frac{\partial a}{\partial x_j}\frac{\partial x_j}{\partial t}\,dV + \int_\Sigma \frac{\partial a^s}{\partial x_j^s}\frac{\partial x_j^s}{\partial t}\,dA \\ & - \int_\Sigma \left(2Ha^s\mathbf{v}^s \cdot \boldsymbol{\xi} + \frac{\partial a^s}{\partial x_j^s}\nabla_s x_j^s \cdot \mathbf{u} + \llbracket a\mathbf{v}^s \cdot \boldsymbol{\xi} \rrbracket\right) dA,\end{aligned} \tag{42}$$

where $\mathbf{u}$ is the speed of displacement of the interface [2], and x_j and x_j^s are the independent bulk and surface excess system variables. Combining this expression with (7), using the expressions for the Poisson and dissipative bracket defined above, and collecting all terms on the left hand side of (7), we obtain (after integration by parts) an expression with two main contributions. The first term is an integral over the bulk domain R, containing terms proportional to the partial derivatives $\partial a/\partial x_j$. The second term is an integral over the interfacial domain Σ, and contains terms proportional to the partial derivatives $\partial a^s/\partial x_j^s$, terms proportional to a^s, and jump terms, proportional to either a or $\partial a/\partial x_j$. Since the observable A and the domains R and Σ were chosen arbitrarily, we must set the integrands of both integrals to zero, in order to satisfy (7) identically. Setting the integrand of the first integral to zero will give us the balance equations for the bulk variables ρ, $\mathbf{m}$, $\bar{U}$, $\rho_{(J)}$, $\bar{\Gamma}$, and $\mathbf{C}$. Setting the integrand of the second integral to zero gives us the balance equations for the corresponding surface excess variables, and a set of consistency requirements for the transport of mass, momentum, energy, and the structural variables to and from the interface [12,13].

Let us first examine the governing equations for the overall bulk density ρ, and the overall surface mass density ρ^s. From the integral over R we obtain (collecting all terms proportional to $\partial a/\partial \rho$, and setting the resulting coefficient to zero)

$$\frac{d_b \rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0, \tag{43}$$

which is the familiar equation of continuity for the bulk phases. The material derivative in this expression is defined as

$$\frac{d_b \psi}{dt} = \frac{\partial \psi}{\partial t} + (\nabla \psi) \cdot \mathbf{v}. \tag{44}$$

Collecting the terms proportional to ρ and $\partial a/\partial \rho$ in the integral over Σ, and setting the result equal to 0, we obtain the consistency requirements ($M = \mathrm{I,II}$)

$$\begin{aligned}&\sum_{J=1}^{N-1} \Lambda_{(J)}^{M}\left(\frac{\check{\mu}_{(J)}^{M}}{T^M} - \frac{\check{\mu}_{(J)}^{s}}{T^s}\right) + \sum_{J=1}^{N-1} \Lambda_{(J)}^{TM}(T^M - T^s) \\ &\quad = -\rho^M(\mathbf{v}^M - \mathbf{v}^s) \cdot \boldsymbol{\xi}^M,\end{aligned} \tag{45}$$

where the modified chemical potentials $\check{\mu}_{(J)}$ and $\check{\mu}_{(J)}^s$ are defined by

$$\frac{\check{\mu}_{(J)}}{T} = -\left(\hat{S}_c + \frac{\partial \bar{S}}{\partial \rho} + \frac{\partial \bar{S}}{\partial \rho_{(J)}} + \frac{\mathbf{v}^2}{2T}\right), \tag{46}$$

$$\frac{\check{\mu}_{(J)}^s}{T^s} = -\left(\hat{S}_c^s + \frac{\partial \bar{S}^s}{\partial \rho^s} + \frac{\partial \bar{S}^s}{\partial \rho_{(J)}^s} + \frac{(\mathbf{v}^s)^2}{2T^s}\right). \tag{47}$$

Finally, collecting all terms proportional to ρ^s and $\partial a^s/\partial \rho^s$ from the surface integral, setting the result to 0, and using (45), we find

$$\frac{d_s \rho^s}{dt} + \rho^s \nabla_s \cdot \mathbf{v}^s + \llbracket \rho(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} \rrbracket = 0. \tag{48}$$

This balance is the overall jump mass balance [2,3]. The surface material derivative in this expression is defined as

$$\frac{d_s \psi}{dt} = \frac{\partial \psi}{\partial t} + (\nabla_s \psi) \cdot \dot{\mathbf{y}}, \tag{49}$$

where $\dot{\mathbf{y}}$ is the intrinsic surface velocity [2]. The consistency requirements (45) are boundary conditions coupling the density field of the adjoining bulk phases to the interfacial density field. This is one of the strengths of the GENERIC framework: it not only provides time evolution equations for the bulk and interfacial system variables, but also generates a complete set of boundary conditions that couple these fields. In other nonequilibrium thermodynamic frameworks these boundary conditions are generated separately on an *ad hoc* basis [2,33].

We now turn our attention to the balance equations for $\mathbf{m}$ and $\mathbf{m}^s$ (the differential momentum balance and differential jump momentum balance [2,3]). From the terms in the integral over R, proportional to $\partial a/\partial\mathbf{m}$, we obtain

$$\rho\frac{d_b\mathbf{v}}{dt}+\nabla(P'+P_E)-\nabla\cdot\boldsymbol{\sigma}_{\text{tot}}=0, \tag{50}$$

where P_E is the contribution from the configurational internal energy to the pressure, defined by

$$P_E=-\bar{U}_c+\rho\frac{\partial\bar{U}_c}{\partial\rho}+\bar{\Gamma}\frac{\partial\bar{U}_c}{\partial\bar{\Gamma}} \tag{51}$$

and $\boldsymbol{\sigma}_{\text{tot}}$ is the total extra stress tensor in the bulk phase, equal to

$$\boldsymbol{\sigma}_{\text{tot}}=\left(\eta_b-\frac{2}{3}\eta\right)[\nabla\cdot\mathbf{v}]\mathbf{I}+2\eta\mathbf{D}+2\mathbf{C}\cdot\frac{\partial\bar{F}_c}{\partial\mathbf{C}}+\mathbf{G}\frac{\partial\bar{F}_c}{\partial\bar{\Gamma}}. \tag{52}$$

In the last expression $\bar{F}_c=\bar{U}_c-T\rho\hat{S}_c$ is the Helmholtz free energy per unit volume of the bulk phase. The terms proportional to $\mathbf{m}$ and $\partial a/\partial\mathbf{m}$ in the surface integral give us the consistency requirement for the transfer of momentum between the interface and the adjacent bulk phases ($M=\text{I,II}$):

$$\begin{aligned}&\sum_{N=\text{I}}^{\text{II}}\boldsymbol{\zeta}^{M,N}T^s\cdot\left(\frac{\mathbf{v}^N}{T^N}-\frac{\mathbf{v}^s}{T^s}\right)\\&\quad=-\rho^M\mathbf{v}^M(\mathbf{v}^M-\mathbf{v}^s)\cdot\boldsymbol{\xi}^M+\sigma_{\text{tot}}^M\cdot\boldsymbol{\xi}^M.\end{aligned} \tag{53}$$

In arriving at this result we used Eq. (33). Note that in this expression we have friction tensors for each side of the interface. This would be required for complex systems in which, for example, the interface is a $2d$ polymer gel, and the adjoining bulk phases are microstructured phases as well [perhaps a liquid crystalline phase or a ($3d$) gel phase]. In such systems we expect a significant effect of the stress-deformation behavior of the interface on the behavior of the adjoining bulk phases, and this effect may be different for each of the bulk phases. In isothermal systems without accumulation of components at the interface we can use a much simpler condition. The entropy balance then suggests we use a single friction tensor $\boldsymbol{\zeta}'$, defined as

$$\boldsymbol{\zeta}'=\left(\frac{\rho^{\text{I}}+\rho^{\text{II}}}{\rho^{\text{I}}-\rho^{\text{II}}}\right)^2\boldsymbol{\zeta}, \tag{54}$$

where $\boldsymbol{\zeta}=\boldsymbol{\zeta}^{\text{I,I}}=\boldsymbol{\zeta}^{\text{I,II}}=\boldsymbol{\zeta}^{\text{II,I}}=\boldsymbol{\zeta}^{\text{II,II}}$. With this choice (53) reduces to (when in addition there is no mass transfer across the interface)

$$\boldsymbol{\zeta}'\cdot(\mathbf{v}^{\text{I}}-\mathbf{v}^{\text{II}})=\left(\frac{1}{\rho^{\text{I}}}-\frac{1}{\rho^{\text{II}}}\right)^{-1}\left(\frac{\sigma_{\text{tot}}^{\text{I}}}{\rho^{\text{I}}}-\frac{\sigma_{\text{tot}}^{\text{II}}}{\rho^{\text{II}}}\right)\cdot\boldsymbol{\xi}. \tag{55}$$

Note that this expression no longer contains any interfacial variables, and couples the adjoining bulk phases directly, as we would expect for simple interfaces without accumulated mass. For simple systems we could have introduced this form directly by changing the second integral in the dissipative bracket in Eq. (29). If we are willing to assume there is no slip between the two bulk phases at the interface (i.e., $\mathbf{v}^{\text{I}}=\mathbf{v}^{\text{II}}$ at the interface), then (55) reduces to

$$\sigma_{\text{tot}}^{\text{I}}=\sigma_{\text{tot}}^{\text{II}}, \tag{56}$$

which states that stresses are continuous across the interface, a boundary condition commonly used in flow problems involving simple interfaces.

From the terms in the surface integral proportional to $\mathbf{m}^s$ and $\partial a^s/\partial\mathbf{m}^s$, we obtain the following form of the jump momentum balance at the interface [using (53)]:

$$\begin{aligned}&\rho^s\frac{d_s\mathbf{v}^s}{dt}-\nabla_s(\gamma'+\gamma_E)-2(\gamma'+\gamma_E)H\boldsymbol{\xi}-\nabla_s\cdot\boldsymbol{\sigma}_{\text{tot}}^s\\&\quad+[\![\rho(\mathbf{v}-\mathbf{v}^s)(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi}-\boldsymbol{\sigma}_{\text{tot}}\cdot\boldsymbol{\xi}+(P'+P_E)\boldsymbol{\xi}]\!]=0,\end{aligned} \tag{57}$$

where the total surface extra stress tensor $\boldsymbol{\sigma}_{\text{tot}}^s$ is defined as

$$\begin{aligned}\boldsymbol{\sigma}_{\text{tot}}^s&=(\varepsilon_d-\varepsilon_s)[\nabla_s\cdot\mathbf{v}^s]\mathbf{P}+2\varepsilon_s\mathbf{D}^s\\&\quad+2\mathbf{C}^s\cdot\frac{\partial\bar{F}_c^s}{\partial\mathbf{C}^s}+\mathbf{G}^s\frac{\partial\bar{F}_c^s}{\partial\bar{\Gamma}^s}.\end{aligned} \tag{58}$$

Here $\bar{F}_c^s=\bar{U}_c^s-T^s\rho^s\hat{S}_c^s$ is the surface Helmholtz free energy per unit area of the interfaces, and γ_E equals

$$\gamma_E=\bar{U}_c^s-\rho^s\frac{\partial\bar{U}_c^s}{\partial\rho^s}-\bar{\Gamma}^s\frac{\partial\bar{U}_c^s}{\partial\bar{\Gamma}^s}. \tag{59}$$

The next two variables we will consider are $\bar{U}$, and $\bar{U}^s$. From the terms in the bulk integral proportional to $\partial a/\partial\bar{U}$ we obtain the differential energy balance for the bulk phases:

$$\begin{aligned}&\frac{d_b\bar{U}}{dt}+(\bar{U}+P')\nabla\cdot\mathbf{v}+\boldsymbol{\Pi}':\nabla\mathbf{v}-2\eta\bar{\mathbf{D}}:\bar{\mathbf{D}}-\eta_b(\text{tr}\mathbf{D})^2-\nabla\cdot(\lambda\nabla T)-\sum_{J=1}^{N-1}\nabla\cdot\left[\tilde{\alpha}_{(J)}T^2\nabla\left(\frac{\mu_{(J)}}{T}\right)\right]\\&\quad-\frac{\partial\bar{U}_c}{\partial\bar{\Gamma}}\frac{R_1}{T}\frac{\partial\bar{F}_c}{\partial\bar{\Gamma}}-\frac{\partial\bar{U}_c}{\partial\mathbf{C}}:\frac{\mathbf{R}_2}{T}:\frac{\partial\bar{F}_c}{\partial\mathbf{C}}+\frac{\partial\bar{U}_c}{\partial\bar{\Gamma}}\nabla\cdot\left[\mathbf{D}_\Gamma\cdot\nabla\left(\frac{1}{T}\frac{\partial\bar{F}_c}{\partial\bar{\Gamma}}\right)\right]+\frac{\partial\bar{U}_c}{\partial\mathbf{C}}:\left\{\nabla\cdot\left[\mathbf{D}_C\,\vdots\,\nabla\left(\frac{1}{T}\frac{\partial\bar{F}_c}{\partial\mathbf{C}}\right)\right]\right\}=0.\end{aligned} \tag{60}$$

The consistency requirement for energy transfer between bulk phases and interface, obtained from the coefficients of the terms proportional to $\bar{U}$ and $\partial a/\partial\bar{U}$ in the surface integral, takes the form [using (45) and (53)] ($M=\text{I,II}$)

$$\begin{aligned}&\frac{T^s-T^M}{R_K^M}-\sum_{J=1}^{N-1}\Lambda_{(J)}^{TM}TT^s\left(\frac{\check{\mu}_{(J)}^M}{T^M}-\frac{\check{\mu}_{(J)}^s}{T^s}\right)\\&\quad=(\bar{U}^M+P'^M)(\mathbf{v}^M-\mathbf{v}^s)\cdot\boldsymbol{\xi}-\mathbf{v}^M\cdot\boldsymbol{\sigma}_{tot}^M\cdot\boldsymbol{\xi}^M+\frac{1}{2}\rho(v^M)^2(\mathbf{v}^M-\mathbf{v}^s)\cdot\boldsymbol{\xi}-\lambda^M\nabla T^M\cdot\boldsymbol{\xi}^M\end{aligned}$$

$$
- \sum_{J=1}^{N-1} \tilde{\alpha}^{M}_{(J)} (T^M)^2 \nabla \left[\frac{\mu^M_{(J)}}{T^M} \right] \cdot \boldsymbol{\xi}^M + \frac{\partial \bar{U}^M_c}{\partial \bar{\Gamma}^M} \left[\mathbf{D}^M_\Gamma \cdot \nabla \left(\frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \bar{\Gamma}^M} \right) \right] \cdot \boldsymbol{\xi}^M + \left[\frac{\partial \bar{U}^M_c}{\partial \mathbf{C}^M} : \mathbf{D}^M_C \vdots \nabla \left(\frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \mathbf{C}^M} \right) \right] \cdot \boldsymbol{\xi}^M
$$

$$
- \left[\boldsymbol{\Phi}^M \frac{\partial \bar{U}^M_c}{\partial \bar{\Gamma}^M} + \frac{\partial \bar{U}^M_c}{\partial \mathbf{C}^M} \right] : \mathbf{J}^M_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}^M}{T^M} \frac{\partial \bar{F}^M_c}{\partial \bar{\Gamma}^M} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \mathbf{C}^M} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right). \tag{61}
$$

And finally, the terms proportional to $\bar{U}^s$ and $\partial a^s / \partial \bar{U}^s$ in the surface integral give us the following expression for the differential jump energy balance:

$$
\frac{d_s \bar{U}^s}{dt} + (\bar{U}^s - \gamma') \nabla_s \cdot \mathbf{v}^s + \boldsymbol{\Pi}'^s : \nabla_s \mathbf{v}^s + 2H \mathbf{v}^s \cdot \boldsymbol{\Pi}'^s \cdot \boldsymbol{\xi} + \nabla_s \cdot \mathbf{q}^s - 2\varepsilon_s \bar{\mathbf{D}}^s : \bar{\mathbf{D}}^s - \varepsilon_d (\mathrm{tr} \mathbf{D}^s)^2
$$

$$
- \frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s} \frac{R^s_1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} - \frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s} : \frac{\mathbf{R}^s_2}{T^s} : \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} + \frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s} \nabla_s \cdot \left[\mathbf{D}^s_\Gamma \cdot \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} \right) \right] + \frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s} : \left\{ \nabla_s \cdot \left[\mathbf{D}^s_C \vdots \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \right] \right\}
$$

$$
+ \Bigg[\rho \left(\hat{U} + \frac{1}{2} [\mathbf{v} - \mathbf{v}^s]^2 \right) (\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \mathbf{q} \cdot \boldsymbol{\xi} - (\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\sigma}_{\mathrm{tot}} \cdot \boldsymbol{\xi} + P' (\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \frac{\partial \bar{U}_c}{\partial \bar{\Gamma}} \left[\mathbf{D}_\Gamma \cdot \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} \right) \right] \cdot \boldsymbol{\xi}
$$

$$
+ \left[\frac{\partial \bar{U}_c}{\partial \mathbf{C}} : \mathbf{D}_C \vdots \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} \right) \right] \cdot \boldsymbol{\xi} - \left[\boldsymbol{\Phi} \frac{\partial \bar{U}_c}{\partial \bar{\Gamma}} - \boldsymbol{\Phi}^s \frac{\partial \bar{U}^s_c}{\partial \bar{\Gamma}^s} + \frac{\partial \bar{U}_c}{\partial \mathbf{C}} - \frac{\partial \bar{U}^s_c}{\partial \mathbf{C}^s} \right]
$$

$$
: \mathbf{J}_{\Gamma C} : \left[\frac{\boldsymbol{\Phi}}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right] \Bigg] = 0, \tag{62}
$$

where $\mathbf{q}$ and $\mathbf{q}^s$ are the bulk and surface energy flux vectors, given by

$$
\mathbf{q} = -\lambda \nabla T - \sum_{J=1}^{N-1} \tilde{\alpha}_{(J)} T^2 \nabla \left(\frac{\mu_{(J)}}{T} \right), \tag{63}
$$

$$
\mathbf{q}^s = -\lambda^s \nabla_s T^s - \sum_{J=1}^{N-1} \tilde{\alpha}^s_{(J)} (T^s)^2 \nabla_s \left(\frac{\mu^s_{(J)}}{T^s} \right). \tag{64}
$$

We now turn our attention to the balance equations for the structural variables. From the integral over R we find that the time evolution of $\bar{\Gamma}$ is given by

$$
\frac{d_b \bar{\Gamma}}{dt} + \bar{\Gamma} \nabla \cdot \mathbf{v} - \mathbf{G} : \nabla \mathbf{v} + \frac{R_1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} - \nabla \cdot \left[\mathbf{D}_\Gamma \cdot \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} \right) \right] = 0. \tag{65}
$$

The consistency requirement for transfer of the scalar structural variable between bulk phase and interface, obtained from the integral over Σ, is given by ($M = \mathrm{I,II}$)

$$
\boldsymbol{\Phi}^M : \mathbf{J}^M_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}^M}{T^M} \frac{\partial \bar{F}^M_c}{\partial \bar{\Gamma}^M} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \mathbf{C}^M} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) = -\bar{\Gamma}^M (\mathbf{v}^M - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \mathbf{D}^M_\Gamma \cdot \nabla \left(\frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \bar{\Gamma}^M} \right) \cdot \boldsymbol{\xi}^M. \tag{66}
$$

The jump balance for $\bar{\Gamma}^s$ takes the form

$$
\frac{d_s \bar{\Gamma}^s}{dt} + \bar{\Gamma}^s \nabla_s \cdot \mathbf{v}^s - \mathbf{G}^s : \nabla_s \mathbf{v}^s - 2H \mathbf{v}^s \cdot \mathbf{G}^s \cdot \boldsymbol{\xi} + \frac{R^s_1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} - \nabla_s \cdot \left[\mathbf{D}^s_\Gamma \cdot \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} \right) \right] - \Bigg[\boldsymbol{\Phi}^s : \mathbf{J}_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \Bigg] = 0. \tag{67}
$$

Likewise we find for the time evolution of the bulk tensorial structural variable

$$
\overset{\square}{\delta_b} \mathbf{C} + \mathbf{R}_2 : \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} \right) - \nabla \cdot \left[\mathbf{D}_C \vdots \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} \right) \right] = 0, \tag{68}
$$

where $\overset{\square}{\delta_b} \mathbf{C}$ denotes the upper convected derivative in the bulk phase, equal to

$$
\overset{\square}{\delta_b} \mathbf{C} = \frac{d_b \mathbf{C}}{dt} - \mathbf{C} \cdot (\nabla_s \mathbf{v})^T - (\nabla_s \mathbf{v}) \cdot \mathbf{C}. \tag{69}
$$

The consistency requirement for transfer of the tensorial structural variable between bulk phase and interface takes the form ($M = \mathrm{I,II}$)

$$
\mathbf{J}^M_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}^M}{T^M} \frac{\partial \bar{F}^M_c}{\partial \bar{\Gamma}^M} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \mathbf{C}^M} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) = \mathbf{D}^M_C \vdots \nabla \left(\frac{1}{T^M} \frac{\partial \bar{F}^M_c}{\partial \mathbf{C}^M} \right) \cdot \boldsymbol{\xi}^M. \tag{70}
$$

For the jump balance for the surface tensorial structural variable we find

$$
\overset{\square}{\delta_s} \mathbf{C}^s - 4H \mathbf{v}^s \cdot \mathbf{C}^s \boldsymbol{\xi} + \mathbf{R}^s_2 : \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) - \nabla_s \cdot \left[\mathbf{D}^s_C \vdots \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \right] - \Bigg[\mathbf{J}_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \Bigg] = 0, \tag{71}
$$

and $\overset{\square}{\delta_s} \mathbf{C}^s$ denotes the upper convected surface derivative, defined as

$$
\overset{\square}{\delta_s} \mathbf{C}^s = \frac{d_s \mathbf{C}^s}{dt} - \mathbf{C}^s \cdot [(\nabla_s \mathbf{v}^s)^T \cdot \mathbf{P}] - [\mathbf{P} \cdot (\nabla_s \mathbf{v}^s)] \cdot \mathbf{C}^s. \tag{72}
$$

The final balance equations we obtain from (7) are those for the bulk and surface species mass densities $\rho_{(J)}$ and $\rho^s_{(J)}$. For these variables we obtain the differential species mass balance

$$\frac{d_b\rho_{(J)}}{dt} + \rho_{(J)}\nabla\cdot\mathbf{v} - \sum_{K=1}^{N-1}\nabla\cdot\left(\tilde{D}_{(JK)}\nabla\left[\frac{\mu_{(J)}}{T}\right]\right) - \nabla\cdot(\tilde{\alpha}_{(J)}\nabla T) = 0, \tag{73}$$

the consistency requirement ($M = \mathrm{I,II}$)

$$\Lambda^M_{(J)}\left(\frac{\check{\mu}^M_{(J)}}{T^M} - \frac{\check{\mu}^s_{(J)}}{T^s}\right) + \Lambda^{TM}_{(J)}(T^M - T^s) = -\rho^M_{(J)}(\mathbf{v}^M - \mathbf{v}^s)\cdot\boldsymbol{\xi}^M + \sum_{K=1}^{N-1}\tilde{D}^M_{(JK)}\nabla\left[\frac{\mu^M_{(J)}}{T^M}\right]\cdot\boldsymbol{\xi}^M + \tilde{\alpha}^M_{(J)}\nabla T^M\cdot\boldsymbol{\xi}^M, \tag{74}$$

and the differential jump species mass balance

$$\frac{d_s\rho^s_{(J)}}{dt} + \rho^s_{(J)}\nabla_s\cdot\mathbf{v}^s - \sum_{K=1}^{N-1}\nabla_s\cdot\left[\tilde{D}^s_{(JK)}\nabla_s\left(\frac{\mu^s_{(J)}}{T^s}\right)\right] - \nabla_s\left(\tilde{\alpha}^s_{(J)}\nabla_s T^s\right) + \Bigg[\rho_{(J)}(\mathbf{v} - \mathbf{v}^s)\cdot\boldsymbol{\xi} - \sum_{K=1}^{N-1}\tilde{D}_{(JK)}\nabla\left[\frac{\mu_{(J)}}{T}\right]\cdot\boldsymbol{\xi} - \tilde{\alpha}_{(J)}\nabla T\cdot\boldsymbol{\xi}\Bigg] = 0. \tag{75}$$

We have now extracted the complete set of time evolution equations for the independent bulk and interfacial variables, a complete set of boundary conditions coupling the bulk and interfacial fields, and a set of constitutive equations for the fluxes appearing in the time evolution equations. This set of equations allows us to construct specific models for a wide range of multiphase systems with a complex microstructure, by choosing specific forms for the bulk and surface configurational Helmholtz free energy, $\bar{F}_c$ and $\bar{F}^s_c$, the scalar relaxation parameters R_1 and R^s_1, the tensorial relaxation and diffusion parameters $\mathbf{R}_2$, $\mathbf{R}^s_2$, $\mathbf{D}_\Gamma$, $\mathbf{D}^s_\Gamma$, $\mathbf{D}_C$ and $\mathbf{D}^s_C$, the second order tensors $\mathbf{G}$ and $\mathbf{G}^s$, and the coupling tensors $\boldsymbol{\Phi}$ and $\boldsymbol{\Phi}^s$. As an example, we will discuss the application of this framework to emulsions stabilized by anisotropic colloidal particles (i.e., Pickering emulsions), in a companion paper. Pickering stabilized emulsions are highly relevant systems for the food, cosmetics, and pharmaceutical industries.

VII. CONCLUSIONS

In this paper we have presented a nonequilibrium thermodynamic model for the dynamics of multiphase systems with a complex microstructure (emulsions, foam, immiscible polymer blends), in the context of the GENERIC framework. The effect of the microstructure on dynamic behavior was incorporated by including scalar and tensorial structural variables in the set of bulk and interfacial system variables. To ensure consistency of our model with the chain rule of functional calculus, a MINT term has to be included in the GENERIC, and to satisfy the entropy degeneracy requirement, this term has to include several new contributions involving the bulk and interfacial tensorial variables. The model produces a complete set of balance and constitutive equations for the bulk and surface fields, and a set of boundary conditions linking bulk to surface fields. By choosing specific forms of the free energies, relaxation parameters, diffusivity tensors, and coupling tensors we can create a wide range of models for specific multiphase systems, which are valid not only close to equilibrium, but also far from equilibrium.

---

[1] L. M. C. Sagis, Rev. Mod. Phys. **83**, 1367 (2011).

[2] J. C. Slattery, L. M. C. Sagis, and E. S. Oh, *Interfacial Transport Phenomena*, 2nd ed. (Springer, New York, 2007).

[3] D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Phenomena and Rheology* (Butterworth-Henemann, Boston, 1991).

[4] L. M. C. Sagis, Physica A **260**, 261 (1998).

[5] E. van der Linden, L. M. C. Sagis, and P. Venema, Curr. Opin. Colloid Interface Sci. **8**, 349 (2003).

[6] L. M. C. Sagis, Appl. Rheol. **20**, 24380 (2010).

[7] L. M. C. Sagis, Physica A **389**, 673 (2010).

[8] L. M. C. Sagis, Soft Matter **17**, 7727 (2011).

[9] M. Grmela and H. C. Öttinger, Phys. Rev. E **56**, 6620 (1997).

[10] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).

[11] H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley-Intersience, Hoboken, 2005).

[12] H. C. Öttinger, D. Bedeaux, and D. C. Venerus, Phys. Rev. E **80**, 021606 (2009).

[13] L. M. C. Sagis, Adv. Colloid Interface Sci. **153**, 58 (2010).

[14] L. M. C. Sagis, Physica A **389**, 1993 (2010).

[15] W. Helfrich, Z. Naturforsch. C **28**, 693 (1973).

[16] L. M. C. Sagis, Physica A **246**, 591 (1997).

[17] J. B. A. F. Smeulders, C. Blom, and J. Mellema, Phys. Rev. A **42**, 3483 (1990).

[18] J. B. A. F. Smeulders, J. Mellema, and C. Blom, Phys. Rev. A **46**, 7708 (1992).

[19] K. H. de Haas, G. J. Ruiter, and J. Mellema, Phys. Rev. E **52**, 1891 (1995).

[20] E. Scholten, L. M. C. Sagis, and E. van der Linden, J. Phys. Chem. B **108**, 12164 (2004).

[21] E. Scholten, L. M. C. Sagis, and E. van der Linden, Macromolecules **38**, 3515 (2005).

[22] E. Scholten, L. M. C. Sagis, and E. van der Linden, J. Phys. Chem. B **110**, 3250 (2006).

[23] L. M. C. Sagis, J. Controlled Release **131**, 5 (2008).

[24] K. Bering, J. Math. Phys. **41**, 7468 (2000).

[25] J. Boussinesq, C. R. Seances Acad. Sci. **156**, 983 (1913).

[26] J. Boussinesq, C. R. Seances Acad. Sci. **156**, 1035 (1913).

[27] J. Boussinesq, C. R. Seances Acad. Sci. **156**, 1124 (1913).

[28] L. M. C. Sagis, Phys. Rev. E **88**, 022150 (2013).

[29] M. Doi and T. Ohta, J. Chem. Phys. **95**, 1242 (1991).

[30] E. A. van der Zeeuw, L. M. C. Sagis, and G. J. M. Koper, Macromolecules **29**, 801 (1996).

[31] E. A. van der Zeeuw, L. M. C. Sagis, G. J. M. Koper, E. K. Mann, M. T. Haarmans, and D. Bedeaux, J. Chem. Phys. **105**, 1646 (1996).

[32] V. M. Kaganer, H. Möhwald, and P. Dutta, Rev. Mod. Phys. **71**, 779 (1999).

[33] B. J. A. Zielinska and D. Bedeaux, Physica A **112**, 265 (1982).