Review

Modeling interfacial dynamics using nonequilibrium thermodynamics frameworks

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Abstract. In recent years several nonequilibrium thermodynamic frameworks have been developed capable of describing the dynamics of multiphase systems with complex microstructured interfaces. In this paper we present an overview of these frameworks. We will discuss interfacial dynamics in the context of the classical irreversible thermodynamics, extended irreversible thermodynamics, extended rational thermodynamics, and GENERIC framework, and compare the advantages and disadvantages of these frameworks.

1 Introduction

In our daily existence we encounter numerous examples of dispersions with complex microstructured interfaces. Examples are, biological fluids like blood, protein or particle stabilized emulsions in food and cosmetics, or dispersions of liposomes or polymer microcapsules used in pharmaceutical and medical diagnostics applications. These dispersions are characterized by very high surface to volume ratios, and their macroscopic rheology is affected significantly by the structure and properties of the interfaces between dispersed and continuous phase. For dispersions with interfaces stabilized by low molecular weight surfactants, the surface tension is typically the only relevant surface property affecting the rheology of the dispersion. But for dispersions with microstructured interfaces also the rheological properties of the interfaces, such as the surface shear modulus, surface dilatational modulus, and bending rigidity, tend to affect the macroscopic response of the dispersion to an applied stress [1–8].

The structures we encounter in microstructured interfaces are very diverse [1]: surface active species can form 2D emulsions and suspensions (mixtures of immiscible lipids), 2D particle gels (globular proteins, colloidal particles), 2D glass phases (globular proteins, colloidal particles), 2D liquid crystalline phases (anisotropic colloidal particles, anisotropic polymers), or even 2D composites (multilayers of flexible polymers and rod-like particles) [9,10]. When these types of microstructured interfaces are deformed, their structure changes, and even at small deformations these interfaces therefore display a highly nonlinear rheological behavior [1]. A detailed fundamental

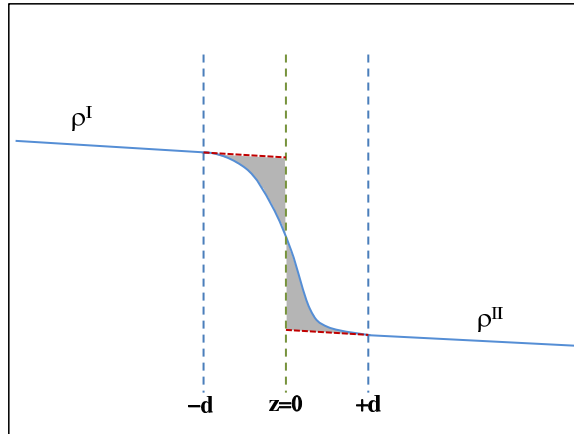---

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Fig. 1. Density profile in the immediate neighborhood of a phase interface. The dividing surface is located at $z = 0$. The shaded areas denote the difference between the extrapolated bulk fields and the actual density field in the interfacial region.

understanding of this highly nonlinear behavior is essential for understanding the complex macroscopic flow behavior of dispersions with structured interfaces.

Various experimental techniques have been developed to characterize the rheological properties of microstructured interfaces [1]. Surface shear moduli are most commonly determined using stress-controlled rheometers, with either bi-cone [11–15] or double-wall ring geometries [16,17]. Alternatively, oscillating needle rheometers [18] can be used, in which the interface is deformed using a thin magnetic needle, displaced by two magnetic coils. Surface dilatational moduli tend to be determined using oscillating drop (or bubble) methods, bubble pressure tensiometry, or Langmuir troughs [19]. Data from surface shear rheological experiments are in general analyzed using linear viscoelastic models [1]. Such models describe the stress-deformation of complex interfaces accurately only in the limit of small departures from equilibrium (i.e. strains typically <0.01). Dilatational data for interfaces stabilized by low molecular weight surfactants tend to be analyzed using the Lucassen and van Tempel model [20,21], which assumes that the stress-deformation behavior of the interface is completely determined by the transfer of surface active components between the bulk phase and the interface. For complex microstructured interfaces both in-plane dynamics, and mass transfer to the interface may affect the response of the interface [22–25], and models have become available that incorporate both effects [26–32]. Again, such models describe the rheology of microstructured interfaces accurately only for small deformations.

Nonequilibrium thermodynamic (NET) frameworks are ideal for constructing constitutive equations for the stress deformation behavior of microstructured interfaces, valid also far from equilibrium. In NET interfaces are typically modeled as two-dimensional dividing surfaces, placed sensibly within the three-dimensional interfacial region (Fig. 1). Fields like the mass or momentum density change rapidly but continuously across this region, from their value in one bulk phase to their value in the other bulk phase. In most multiphase NET frameworks the bulk fields are extrapolated up to the dividing surface (Fig. 1), and the differences between actual fields and extrapolated fields are accounted for by associating excess fields, like a surface mass density or a surface momentum density, with every point on the dividing surface.

Including these excess variables in the conservation principles for mass, momentum, energy, and entropy, we obtain, apart from the well known balance equations for the bulk fields, an additional set of equations for the time evolution of the surface

mass density, the surface momentum, the surface energy, and surface entropy. For multicomponent systems we also obtain additional time evolution equations for each component in the system. There are now several NET frameworks available that include surface excess variables in the set of independent system variables: rational thermodynamics [15], classical irreversible thermodynamics [33–36], extended irreversible thermodynamics [37], extended rational thermodynamics [38], and GENERIC [39–41] have all been generalized to multiphase systems with excess variables associated with the dividing surfaces. All these frameworks give identical expressions for the time evolutions for surface mass density, surface momentum, and surface energy. They differ however significantly in the types of constitutive equations that can be constructed, for the fluxes that appear in these time evolution equations.

Before we compare the constitutive equations that can be generated with these NET frameworks, let us first discuss the properties we would like these equations to have. First of all, for microstructured interfaces we would like to have a direct link between the response of the system to an applied force, and the evolution of its microstructure. This can be accomplished by including structural variables in the set of independent system variables. These variables can have a scalar, vectorial, or tensorial nature, and are continuous fields describing some characteristic and locally averaged properties of the microstructure. For example, for interfaces stabilized by polymers, the structure could be characterized by one or more scalar variables, representing the local segment density, or local stretching of polymer segments. The orientation of the segments could be characterized by a tensorial variable, for example, the second moment of the segment end-to-end vector distribution.

This type of structural modeling has been applied successfully to the rheological modeling of complex bulk phases, such as polymer melts and solutions, liquid crystalline phases [42,43], and biopolymer solutions [44]. Sofar structural models have found only limited application in the analysis of surface rheological data. Rey [45–47] used structural variables to model the interfacial dynamics of interfaces between a nematic polymer phase, and a viscous fluid. Oh and Slattery [48] used a structural model to describe the interfacial behavior in single wall carbon nanotubes. Sagis [49] developed a model for the surface extra stress tensor for an interface stabilized by anisotropic colloidal particles.

Of the four NET frameworks we will compare in this paper (classical irreversible thermodynamics (CIT), extended irreversible thermodynamics (EIT), extended rational thermodynamics (ERT), and GENERIC) microstructural variables can be incorporated most easily in the CIT and GENERIC formalism. We will see that in EIT and ERT the coupling with the microstructure is introduced implicitly, by using the stress (and other fluxes) as independent system variables. We will not discuss the rational thermodynamics framework here, since the resulting constitutive models obtained from it are quite similar to those obtained with the CIT framework.

A second property we would like constitutive models for the surface fluxes to have is that the expressions for the surface fluxes should contain a coupling with the corresponding fluxes in the adjoining bulk phases. In systems where both the interfaces and the adjoining bulk phases have a complex microstructure, we may expect that the bulk structure in the immediate neighborhood of the interface will affect the structure of the interface, and vice versa. For example, in a system with an interface stabilized by anisotropic particles, separating a dense anisotropic particle phase from a dilute particle phase, we may expect that the orientation of the particles in the concentrated phase, close to the interface, will affect the orientation of the particles in the interface. As we will see this coupling is most easily introduced in the ERT and GENERIC frameworks.

A third and obvious property we would like the constitutive models for the surface fluxes to have, is that they are valid also far from equilibrium. For constitutive

equations for the surface extra stress tensor this implies that they should describe experimental data appropriately also for strains $\gg 1$.

In the remainder of this paper we will compare the constitutive models that can be constructed for interfaces with a complex microstructure, using the CIT, EIT, ERT, and GENERIC frameworks, using the three criteria we discussed above. We will limit ourselves to constitutive models for the surface extra stress tensor. Constitutive models for the other fluxes (the surface heat flux vector, and surface mass flux vectors) can be derived in a similar manner. We will consider only systems in which bulk or interfacial chemical reactions between components are absent.

2 Classical irreversible thermodynamics

The classical irreversible thermodynamics framework is the oldest of the currently available NET frameworks, and dates back to Onsager [50,51] (see also [52]). This framework was generalized to multiphase systems with excess properties associated with the interfaces in the 1970s and 80s by Bedeaux et al. [33], Zielinska and Bedeaux, [34], Bedeaux [35], Albano and Bedeaux [53], Bedeaux and Vlieger [36], and Kjelstrup and Bedeaux [54]. In the classical irreversible thermodynamics framework for multiphase systems we start with expressions for the time rate of change of the bulk and surface entropy per unit mass, $\hat{S}$ and $\hat{S}^s$. Since here we are interested only in interfacial dynamics we will consider only the balance equation for the latter. This has the following form [34,54]:

$$\rho^s \frac{d_s \hat{S}^s}{dt} = -\nabla_s \cdot \mathbf{j}_S^s + \rho^s \hat{\mathcal{E}}^s - [\![\rho(\hat{S} - \hat{S}^s)(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \mathbf{j}_S \cdot \boldsymbol{\xi}]\!]. \tag{1}$$

Here $\hat{\mathcal{E}}^s$ is the rate of surface entropy production per unit mass. To satisfy the second law of thermodynamics we must require $\hat{\mathcal{E}}^s \geq 0$. The vector $\mathbf{j}_S^s$ is the surface entropy flux vector, $\mathbf{j}_S$ is the entropy flux vector in the bulk phase, and ρ and ρ^s are respectively the overall bulk and surface mass densities. The operator ∇_s is the surface gradient operator, defined as $\nabla_s \Psi = (\partial \Psi / \partial y^\alpha) \mathbf{a}^\alpha$, where y^α ($\alpha = 1, 2$) are the surface coordinates, and $\mathbf{a}^\alpha$ the dual tangential basis vector fields of the interface. The vectors $\mathbf{v}$ and $\mathbf{v}^s$ denote the bulk and surface velocities, and $\boldsymbol{\xi}$ is the unit vector, normal to the surface. The time derivative in (1) is the surface material derivative, defined by [15]

$$\frac{d_s \hat{S}^s}{dt} = \frac{\partial \hat{S}^s}{\partial t} + (\nabla_s \hat{S}^s) \cdot \dot{\mathbf{y}} \tag{2}$$

where $\dot{\mathbf{y}}$ is the intrinsic surface velocity, defined by $(d_s y^\alpha / dt) \mathbf{a}^\alpha$ [15]. The boldface brackets describe contributions to surface balances from the adjoining bulk phases, and this notation is defined as

$$[\![\Psi \boldsymbol{\xi}]\!] = \Psi^{(I)} \boldsymbol{\xi}^{(I,II)} + \Psi^{(II)} \boldsymbol{\xi}^{(II,I)} \tag{3}$$

where $\Psi^{(I)}$ is the value of the arbitrary observable Ψ in bulk phase I, evaluated at the interface $\Sigma^{(I,II)}$, and $\boldsymbol{\xi}^{(I,II)}$ is the unit vector normal to that interface, pointing in the direction of phase I.

The next step in the classical irreversible thermodynamics framework is to choose a functional dependence for the surface entropy. A general practice is to assume local equilibrium, which implies that locally the surface entropy depends on the same variables as the entropy of an interface in global equilibrium. For the surface entropy per unit mass of an N-component microstructured interface this assumption implies

$$\hat{S}^s = \hat{S}^s(\hat{U}^s, \hat{\mathcal{A}}, \omega_{(1)}^s, ..., \omega_{(N-1)}^s, \Gamma^s, \mathbf{C}^s) \tag{4}$$

where $\hat{U}^s$ is the surface internal energy per unit mass, $\hat{\mathcal{A}}$ is the area per unit mass $(= 1/\rho^s)$, $\omega_{(A)}^s$ $(A = 1, N)$ denotes the surface mass fraction of species A, and Γ^s and $\mathbf{C}^s$ are respectively scalar and tensorial structural variables describing the microstructure of the interface. Note that here we assume that all surface excess variables are curvature dependent [15], and we therefore do not include curvature variables such as the mean or Gaussian in the set of independent variables. We have limited ourselves here to a system described by one scalar and one tensorial variable. The extension to systems with multiple scalar or tensorial variables, or even vectorial variables, is straightforward. From equation (4) we find that the left hand side of (1) equals

$$\rho^s \frac{d_s \hat{S}^s}{dt} = \frac{\rho^s}{T^s} \frac{d_s \hat{U}^s}{dt} - \frac{\gamma \rho^s}{T^s} \frac{d_s \hat{\mathcal{A}}}{dt} - \frac{\rho^s}{T^s} \sum_{A=1}^{N} \mu_{(A)}^s \frac{d_s \omega_{(A)}^s}{dt}$$
$$- \frac{\rho^s \Xi^s}{T^s} \frac{d_s \Gamma^s}{dt} - \frac{\rho^s}{T^s} \mathbf{W}^s : \frac{d_s \mathbf{C}^s}{dt} \quad (5)$$

where T^s is the surface temperature, γ is the surface tension, and $\mu_{(A)}^s$ is the surface chemical potential per unit mass of species A. The coefficients Ξ^s and $\mathbf{W}^s$ are defined as

$$\Xi^s \equiv T^s \left(\frac{\partial \hat{S}^s}{\partial \Gamma^s} \right)_{\hat{U}^s, \hat{\mathcal{A}}, \omega_{(A)}^s, \mathbf{C}^s} \quad (6)$$

$$\mathbf{W}^s \equiv T^s \left(\frac{\partial \hat{S}^s}{\partial \mathbf{C}^s} \right)_{\hat{U}^s, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s} . \quad (7)$$

The surface material derivatives of $\hat{U}^s$, $\hat{\mathcal{A}}$, and $\omega_{(A)}^s$ in (5) can be eliminated using the jump energy balance [15,34], the overall jump mass balance [15,34], and the species jump mass balance [15,34]. After elimination of these three surface material derivatives the right hand side of the resulting equation is set equal to the right hand side of (1), which allows us to determine an expression for $\hat{\mathcal{E}}^s$ and $\mathbf{j}_S^s$. The expression for $\hat{\mathcal{E}}^s$ has the general form [34]

$$\rho^s \hat{\mathcal{E}}^s = \sum_k J_k^s X_k^s + \left[\!\!\left[\mathcal{C} \left(\mathbf{v} - \mathbf{v}^s \right) \cdot \boldsymbol{\xi} + \sum_k \left(J_k \cdot \boldsymbol{\xi} \right) X_k \right]\!\!\right] \geq 0 \quad (8)$$

where J_k and J_k^s represent the bulk and surface fluxes in the system (either scalar, vectorial, or tensorial), and X_k and X_k^s are their respective driving forces. The first contribution to the boldface bracket term describes the entropy production associated with convective transport of mass, momentum, energy, and entropy between the interface and the adjoining bulk phases (all these contributions are collected in $\mathcal{C}$, which in view of its lengthy form, we will not specify here). Based on (8) and the Curie principle [52], coupled linear constitutive equations for the in-plane interfacial fluxes are constructed of the general form [15,34]

$$J_k^s = \sum_m L_{km}^s X_m^s. \quad (9)$$

The Curie principle implies that fluxes in (9) couple only to driving forces of equal tensorial order. Equation (8) also allows us to construct constitutive equations for the fluxes $J_k \cdot \boldsymbol{\xi}$ describing transport perpendicular to the interface, but these are outside the scope of the current paper. They are discussed in detail in the papers

by Zielinska and Bedeaux [34], and Bedeaux [35]. Note that the contraction with the normal vector $\boldsymbol{\xi}$ reduces the order of the original flux J_k by one, and therefore for vectorial fluxes $J_k \cdot \boldsymbol{\xi}$ will couple to scalar driving forces. The constitutive equations in (9) can be simplified using the Onsager reciprocal relations, which require that the phenomenological coefficients L_{km}^s satisfy [34,52]

$$L_{km}^s = \pm L_{mk}^s \tag{10}$$

where a positive sign describes the case where k and m are both even (or both odd) under time reversal, and the negative sign must be used when k is even and m is odd (or vise versa) under reversal of time. For the surface extra stress tensor of an interface with a microstructure described by a single scalar and tensorial structural variable, this analysis leads to the following set of constitutive equations (retaining only terms linear in the driving forces) [34,49]:

$$\bar{\boldsymbol{\sigma}}^s = \mathbf{L}_{\sigma d}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s) : \nabla_s \mathbf{v}^s + \mathbf{L}_{\sigma w}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s) : \mathbf{W}^s \tag{11}$$

$$\mathrm{tr}\boldsymbol{\sigma}^s = 2L_{\sigma d}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\mathrm{tr}(\nabla_s \mathbf{v}^s)$$
$$+ 2L_{\sigma w}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\mathrm{tr}\mathbf{W}^s + 2L_{\sigma\xi}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\Xi^s \tag{12}$$

$$\rho^s \frac{d_s \mathbf{C}^s}{dt} = \mathbf{L}_{cd}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s) : \nabla_s \mathbf{v}^s + \mathbf{L}_{cw}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s) : \mathbf{W}^s \tag{13}$$

$$\rho^s \frac{d_s \Gamma^s}{dt} = 2L_{\gamma d}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\mathrm{tr}(\nabla_s \mathbf{v}^s)$$
$$+ 2L_{\gamma w}(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\mathrm{tr}\mathbf{W}^s + 2L_{\gamma\xi}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\Xi^s \tag{14}$$

where $\bar{\boldsymbol{\sigma}}^s$ is the traceless symmetric part of the surface extra stress tensor, equal to $\boldsymbol{\sigma}^s - \frac{1}{2}(\mathrm{tr}\boldsymbol{\sigma}^s)\mathbf{P}$, and $\mathbf{P}$ is the surface projection tensor. According to equation (10) the fourth order tensors $\mathbf{L}_{\sigma w}^s$ and $\mathbf{L}_{cd}^s$ are related by

$$\mathbf{L}_{\sigma w}^s = -\mathbf{L}_{cd}^s \tag{15}$$

and the scalars $L_{\sigma\xi}^s$ and $L_{\gamma d}^s$ by

$$L_{\sigma\xi}^s = -L_{\gamma d}^s. \tag{16}$$

When the interface was initially in an isotropic state, and deformations are sufficiently small for effects of anisotropy in the response of the interface to be negligible, the fourth order tensors in (11) and (13) can be written as:

$$\mathbf{L}_{km}^s = 2\tilde{L}_{km}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \Gamma^s, \mathbf{C}^s)\mathbf{P}^{(4)} \tag{17}$$

where $\tilde{L}_{km}^s$ are scalar coefficients, and the fourth order isotropic surface tensor $\mathbf{P}^{(4)}$ is equal to

$$\mathbf{P}^{(4)} \equiv \frac{1}{2}\left(a_{\alpha\mu}a_{\beta\nu} + a_{\alpha\nu}a_{\beta\mu} - a_{\alpha\beta}a_{\mu\nu}\right)\mathbf{a}^\alpha\mathbf{a}^\beta\mathbf{a}^\mu\mathbf{a}^\nu. \tag{18}$$

In this expression $a_{\alpha\beta}$ denote the components of the surface metric tensor [15]. This tensor transforms every second order surface tensor field into a symmetric traceless tangential surface tensor field. With (17) equations (11) and (13) reduce to (for the sake of brevity, omitting the dependencies of the coefficients on the system variables):

$$\bar{\boldsymbol{\sigma}}^s = -[\tilde{L}_{\sigma d}^s\mathrm{tr}\mathbf{D}^s - \tilde{L}_{cd}^s\mathrm{tr}\mathbf{W}^s]\mathbf{P} + 2\tilde{L}_{\sigma d}^s\mathbf{D}^s - 2\tilde{L}_{cd}^s\mathbf{W}^s \tag{19}$$

$$\rho^s \frac{d_s \mathbf{C}^s}{dt} = -[\tilde{L}_{cd}^s \mathrm{tr}\mathbf{D}^s + \tilde{L}_{cw}^s \mathrm{tr}\mathbf{W}^s]\mathbf{P} + 2\tilde{L}_{cd}^s \mathbf{D}^s + 2\tilde{L}_{cw}^s \mathbf{W}^s. \tag{20}$$

Here $\mathbf{D}^s$ is the surface rate of deformation tensor defined by [15]

$$\mathbf{D}^s \equiv \mathbf{P} \cdot \nabla_s \mathbf{v}^s + (\nabla_s \mathbf{v}^s)^T \cdot \mathbf{P} \tag{21}$$

where the superscript-T denotes the transpose of a tensor. Combining equations (12) and (19) we find for the surface extra stress tensor

$$\boldsymbol{\sigma}^s = (L_{\sigma d}^s - \tilde{L}_{\sigma d}^s)\left[\mathrm{tr}\mathbf{D}^s\right]\mathbf{P} + 2\tilde{L}_{\sigma d}^s \mathbf{D}^s - 2\tilde{L}_{cd}^s \mathbf{W}^s$$
$$+([L_{\sigma w}^s - \tilde{L}_{\sigma w}^s]\mathrm{tr}\mathbf{W}^s + L_{\sigma\xi}^s \Xi^s)\mathbf{P}. \tag{22}$$

Note that when contributions of the interfacial microstructure to the surface extra stress can be neglected, and we identify $L_{\sigma d}^s = \varepsilon_d$ and $\tilde{L}_{\sigma d}^s = \varepsilon_s$, where ε_d and ε_s are the surface dilatational and shear viscosities, we recover the familiar Boussinesq model for viscous interfaces [55–57].

Equations (14), (20), and (22) need to be closed with expressions for $\mathbf{W}^s$ and Ξ^s. For this we need to choose an expression for the surface entropy per unit mass in terms of the structural variables. For small departures from equilibrium we can express $\hat{S}^s$ as a Taylor expansion in these variables:

$$\hat{S}^s = \hat{S}_0^s(\hat{U}^s, \hat{\mathcal{A}}, \omega_{(A)}^s) + \frac{1}{2}\alpha_{\gamma\gamma}\left(\Gamma^s\right)^2 + \alpha_{\gamma c}\Gamma^s \mathrm{tr}\mathbf{C}^s + \frac{1}{2}\alpha_{cc}\mathbf{C}^s : \mathbf{C}^s + \mathcal{O}\left([\Gamma^s]^3, [\mathbf{C}^s]^3\right) \tag{23}$$

where $\hat{S}_0^s(\hat{U}^s, \hat{\mathcal{A}}, \omega_{(A)}^s)$ is the entropy of the non-deformed interface, and the α_{ij} ($i, j = \gamma, c$) are coefficients which depend on composition and temperature of the interface. With this expression, and equations (6) and (7), we find up to second order in the structural variables Γ^s and $\mathbf{C}^s$

$$\frac{\Xi^s}{T^s} = \alpha_{\gamma\gamma}\Gamma^s + \alpha_{\gamma c}\mathrm{tr}\mathbf{C}^s \tag{24}$$

$$\frac{\mathbf{W}^s}{T^s} = \alpha_{\gamma c}\Gamma^s \mathbf{P} + \alpha_{cc}\mathbf{C}^s. \tag{25}$$

Substituting these expressions in equations (14), (20), and (22) we find the following set of coupled nonlinear equations for the rheological behavior of a microstructured interface:

$$\boldsymbol{\sigma}^s = (\varepsilon_d - \varepsilon_s)\left[\mathrm{tr}\mathbf{D}^s\right]\mathbf{P} + 2\varepsilon_s \mathbf{D}^s - 2\tilde{L}_{cd}^s T^s \alpha_{cc}\mathbf{C}^s$$
$$+[2L_{\sigma w}^s T^s \alpha_{\gamma c}\Gamma^s + (L_{\sigma w}^s - \tilde{L}_{\sigma w}^s)T^s \alpha_{cc}\mathrm{tr}\mathbf{C}^s]\mathbf{P}$$
$$+L_{\sigma\xi}^s T^s \left(\alpha_{\gamma\gamma}\Gamma^s + \alpha_{\gamma c}\mathrm{tr}\mathbf{C}^s\right)\mathbf{P} \tag{26}$$

$$\rho^s \frac{d_s \Gamma^s}{dt} = 2L_{\gamma d}^s \mathrm{tr}\mathbf{D}_s + 2\left(2L_{\gamma w}^s \alpha_{\gamma c} + L_{\gamma\xi}^s \alpha_{\gamma\gamma}\right)T^s \Gamma^s$$
$$+ \left(L_{\gamma w}^s \alpha_{cc} + L_{\gamma\xi}^s \alpha_{\gamma c}\right)T^s \mathrm{tr}\mathbf{C}_s \tag{27}$$

$$\rho^s \frac{d_s \mathbf{C}^s}{dt} = \tilde{L}_{cd}^s \left(2\mathbf{D}^s - [\mathrm{tr}\mathbf{D}^s]\mathbf{P}\right) + \tilde{L}_{cw}^s \alpha_{cc}T^s \left(2\mathbf{C}^s - [\mathrm{tr}\mathbf{C}^s]\mathbf{P}\right). \tag{28}$$

We see that the expression for the surface extra stress tensor depends on both Γ^s and $\mathbf{C}^s$, and through equations (27) and (28) depends on the time evolution of the

structural variables. The latter equations have a similar structure. The first term on the right hand side of these equations describes the time rate of change of the structural variables as a result of an imposed deformation field. The second term in these equations is a relaxation term, which after cessation of flow will drive the system back to its equilibrium state.

Sagis [49] examined a model of this type for an interface stabilized by anisotropic colloidal particles. The structural scalar parameter was chosen to be the particle concentration (assumed to be constant in time), and the tensorial structural variable was chosen to be the orientation tensor $\mathbf{Q}^s = \langle \mathbf{n}^s \mathbf{n}^s - \frac{1}{2}\mathbf{P} \rangle_s$, where $\mathbf{n}^s$ is a tangential vector field characterizing the orientation of the particles in the interface, and $\langle ... \rangle_s$ denotes a local average over a portion of the interface. When assuming constant coefficients in this model, it predicts thixotropic behavior: exposing the interface to a steady surface shear field causes the effective surface shear viscosity of the interface to decrease in time until a steady state value is reached [49]. With constant coefficients the model did not predict the often observed shear thinning behavior, a decrease of the effective surface shear viscosity with increasing applied shear rate. Such a dependence on shear rate can be included in the model in two ways. The first option is to expand equation (23) to higher orders in both Γ^s and $\mathbf{C}^s$. The second option is to include a dependence on the tensor $\mathbf{Q}^s$ in the expression for the tensorial coefficients in equation (17). These coefficients then take a form equal to

$$\mathbf{L}_{km}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s, \mathbf{Q}^s) = 2L_{km1}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s)\mathbf{P}^{(4)} + 2L_{km2}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s)\mathbf{P}_Q^{(4)}$$
$$+ 2L_{km3}^s(T, \hat{\mathcal{A}}, \omega_{(A)}^s)\mathbf{P}_{QQ}^{(4)} \tag{29}$$

where the tensors $\mathbf{P}_Q^{(4)}$, and $\mathbf{P}_{QQ}^{(4)}$ are given by

$$\mathbf{P}_Q^{(4)} = \frac{1}{2}[Q_{\alpha\mu}^s a_{\beta\nu} + Q_{\alpha\nu}^s a_{\beta\mu} + Q_{\alpha\beta}^s a_{\mu\nu} + a_{\alpha\mu}Q_{\beta\nu}^s$$
$$+ a_{\alpha\nu}Q_{\beta\mu}^s + a_{\alpha\beta}Q_{\mu\nu}^s]\mathbf{a}^\alpha\mathbf{a}^\beta\mathbf{a}^\mu\mathbf{a}^\nu \tag{30}$$

$$\tilde{\mathbf{P}}_{QQ}^{(4)} = \left(\frac{1}{2}\Big[Q_{\alpha\mu}^s Q_{\beta\nu}^s + Q_{\alpha\nu}^s Q_{\beta\mu}^s + Q_{\alpha\beta}^s Q_{\mu\nu}^s\Big] - \frac{1}{4}[a_{\alpha\beta}Q_{\mu\epsilon}^s Q_{\epsilon\nu}^s \right.$$
$$+ a_{\mu\nu}Q_{\alpha\epsilon}^s Q_{\epsilon\beta}^s + a_{\alpha\nu}Q_{\mu\epsilon}^s Q_{\epsilon\beta}^s + a_{\alpha\mu}Q_{\beta\epsilon}^s Q_{\epsilon\nu}^s + a_{\beta\nu}Q_{\alpha\epsilon}^s Q_{\epsilon\mu}^s + a_{\beta\mu}Q_{\alpha\epsilon}^s Q_{\epsilon\nu}^s]$$
$$\left. + \frac{1}{8}[a_{\alpha\mu}a_{\beta\nu}Q_{\delta\epsilon}^s Q_{\epsilon\delta}^s + a_{\alpha\nu}a_{\beta\mu}Q_{\delta\epsilon}^s Q_{\epsilon\delta}^s + a_{\alpha\beta}a_{\mu\nu}Q_{\delta\epsilon}^s Q_{\epsilon\delta}^s]\right)\mathbf{a}^\alpha\mathbf{a}^\beta\mathbf{a}^\mu\mathbf{a}^\nu. \tag{31}$$

Both tensors are traceless, symmetric in the index pairs $\alpha\beta$ and $\mu\nu$, and symmetric under exchange of $\alpha \to \mu$ and $\beta \to \nu$. Sagis showed that with expressions of the form of (29) the resulting model for the surface extra stress tensor does predict shear thinning behavior [49]. However, the model gives realistic predictions for the orientation of the particles only for shear rates $<0.1\,\mathrm{s}^{-1}$. It is not surprising that this model is valid only for small deformation rates. After all, it is based on linear flux-driving force relations, and both the entropy as well as the coefficients in the model are all expanded in Taylor series in terms of the structural variables, around the equilibrium state.

Another drawback of this CIT approach is the high number of coefficients that appear in the constitutive equations. There are no clear procedures on how to determine all these phenomenological coefficients. Finally, the desired coupling of the surface structural variables with the bulk phase structural variables cannot easily be constructed in this framework. An advantage of this framework is that constitutive

equations are easy to construct, without the considerable mathematical effort typically involved in deriving models using the GENERIC framework. The simple models we have shown in this section do provide a lot of insight in how microstructural changes cause nonlinear behavior in surface rheological experiments.

3 Extended irreversible thermodynamics

Since interfacial regions typically have a thickness of only a few nanometers, information on the microstructure of the interface is hard to obtain. If such information is not available a more phenomenological approach can be used. We see in equation (26) that at least for small departures from equilibrium the stress has a linear dependence on the structural tensor $\mathbf{C}^s$. This suggest that rather than the true structural parameters Γ^s and $\mathbf{C}^s$, we choose the trace of the surface extra stress tensor, and its traceless part as independent system variables. This would mean we replace (4) by

$$\hat{S}^s = \hat{S}^s(\hat{U}^s, \hat{\mathcal{A}}, \omega^s_{(1)}, ..., \omega^s_{(N-1)}, \mathrm{tr}\boldsymbol{\sigma}^s, \bar{\boldsymbol{\sigma}}^s). \tag{32}$$

Of course other fluxes could also be included in this expression, but here we will limit ourselves to the rheological fluxes. Equation (32) is the starting point for the extended irreversible thermodynamics framework [58,59], which was recently generalized to multiphase systems with excess variables associated with the dividing surfaces [37].

To construct constitutive equations for the surface extra stress tensor within the EIT framework, we proceed in the same manner presented in the previous section. We take the material time derivative of (32), eliminate the surface material derivatives of $\hat{U}^s$, $\hat{\mathcal{A}}$, and $\omega^s_{(A)}$ using the jump energy balance [15,34], the overall jump mass balance [15,34], and the species jump mass balance [15,34], and substitute the result in (1). We then obtain an expression for the surface entropy production per unit mass of the form

$$\rho^s \hat{\mathcal{E}}^s = \sum_k J^s_k \left(X^s_k - \sum_m \alpha_{km} \frac{d_s J^s_m}{dt} \right) + [\![\mathcal{C}' \left(\mathbf{v} - \mathbf{v}^s \right) \cdot \boldsymbol{\xi} + \sum_k \left(J_k \cdot \boldsymbol{\xi} \right) X_k]\!] \geq 0 \tag{33}$$

where α_{km} is a scalar coefficient, associated with the material time derivative of the surface flux J^s_m. Equation (33) suggests the following form for the constitutive equations for the traceless part of the surface extra stress, and its trace:

$$\bar{\boldsymbol{\sigma}}^s = \bar{\boldsymbol{\sigma}}^s \left(\bar{\mathbf{D}}^s, \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} \right) \tag{34}$$

and

$$\mathrm{tr}\boldsymbol{\sigma}^s = \mathrm{tr}\boldsymbol{\sigma}^s \left(\mathrm{tr}\mathbf{D}^s, \frac{d_s \mathrm{tr}\boldsymbol{\sigma}^s}{dt} \right). \tag{35}$$

Expanding these functionals up to linear order in their arguments, we obtain

$$\bar{\boldsymbol{\sigma}}^s + \tau_s \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} = 2\varepsilon_s \bar{\mathbf{D}}^s \tag{36}$$

$$\mathrm{tr}\boldsymbol{\sigma}^s + \tau_d \frac{d_s \mathrm{tr}\boldsymbol{\sigma}^s}{dt} = 2\varepsilon_d \mathrm{tr}(\nabla_s \mathbf{v}^s) \tag{37}$$

where the coefficients ε_s and ε_d again denote the surface shear and dilatational viscosities, and τ_s and τ_d are the surface shear and dilatational relaxation times. Combining (36) and (37) we find that the surface extra stress tensor is given by

$$\tau_s \frac{d_s\boldsymbol{\sigma}^s}{dt} + \boldsymbol{\sigma}^s + \frac{1}{2}(\tau_d-\tau_s)\mathbf{P}\frac{d_s\mathrm{tr}\boldsymbol{\sigma}^s}{dt} - \frac{1}{2}\tau_s\mathrm{tr}\boldsymbol{\sigma}^s\frac{d_s\mathbf{P}}{dt} = 2\varepsilon_s\mathbf{D}^s + (\varepsilon_d - \varepsilon_s)[\mathrm{tr}\mathbf{D}^s]\mathbf{P}. \quad (38)$$

This is the surface equivalent of the linear viscoelastic fluid model, also referred to as linear Maxwell fluid model. This type of model, or simplified versions of it, are often used in the analysis of surface rheological experiments [1]. The simplified versions are usually straightforward generalizations of the 3D linear Maxwell model to 2D interfaces, and tend to neglect the fact the stress response may have contributions from both shear and dilatational deformations, as illustrated by equation (38). This is particularly true for dilatational experiments using Langmuir troughs or oscillating bubble methods [1].

For microstructured interfaces, equations (36) and (37) are not particularly useful, since these linear equations are not capable of describing the highly nonlinear response of these interfaces. We can however make several simple modifications to these expressions to make them nonlinear. Let us first consider (36). The surface material derivative of the stress tensor appearing in this equation is not invariant under orthogonal changes of the frame of observation. We can alleviate this problem by replacing the surface material derivative by an invariant derivative such as the co-rotational or upper-convective derivatives. These are defined as, respectively

$$\overset{\triangledown}{\delta}\,\bar{\boldsymbol{\sigma}}^s = \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} - \boldsymbol{\Omega}^s\cdot\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s\cdot\boldsymbol{\Omega}^s \quad (39)$$

$$\overset{\square}{\delta}\,\bar{\boldsymbol{\sigma}}^s = \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} - ([\nabla_s\mathbf{v}^s]^T\cdot\mathbf{P})\cdot\bar{\boldsymbol{\sigma}}^s - \bar{\boldsymbol{\sigma}}^s\cdot(\mathbf{P}\cdot\nabla_s\mathbf{v}^s). \quad (40)$$

Here the surface vorticity tensor is defined as

$$\boldsymbol{\Omega}^s = \frac{1}{2}(\mathbf{P}\cdot\nabla_s\mathbf{v}^s - [\nabla_s\mathbf{v}^s]^T\cdot\mathbf{P}). \quad (41)$$

If we choose to use an upper-convective derivative, (36) is modified to

$$\tau_s\overset{\square}{\delta}\,\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s. \quad (42)$$

This is the surface rheological equivalent of the upper-convected Maxwell model. A further modification we can make to this model is, to replace it by

$$\tau_s\overset{\square}{\delta}\,\bar{\boldsymbol{\sigma}}^s + \mathbf{B}^s\cdot\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s \quad (43)$$

where the anisotropic surface mobility tensor $\mathbf{B}^s$ is defined as

$$\mathbf{B}^s = \mathbf{P} + \alpha_s\left(\mathbf{C}^s - \mathbf{P}\right) = (1 - \alpha_s)\mathbf{P} + \alpha_s\mathbf{C}^s \quad (44)$$

where α_s is a dimensionless parameter, and $\mathbf{C}^s$ is again a configuration tensor, assumed to be related to the surface extra stress tensor by

$$\boldsymbol{\sigma}^s = \frac{\varepsilon_s}{\tau_s}\left(\mathbf{C}^s - \mathbf{P}\right). \quad (45)$$

Substituting (44) and (45) in (43) we obtain

$$\tau_s\overset{\square}{\delta}\,\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s + \frac{\alpha_s\tau_s}{\varepsilon_s}\bar{\boldsymbol{\sigma}}^s\cdot\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s \quad (46)$$

which is the surface version of the single mode Giesekus model [60]. In a similar manner we can extend equation (37) to find

$$\tau_d \left(\frac{d_s \mathrm{tr}\boldsymbol{\sigma}^s}{dt} \right) + \mathrm{tr}\boldsymbol{\sigma}^s + \frac{\alpha_d \tau_d}{\varepsilon_d} \left(\mathrm{tr}\boldsymbol{\sigma}^s \right)^2 = 2\varepsilon_d \mathrm{tr}\mathbf{D}^s. \tag{47}$$

Using the entropy balance we can show that the coefficients α_s and α_d should satisfy $0 \leq \alpha_d, \alpha_s \leq 1$ [37]. The Giesekus model and its multi-mode generalizations have been used successfully to model the rheological behavior of 3D bulk phases with a complex microstructure, such as polymer melts and polymer solutions. It has so far not found widespread application in surface rheology, in spite of the significant number of experimental studies on polymer stabilized interfaces, currently reported in the literature on surface rheology [1].

When comparing the constitutive equations we derived with the EIT framework to those in the previous section derived within the CIT framework, we see that the former are much simpler and contain fewer coefficients, which need to be determined by experiment. However, these more phenomenological EIT models do not provide a direct coupling to the microstructure of the surface, and therefore provide less fundamental insight on the structural rearrangements responsible for the highly nonlinear rheological behavior of microstructured interfaces. Moreover, just like in the CIT models, the coupling of the surface stresses with stresses in the adjoining bulk phases is not present in these models. In the next section we will show how to incorporate such a coupling within the ERT framework.

4 Extended rational thermodynamics

In the recent literature on nonequilibrium thermodynamics there are a number of frameworks which are commonly referred to as extended rational thermodynamics. A well know version is the one developed by Liu and Müller [61], and Liu [62], who add balance equations for the momentum flux density $\rho\mathbf{vv}$, and energy flux density $\rho\mathbf{vv}\cdot\mathbf{v}$, to the set of classical balance equations for the density, momentum density, and energy density. This approach is inspired by kinetic theory.

Here we will use a simpler version of ERT, suggested by Lebon and Rubi [63], Jou and Perez-Garcia [64], Lebon and Jou [65], Boukary and Lebon [66], and Lebon and Boukary [67]. In this version of ERT, which was recently generalized to multiphase systems [38], the total traceless extra stress is defined as

$$\boldsymbol{\Sigma} \equiv \int_R \rho\bar{\boldsymbol{\sigma}} \, dV + \int_\Sigma \rho^s \bar{\boldsymbol{\sigma}}^s \, dA. \tag{48}$$

and the total trace of the extra stress tensor is defined as

$$\Theta \equiv \int_R \rho\mathrm{tr}\boldsymbol{\sigma} \, dV + \int_\Sigma \rho^s \mathrm{tr}\boldsymbol{\sigma}^s \, dA. \tag{49}$$

Here R denotes the bulk domain of the system, Σ is the domain of the interior interfaces, and dV and dA denote an integration over respectively volume, and area. Subsequently it is assumed the time rate of change of the total traceless extra stress is equal to a flux term through the boundaries of the system, and a source term, describing generation in the interior of the body. For the traceless part of the total extra stress, this assumption leads to

$$\frac{d\boldsymbol{\Sigma}}{dt} = -\int_S \mathbf{J}_\sigma\cdot\mathbf{n} \, dA + \int_R \mathbf{S}_\sigma \, dV - \int_C \mathbf{J}_\sigma^s\cdot\boldsymbol{\mu} \, ds + \int_\Sigma \mathbf{S}_\sigma^s \, dA \tag{50}$$

where S is the outer bounding surface of the system, C is the line of intersection between Σ and S, and $\mathbf{J}_\sigma$ is a third order tensor field, describing the flux of the symmetric traceless part of the extra stress tensor to the bulk phase through the bounding surface. The second order tensor field $\mathbf{S}_\sigma$ is the source term for the symmetric traceless part of the extra stress tensor in the bulk phase. The third order tangential surface tensor $\mathbf{J}_\sigma^s$ and second order tangential surface tensor $\mathbf{S}_\sigma^s$ represent the flux and source term for the traceless symmetric part of the surface extra stress tensor. The vector $\mathbf{n}$ is the outwardly directed unit normal vector on S, and $\boldsymbol{\mu}$ is the unit vector normal to the curve C, tangential to Σ, and directed outwardly from the system. The symbol ds denotes an integration over arc length.

Using the transport theorem for multiphase systems [15], the divergence theorem, and the surface divergence theorem, we find the following balance equations for the traceless symmetric parts of the extra stress tensor and the surface extra stress tensor:

$$\rho \frac{d_b \bar{\boldsymbol{\sigma}}}{dt} = -\nabla \cdot \mathbf{J}_\sigma + \mathbf{S}_\sigma \tag{51}$$

$$\rho^s \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} = -\nabla_s \cdot \mathbf{J}_\sigma^s + \mathbf{S}_\sigma^s - [\![\rho \left(\bar{\boldsymbol{\sigma}} - \bar{\boldsymbol{\sigma}}^s \right) \left(\mathbf{v} - \mathbf{v}^s \right) \cdot \boldsymbol{\xi} + \mathbf{J}_\sigma \cdot \boldsymbol{\xi}]\!]. \tag{52}$$

The material derivative appearing in equation (51) is defined as [15]

$$\frac{d_b \psi}{dt} = \frac{\partial \psi}{\partial t} + (\nabla \psi) \cdot \mathbf{v}. \tag{53}$$

The operator ∇ denotes the three dimensional gradient operator.

The jump terms give us the explicit connection between the surface fluxes, and their corresponding fluxes in the adjacent bulk phases. In (52) the first contribution to the jump term represents the convective transfer of $\bar{\boldsymbol{\sigma}}$ from the bulk to the interface, and the second term represents the flux of $\bar{\boldsymbol{\sigma}}$ from the bulk to the interface. The physical interpretation of these contributions will become more clear when we discuss specific forms of the balances for the extra stresses.

Applying the same approach to the traces of the extra stress tensors we obtain

$$\rho \frac{d_b \mathrm{tr} \boldsymbol{\sigma}}{dt} = -\nabla \cdot \mathbf{j}_{\mathrm{tr}\sigma} + S_{\mathrm{tr}\sigma} \tag{54}$$

$$\rho^s \frac{d_s \mathrm{tr} \boldsymbol{\sigma}^s}{dt} = -\nabla_s \cdot \mathbf{j}_{\mathrm{tr}\sigma}^s + S_{\mathrm{tr}\sigma}^s - [\![\rho \left(\mathrm{tr}\boldsymbol{\sigma} - \mathrm{tr}\boldsymbol{\sigma}^s \right) \left(\mathbf{v} - \mathbf{v}^s \right) \cdot \boldsymbol{\xi} + \mathbf{j}_{\mathrm{tr}\sigma} \cdot \boldsymbol{\xi}]\!]. \tag{55}$$

Here the vectors $\mathbf{j}_{\mathrm{tr}\sigma}$ and $\mathbf{j}_{\mathrm{tr}\sigma}^s$ denote the flux vectors for the trace of the extra stress tensor and trace of the surface extra stress tensor. Finally, the scalars $S_{\mathrm{tr}\sigma}$ and $S_{\mathrm{tr}\sigma}^s$ are the source terms for the trace of the extra stress tensor and trace of the surface extra stress tensor.

To construct expressions for the fluxes and sources in the above equations, we proceed in the same manner as we did in the CIT and EIT frameworks. We derive an expression for the bulk and surface entropy production, and use those balances to guide us in the construction of the constitutive relations for the fluxes and sources. Proceeding in this manner we find for the surface fluxes [38]

$$\mathbf{J}_\sigma^s = \mathbf{J}_\sigma^s \left(\nabla_s \bar{\boldsymbol{\sigma}}^s \right) \tag{56}$$

$$\mathbf{j}_{\mathrm{tr}\sigma}^s = \mathbf{j}_{\mathrm{tr}\sigma}^s \left(\nabla_s \mathrm{tr} \boldsymbol{\sigma}^s \right) \tag{57}$$

and for the surface sources

$$\mathbf{S}_\sigma^s = \mathbf{S}_\sigma^s \left(\bar{\boldsymbol{\sigma}}^s, \nabla_s \mathbf{v}^s \right) \tag{58}$$

$$S_{\text{tr}\sigma}^s = S_{\text{tr}\sigma}^s \left(\text{tr}\boldsymbol{\sigma}^s, \text{tr}[\nabla_s \mathbf{v}^s]\right). \tag{59}$$

Expanding these functionals up to linear order in their arguments, we find

$$\mathbf{J}_\sigma^s = \alpha_J \nabla_s \bar{\boldsymbol{\sigma}}^s \tag{60}$$

$$\mathbf{j}_{\text{tr}\sigma}^s = \alpha_j \nabla_s \left[\text{tr}\boldsymbol{\sigma}^s\right] \tag{61}$$

$$\mathbf{S}_\sigma^s = -\frac{\rho^s}{\tau_s} \bar{\boldsymbol{\sigma}}^s + \frac{2\rho^s \varepsilon_s}{\tau_s} \bar{\mathbf{D}}^s \tag{62}$$

$$S_{\text{tr}\sigma}^s = -\frac{\rho^s}{\tau_d} \text{tr}\boldsymbol{\sigma}^s + \frac{\rho^s \varepsilon_d}{\tau_d} \text{tr}[\nabla_s \mathbf{v}^s] \tag{63}$$

where α_J and α_j are scalar coefficients, and again, ε_s is the surface shear viscosity, τ_s is the surface shear relaxation time, ε_d is the surface dilatational viscosity, and τ_d is the surface dilatational relaxation time. Substituting these expressions in equations (52) and (55), we obtain

$$\rho^s \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} + \frac{\rho^s}{\tau_s} \bar{\boldsymbol{\sigma}}^s = -\alpha_J \nabla_s^2 \bar{\boldsymbol{\sigma}}^s - \nabla_s \alpha_J \cdot \nabla_s \bar{\boldsymbol{\sigma}}^s$$
$$+ \frac{2\rho^s \varepsilon_s}{\tau_s} \bar{\mathbf{D}}^s - \left[\!\left[\rho \left(\bar{\boldsymbol{\sigma}} - \bar{\boldsymbol{\sigma}}^s\right) \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi} + \mathbf{J}_\sigma \cdot \boldsymbol{\xi} \right]\!\right] \tag{64}$$

and

$$\rho^s \frac{d_s \text{tr}\boldsymbol{\sigma}^s}{dt} + \frac{\rho^s}{\tau_d} \text{tr}\boldsymbol{\sigma}^s = -\alpha_j \nabla_s^2 \left[\text{tr}\boldsymbol{\sigma}^s\right] - \nabla_s \alpha_j \cdot \nabla_s \left[\text{tr}\boldsymbol{\sigma}^s\right]$$
$$+ \frac{\rho^s \varepsilon_d}{\tau_d} \text{tr}[\nabla_s \mathbf{v}^s] - \left[\!\left[\rho \left(\text{tr}\boldsymbol{\sigma} - \text{tr}\boldsymbol{\sigma}^s\right) \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi} + \mathbf{j}_{\text{tr}\sigma} \cdot \boldsymbol{\xi} \right]\!\right]. \tag{65}$$

To complete these balances we need to specify the constitutive relations for the bulk fluxes appearing in the jump terms. Again using the entropy balance as a guide, we assume these to be given by

$$\mathbf{J}_\sigma^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = k_\sigma^{(I)} (\bar{\boldsymbol{\sigma}}^{(I)} - \bar{\boldsymbol{\sigma}}^s) - \rho^{(I)} \bar{\boldsymbol{\sigma}}^{(I)} \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi}^{(I,J)} \tag{66}$$

and

$$\mathbf{j}_{\text{tr}\sigma}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = k_{\text{tr}\sigma}^{(I)} (\text{tr}\boldsymbol{\sigma}^{(I)} - \text{tr}\boldsymbol{\sigma}^s) - \rho^{(I)} \text{tr}\boldsymbol{\sigma}^{(I)} \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi}^{(I,J)} \tag{67}$$

where k_σ and $k_{\text{tr}\sigma}$ are scalar coefficients. This gives us the final form of our balance equations for the traceless part of the surface extra stress tensor, and the trace of this tensor:

$$\rho^s \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} = -\frac{\rho^s}{\tau_s} \bar{\boldsymbol{\sigma}}^s - \alpha_3 \nabla_s^2 \bar{\boldsymbol{\sigma}}^s - \nabla_s \alpha_3 \cdot \nabla_s \bar{\boldsymbol{\sigma}}^s$$
$$+ \frac{2\rho^s \varepsilon_s}{\tau_s} \bar{\mathbf{D}}^s + \left[\!\left[\rho \bar{\boldsymbol{\sigma}}^s \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi} - k_\sigma \left(\bar{\boldsymbol{\sigma}} - \bar{\boldsymbol{\sigma}}^s\right) \right]\!\right] \tag{68}$$

$$\rho^s \frac{d_s \text{tr}\boldsymbol{\sigma}^s}{dt} = -\frac{\rho^s}{\tau_d} \text{tr}\boldsymbol{\sigma}^s - \alpha_4 \nabla_s^2 \left[\text{tr}\boldsymbol{\sigma}^s\right] - \nabla_s \alpha_4 \cdot \nabla_s \left[\text{tr}\boldsymbol{\sigma}^s\right]$$
$$+ \frac{\rho^s \varepsilon_d}{\tau_d} \text{tr}[\nabla_s \mathbf{v}^s] + \left[\!\left[\rho \text{tr}\boldsymbol{\sigma}^s \left(\mathbf{v} - \mathbf{v}^s\right) \cdot \boldsymbol{\xi} - k_{\text{tr}\sigma} \left(\text{tr}\boldsymbol{\sigma} - \text{tr}\boldsymbol{\sigma}^s\right) \right]\!\right]. \tag{69}$$

Looking at the structure of these equations, we see that they have the form of a relaxation-diffusion equation. In both equations the first term on the right hand side is a relaxation term. When the flow is stopped these terms are responsible for the relaxation of the stress back to is equilibrium value (typically zero). The second and third terms on the right hand side of both equations are important when an imposed deformation field causes inhomogeneities in the stress fields, for example, as a result of gradients in the structural elements that stabilize the interface. Examples of such gradients can be seen in particle stabilized droplets deformed in a flow field, where particles tend to accumulate at the ends of a spheroidally shaped droplet. The diffusive terms in both equations tend to smoothen any gradients in the stress field, that originate from the imposed deformation field. Terms like these arise naturally in the ERT framework, and are much harder to incorporate in the CIT and EIT frameworks. The forth term on the right hand side of these equations represents the applied deformation, driving the interface out of equilibrium. The boldface bracket terms couple the surface stresses to the stresses in the adjoining bulk phases, and these represent a simple phenomenological example of this type of coupling, through the stress tensors, rather than through the microstructural variables. They describe the "transfer of stress" between the bulk phases and the interface. As we see, these coupling terms arise naturally in the ERT framework, whereas in the CIT and EIT these couplings did not appear.

Let us now take a closer look at equation (68), and assume that the surface stress diffusion coefficient in this expression is independent of position on the interface. In addition, we replace the surface material derivative on the left hand side of this equation by an upper-convected derivative (since the surface material derivative of a tensor is not invariant under orthogonal changes of the frame of observation). We then find

$$\rho^s \overset{\square}{\delta} \bar{\boldsymbol{\sigma}}^s = -\frac{\rho^s}{\tau_s}\bar{\boldsymbol{\sigma}}^s - \alpha_3\nabla_s^2\bar{\boldsymbol{\sigma}}^s + \frac{2\rho^s\varepsilon_s}{\tau_s}\bar{\mathbf{D}}^s + \left[\!\left[\rho\bar{\boldsymbol{\sigma}}^s\left(\mathbf{v}-\mathbf{v}^s\right)\cdot\boldsymbol{\xi} - k_\sigma\left(\bar{\boldsymbol{\sigma}}-\bar{\boldsymbol{\sigma}}^s\right)\right]\!\right]. \quad (70)$$

If we now replace $\bar{\boldsymbol{\sigma}}^s$ in the first term on the right hand side of (70) by $\mathbf{B}^s\cdot\bar{\boldsymbol{\sigma}}^s$, where $\mathbf{B}^s$ is again the surface mobility tensor defined in equation (44), we obtain

$$\rho^s \overset{\square}{\delta} \bar{\boldsymbol{\sigma}}^s = -\frac{\rho^s}{\tau_s}\bar{\boldsymbol{\sigma}}^s - \frac{\rho^s\alpha_s}{\varepsilon_s}\bar{\boldsymbol{\sigma}}^s\cdot\bar{\boldsymbol{\sigma}}^s - \alpha_3\nabla_s^2\bar{\boldsymbol{\sigma}}^s$$
$$+\frac{2\rho^s\varepsilon_s}{\tau_s}\bar{\mathbf{D}}^s + \left[\!\left[\rho\bar{\boldsymbol{\sigma}}^s\left(\mathbf{v}-\mathbf{v}^s\right)\cdot\boldsymbol{\xi} - k_\sigma\left(\bar{\boldsymbol{\sigma}}-\bar{\boldsymbol{\sigma}}^s\right)\right]\!\right]. \quad (71)$$

We see that we have now obtained a generalization of the surface Giesekus model we derived in the previous section. This version accounts for the smoothing of inhomogeneities in the surface stress field by a diffusive process, and introduces a coupling of the surface stresses with the stresses in the adjoining bulk phases. So far this type of equation has not been applied to the analysis of surface rheological data, so its true value still needs to be established. We have seen that the incorporation of these additional effects in the time evolution of the surface stresses is relatively straightforward within the ERT framework. This type of model satisfies most of the requirements we outlined in the introduction. A drawback of this approach is that the model is purely phenomenological, since it produces time evolution equations for the surface stresses, and not for the underlying microstructural changes responsible for this stress evolution. To find similar models, but in terms of microstructural tensors we can use the GENERIC framework, discussed in the next section.

5 GENERIC

General Equation for the Nonequilibrium Reversible Irreversible Coupling (GENERIC) is a nonequilibrium thermodynamic framework in which the dynamics of a system is expressed by a single equation. The framework was developed in the mid 90s of the previous century by Grmela and Öttinger [68, 69], and recently extended to multiphase systems with inviscid interfaces [39]. Sagis extended it to systems with viscous interfaces [40], and systems with interfaces with a complex microstructure [1, 41].

For multiphase systems with a complex microstructure, the GENERIC takes the following form [39–41]

$$\frac{dA}{dt} = \{A, E\} + [A, S] + \{A, E\}^{\mathrm{mint}}. \tag{72}$$

Here A is an arbitrary observable of the system (for example its total mass, or its total energy), the first term on the right hand side is a Poisson bracket, describing the reversible part of the dynamics, and the second term (square brackets) describes the irreversible or dissipative contributions to the dynamics of the system. E is the total Hamiltonian of the system, and S is its total entropy. The term $\{A, E\}^{\mathrm{mint}}$ is the moving interface normal transfer term, a term that is needed to guarantee consistency of the GENERIC with the chain rule of functional calculus, when moving interfaces are present in the system [39]. The Poisson bracket is defined by

$$\{A, B\} \equiv \frac{\delta A(\mathbf{x})}{\delta \mathbf{x}} \cdot \mathbf{L} \cdot \frac{\delta B(\mathbf{x})}{\delta \mathbf{x}} \tag{73}$$

where $\mathbf{L}$ is the Poisson matrix, and $\mathbf{x}$ denotes a vector whose components are the independent system variables. The derivatives in this expression are functional derivatives. The Poisson bracket must satisfy the following two conditions:

$$\{A, B\} = -\{B, A\} \tag{74}$$

$$\{A, \{B, C\}\} + \{C, \{A, B\}\} + \{B, \{C, A\}\} = 0. \tag{75}$$

The first condition implies the bracket (and hence $\mathbf{L}$) is antisymmetric, and the second condition is referred to as the Jacobi identity. The Poisson bracket is further restricted by the degeneracy conditions

$$\{S, B\} + \{S, B\}^{\mathrm{mint}} = 0 \tag{76}$$

$$\{\mathcal{M}, B\} + \{\mathcal{M}, B\}^{\mathrm{mint}} = 0 \tag{77}$$

where $\mathcal{M}$ is the total momentum of the system. The dissipative bracket is defined as

$$[A, B] \equiv \frac{\delta A(\mathbf{x})}{\delta \mathbf{x}} \cdot \mathbf{M} \cdot \frac{\delta B(\mathbf{x})}{\delta \mathbf{x}} \tag{78}$$

where $\mathbf{M}$ is a symmetric positive semi-definite matrix. The dissipative bracket must be constructed in such a way that

$$[A, B] = [B, A] \tag{79}$$

$$[A, A] \geq 0 \tag{80}$$

which ensures that $\mathbf{M}$ is indeed a symmetric positive semi-definite matrix.

An important step in every GENERIC model is the selection of the independent system variables. For a multiphase material in which both bulk phases and interfaces have a complex microstructure, we will choose the set of system variables to be

$$\left\{ \rho, \mathbf{m}, \bar{U}^*, \rho_{(1)}, ..., \rho_{(N-1)}, \bar{\Gamma}, \mathbf{C}, \rho^s, \mathbf{m}^s, \bar{U}^{s*}, \rho^s_{(1)}, ..., \rho^s_{(N-1)}, \bar{\Gamma}^s, \mathbf{C}^s \right\} \qquad (81)$$

where $\mathbf{m} = \rho \mathbf{v}$ is the momentum density, $\rho_{(J)}$ $(J = 1, ..., N)$ are the mass densities of the individual components in the bulk phase, $\bar{\Gamma}$ is a scalar density characterizing the microstructure of the bulk phases, $\mathbf{C}$ is a tensorial variable describing the microstructure of the bulk phase, $\mathbf{m}^s = \rho^s \mathbf{v}^s$ is the surface momentum density, $\rho^s_{(J)}$ $(J = 1, ..., N)$ are the mass densities of the individual components in the interface, $\bar{\Gamma}^s$ is a scalar density characterizing the microstructure of the interfaces, and $\mathbf{C}^s$ is again a tensorial variable describing the microstructure of the interfaces. The symbol $\bar{U}^* = \bar{U} + \bar{U}_c$ is the total internal energy per unit mass of the bulk phase, split in a non-configurational contribution $\bar{U}$ and a configurational contribution $\bar{U}_c$. The surface equivalent of this variable is $\bar{U}^{s*} = \bar{U}^s + \bar{U}^s_c$.

Next we assume that the Hamiltonian and total entropy of the system is given by

$$E = \int_R \left(\frac{\mathbf{m}^2}{2\rho} + \bar{U}(\mathbf{r}) + \bar{U}_c(\rho(\mathbf{r}), \bar{\Gamma}^s(\mathbf{r}), \mathbf{C}^s(\mathbf{r})) \right) dV$$
$$+ \int_\Sigma \left(\frac{(\mathbf{m}^s)^2}{2\rho^s} + \bar{U}^s(\mathbf{r}) + \bar{U}^s_c(\rho^s(\mathbf{r}), \bar{\Gamma}^s(\mathbf{r}), \mathbf{C}^s(\mathbf{r})) \right) dA \qquad (82)$$

$$S = \int_R [\bar{S}\left(\rho, \bar{U}, \rho_{(1)}, ..., \rho_{(N-1)} \right) + \rho \hat{S}_c \left(\bar{\Gamma}(\mathbf{r}), \mathbf{C}(\mathbf{r}) \right)] dV$$
$$+ \int_\Sigma [\bar{S}^s \left(\rho^s, \bar{U}^s, \rho^s_{(1)}, ..., \rho^s_{(N-1)} \right) + \rho^s \hat{S}^s_c(\bar{\Gamma}^s(\mathbf{r}), \mathbf{C}^s(\mathbf{r}))] dA \qquad (83)$$

where the parameter $\hat{S}_c$ is the configurational contribution to the entropy per unit mass, $\hat{S} = \bar{S}/\rho$, and $\hat{S}^s_c$ denotes the contribution of the microstructure of the interface to the surface entropy per unit mass, $\hat{S}^s$. We will assume that the separation in terms of bulk and interfacial contributions introduced in (82) and (83), can also be applied to the observable A in equation (72), which implies that this observable can by written as

$$A = \int_R a\,dV + \int_\Sigma a^s\,dA \qquad (84)$$

where a denotes the density of A in the bulk phase, and a^s the surface density of A in the interface. With such an expression for the observable A, the left hand side of equation (72) reduces to

$$\frac{dA}{dt} = \int_R \frac{\partial a}{\partial x_j} \frac{\partial x_j}{\partial t}\,dV + \int_\Sigma \frac{\partial a^s}{\partial x^s_j} \frac{\partial x^s_j}{\partial t}\,dA$$
$$- \int_\Sigma \left(2H a^s \mathbf{v}^s \cdot \boldsymbol{\xi} + \frac{\partial a^s}{\partial x^s_j} \nabla_s x^s_j \cdot \mathbf{u} + [\![a \mathbf{v}^s \cdot \boldsymbol{\xi}]\!] \right) dA \qquad (85)$$

where x_j denote the bulk variables from the set of independent system variables, defined in (81), x^s_j are the surface variables, H is the mean curvature of the interface, and $\mathbf{u}$ is the speed of displacement of the interface [15].

With equations (73), (78), and (81) through (83) we can construct the Poisson and dissipative brackets appearing in (72), consistent with equations (74) through (77), (79), and (80). In view of the length of these expressions we will not repeat these here, and instead refer the reader to references [39–41, 70]. Substituting (85) in (72), and using the expressions for the Poisson and dissipative brackets, we obtain, after collecting all terms on the left hand side of (72) and integrating 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 (72) 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 [39, 40]. Here we will focus only on the constitutive equations for the surface extra stress tensor generated by this approach. For the complete set of balance equations, consistency requirements and constitutive relations produced by (72) we refer the reader to reference [70]. The total surface extra stress tensor for an interface with complex microstructure described by (72), is given by:

$$\boldsymbol{\sigma}_{\text{tot}}^s = (\varepsilon_d - \varepsilon_s)\left[\nabla_s \cdot \mathbf{v}^s\right]\mathbf{P} + 2\varepsilon_s \mathbf{D}^s + 2\mathbf{C}^s \cdot \frac{\partial \bar{F}_c^s}{\partial \mathbf{C}^s} + \mathbf{G}^s \frac{\partial \bar{F}_c^s}{\partial \bar{\Gamma}^s}. \tag{86}$$

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. The tensor $\mathbf{G}^s$ describes the coupling of the scalar structural field $\bar{\Gamma}^s$ with the surface velocity gradient, and a typical choice for this tensor is [43]

$$\mathbf{G}^s = g_1^s \mathbf{C}^s + g_2^s \mathbf{I} + g_3^s \left(\mathbf{C}^s\right)^{-1} \tag{87}$$

where the coefficients g_i^s, are functions of $\bar{\Gamma}^s$, and the three invariants of $\mathbf{C}^s$. The first two terms in equation (86) represent the contributions from the bare interface to the total surface extra stress tensor, and this contribution is described by a linear Boussinesq model. For interfaces stabilized by colloidal particles or polymers, in the high surface loading regime, these contributions will be negligible and can be omitted.

To complete the model we need time evolution equations for the structural variables. For the GENERIC we introduced here, the jump balance for $\bar{\Gamma}^s$ takes the form [70]

$$\begin{aligned}
\frac{d_s \bar{\Gamma}^s}{dt} &+ \bar{\Gamma}^s \nabla_s \cdot \mathbf{v}^s - \mathbf{G}^s : \nabla_s \mathbf{v}^s - 2H\mathbf{v}^s \cdot \mathbf{G}^s \cdot \boldsymbol{\xi} + \frac{R_1^s}{T^s} \frac{\partial \bar{F}_c^s}{\partial \bar{\Gamma}^s} \\
&- \nabla_s \cdot \left[\mathbf{D}_{\bar{\Gamma}}^s \cdot \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}_c^s}{\partial \bar{\Gamma}^s}\right)\right] - \left[\!\!\left[\boldsymbol{\Phi}^s : \mathbf{J}_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}}\right.\right.\right. \\
&\left.\left.\left. - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}_c^s}{\partial \bar{\Gamma}^s} + \frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} - \frac{1}{T^s} \frac{\partial \bar{F}_c^s}{\partial \mathbf{C}^s}\right)\right]\!\!\right] = 0
\end{aligned} \tag{88}$$

where R_1^s is a scalar characterizing relaxation processes for $\bar{\Gamma}^s$, $\mathbf{D}_{\bar{\Gamma}}^s$ is a second order surface tensor, describing diffusion process for $\bar{\Gamma}^s$, $\mathbf{J}_{\Gamma C}$ is a forth order tensor field quantifying the transfer of $\bar{\Gamma}$, and $\mathbf{C}$ between the interface and the adjoining bulk phases, and $\boldsymbol{\Phi}^s$ is second order surface tensor, describing the coupling between the transfer of these two variables. From dimensional arguments we find that this tensor

satisfies $\boldsymbol{\Phi}^s \sim \bar{\Gamma}^s (\mathbf{C}^s)^{-1}$. This type of coupling is important in systems where $\bar{\Gamma}^s$ represents a surface concentration, and particles or polymer segments first have to adopt a preferred orientation, before they can adsorb to an interface. 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 = I, II) [70]

$$
\begin{aligned}
\boldsymbol{\Phi}^{\mathrm{M}} \; &: \; \mathbf{J}^{\mathrm{M}}_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}^{\mathrm{M}}}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \bar{\Gamma}^{\mathrm{M}}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \mathbf{C}^{\mathrm{M}}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \\
&= -\bar{\Gamma}^{\mathrm{M}} \left(\mathbf{v}^{\mathrm{M}} - \mathbf{v}^s \right) \cdot \boldsymbol{\xi} + \mathbf{D}^{\mathrm{M}}_{\Gamma} \cdot \nabla \left(\frac{1}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \bar{\Gamma}^{\mathrm{M}}} \right) \cdot \boldsymbol{\xi}^{\mathrm{M}}.
\end{aligned}
\tag{89}
$$

These consistency requirements (one for each adjoining bulk phase) are boundary conditions that couple equation (88) to the corresponding equations for the bulk variables $\bar{\Gamma}$ in the adjoining bulk phases. Here $\boldsymbol{\Phi}^{\mathrm{M}}$ is the bulk coupling tensor in phase M, proportional to $\bar{\Gamma}(\mathbf{C})^{-1}$, and $\mathbf{D}^{\mathrm{M}}_{\Gamma}$ is a second order tensor field describing diffusion processes for $\bar{\Gamma}$ in bulk phase M.

For the jump balance for the surface tensorial structural variable we find [70]:

$$
\begin{aligned}
&\overset{\square}{\delta}_s \, \mathbf{C}^s - 4H \mathbf{v}^s \cdot \mathbf{C}^s \boldsymbol{\xi} + \mathbf{R}^s_2 : \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) - \nabla_s \cdot \left[\mathbf{D}^s_C \vdots \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \right] \\
&\qquad - \left[\mathbf{J}_{\Gamma C} : \left(\frac{\boldsymbol{\Phi}}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T} \frac{\partial \bar{F}_c}{\partial \mathbf{C}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \right] = 0
\end{aligned}
\tag{90}
$$

where $\overset{\square}{\delta}_s \, \mathbf{C}^s$ denotes the upper convected surface derivative, defined in Section 3. The forth order surface tensor $\mathbf{R}^s_2$ characterizes relaxation processes for the tensor variable $\mathbf{C}^s$, and the sixth order surface tensor $\mathbf{D}^s_C$ is associated with diffusion processes of $\mathbf{C}^s$. The triple dots in the last term of the first line of this expression denote a triple contraction. The consistency requirements for transfer of the tensorial structural variable between bulk phases and interface take the form (M = I, II) [70]

$$
\begin{aligned}
\mathbf{J}^{\mathrm{M}}_{\Gamma C} \; &: \; \left(\frac{\boldsymbol{\Phi}^{\mathrm{M}}}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \bar{\Gamma}^{\mathrm{M}}} - \frac{\boldsymbol{\Phi}^s}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} + \frac{1}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \mathbf{C}^{\mathrm{M}}} - \frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \mathbf{C}^s} \right) \\
&= \mathbf{D}^{\mathrm{M}}_C \vdots \nabla \left(\frac{1}{T^{\mathrm{M}}} \frac{\partial \bar{F}^{\mathrm{M}}_c}{\partial \mathbf{C}^{\mathrm{M}}} \right) \cdot \boldsymbol{\xi}^{\mathrm{M}}
\end{aligned}
\tag{91}
$$

where $\mathbf{D}^{\mathrm{M}}_C$ is a sixth order tensor field associated with diffusive processes for $\mathbf{C}$ in bulk phase M. Again, equation (91) couples (90) to the corresponding equations for $\mathbf{C}$ in the adjoining bulk phases.

With equations (86) through (91), supplemented with equations for the bulk structural variables [70], we have a general model for the rheological behavior of interfaces in multiphase materials with a complex microstructure. By choosing specific forms for the configurational Helmholtz free energies $\bar{F}_c$ and $\bar{F}^s_c$, the scalar R^s_1, and the tensors $\mathbf{R}^s_2$, $\mathbf{D}_{\Gamma}$, $\mathbf{D}^s_{\Gamma}$, $\mathbf{D}_C$, $\mathbf{D}^s_C$, and $\mathbf{J}_{\Gamma C}$, we can construct models for specific systems, such as materials with particle or polymer stabilized interfaces.

A simple example of such a specific model was recently presented in reference [71], for a system with simple Newtonian bulk phases, and interfaces stabilized by rigid anisotropic colloidal particles, in the dilute surface concentration regime. The relevant structural variables for this system are $\bar{\Gamma}^s = \rho^s_p$, where ρ^s_p is the surface mass density of the particles, and $\mathbf{C}^s = 2\langle \mathbf{n}^s \mathbf{n}^s \rangle_s$, the second moment of the distribution of the vector $\mathbf{n}^s$, which denotes the direction of the length axis of the particles. Since

the bulk phases in such a system do not have a complex microstructure, $\bar{F}_c = 0$. For the configurational Helmholtz free energy of the interface an expression was chosen of the form [43, 72]

$$\bar{F}_c^s = \frac{k_B T^s \rho^s \omega_p^s}{m} \left(\ln \omega_p^s - \frac{1}{2} \left[\mathrm{tr} \left(\mathbf{P} - \mathbf{C}^s \right) + \ln \det \mathbf{C}^s \right] \right) \tag{92}$$

where k_B is the Boltzmann constant, ω_p^s is the surface mass fraction of the particles, and m is the mass of a single colloidal particle. The tensor $\mathbf{R}_2^s$ was set equal to

$$\mathbf{R}_2^s = \frac{m}{k_B \rho^s \omega_p^s} \frac{1}{\tau} (a_{\alpha\mu} C_{\beta\nu}^s + a_{\alpha\nu} C_{\beta\mu}^s + \beta \left[C_{\alpha\mu}^s C_{\beta\nu}^s + C_{\alpha\nu}^s C_{\beta\mu}^s \right]) \, \mathbf{a}^\alpha \mathbf{a}^\beta \mathbf{a}^\mu \mathbf{a}^\nu \tag{93}$$

where τ is a relaxation time associated with in-plane orientational relaxation processes of the particles. The coefficient β characterizes the magnitude of the nonlinear corrections for the linear relaxation behavior described by the first two terms on de right hand side of (93). These corrections become important when the system is highly anisotropic [43].

The model in [71] further assumes that the imposed surface shear and dilatational deformations do not cause in-plane spacial inhomogeneities in the particle concentration or orientation of the particles. Another assumption is that there is no exchange of the structural variables between bulk phases and interface. These assumptions imply that the balance equation for $\bar{\Gamma}^s$ is satisfied identically, and that the diffusion and boldface bracket terms in equation (90) can be neglected. Together with (92) and (93) the assumptions result in the following specific forms of (86) and (90):

$$\boldsymbol{\sigma}_{tot}^s = (\varepsilon_d - \varepsilon_s) \left[\nabla_s \cdot \mathbf{v}^s \right] \mathbf{P} + 2\varepsilon_s \mathbf{D}^s + \frac{k_B T^s \rho^s \omega_P^s}{m} \left(\mathbf{C}^s - \mathbf{P} \right) \tag{94}$$

$$\frac{\partial \mathbf{C}^s}{\partial t} - \mathbf{C}^s \cdot \left(\nabla_s \mathbf{v}^s \right)^T - \left(\nabla_s \mathbf{v}^s \right) \cdot \mathbf{C}^s - 4H \mathbf{v}^s \cdot \mathbf{C}^s \boldsymbol{\xi}$$
$$+ \frac{1}{\tau} \left([1 - \beta] \mathbf{C}^s - \mathbf{P} + \beta \mathbf{C}^s \cdot \mathbf{C}^s \right) = 0. \tag{95}$$

This two parameter model was compared to a model derived using the CIT framework discussed in Sect. 2 [49], for a flat interface deformed in both surface shear and dilatational mode. The model produced by the GENERIC framework is clearly superior to the one derived using the CIT framework. Realistic predictions for the average orientation of the particles are obtained even for shear rates much higher than $1\,\mathrm{s}^{-1}$, whereas the CIT model gives accurate predictions only for shear rates lower than $0.1\,\mathrm{s}^{-1}$ [71]. The GENERIC model also has fewer adjustable parameters, which makes it easier to use in the evaluation of experimental data.

We see that the GENERIC framework produces models for the dynamics of materials with microstructured interfaces, which are valid also far from equilibrium (strains $\gg 1$). They link the nonlinear stress deformation of complex interfaces directly to microstructural changes induced by the applied deformation, and include a coupling of the time evolution of the interfacial microstructure with the evolution of the microstructure of the adjoining bulk phases. The GENERIC framework satisfies best the desired properties of surface rheological constitutive equations we outlined in the introduction of this paper. An obvious drawback of the framework is that it is mathematically very involved, which may hamper its widespread use in surface rheology. It also requires detailed knowledge of the physics of the interfaces on microscopic length scales, to produce specific models from the general balance equations. Here kinetic theory, mesoscopic nonequilibrium thermodynamics, and computational methods on both molecular and mesoscopic length scales, could play an important role, by providing input for the development of the coarse-grained continuum models we discussed here.

6 Conclusions and outlook

In this paper we compared four nonequilibrium thermodynamics frameworks with respect to their capability of generating constitutive equations capable of describing the highly nonlinear rheology of interfaces with a complex microstructure. We examined the classical irreversible thermodynamics framework and found that although in CIT it is straightforward to incorporate a dependence of the surface stresses on the time evolution of the interfacial microstructure, the resulting equations are valid only for small departures from equilibrium (strains smaller than 0.1). The extended irreversible thermodynamics framework incorporates the stresses in the set of independent system variables, instead of structural variables describing the microstructure. We have seen that it is relatively straightforward to generate nonlinear viscoelastic models like the surface upper-convected Maxwell model or surface Giesekus model within this framework. But these models are phenomenological and do not have an explicit coupling with the microstructure of the interface. In both the CIT and EIT framework it is not straightforward to introduce a coupling of the surface stresses with the stresses in the adjoining bulk phases. This can easily be done in the extended rational thermodynamics framework. With expressions generated within this framework we can also describe interfaces with inhomogeneous stress distributions. Again these expressions do not have a direct link to the microstructure of the interface. For similar expressions in terms of scalar and tensorial structural variables GENERIC is the most suited framework. Although this framework is the most ideal framework to create constitutive equations for the surface stresses, that link the stresses directly to the time evolution equations for the structural variables, are capable of dealing with structural inhomogeneities, and include contributions from the adjoining bulk phases, it is also the most mathematically involved framework. This may hamper its future use in surface rheology.

We have seen that with the recent progress in nonequilibrium thermodynamics of multiphase systems it is now possible to construct nonlinear constitutive equations to model the stress-deformation behavior of complex fluid-fluid interfaces. An important questions that remains to be discussed is how to implement these equations in the analysis of surface rheology experiments, or in the analysis of droplet deformation studies. Most of the expressions we discussed are highly nonlinear, and will have to be solved numerically, along with the mass and momentum balances for the interfaces and bulk phases of the system. Recent advances in numerical simulations (see for example the reviews by Gross and Reusken [73], Krüger et al. [74], and Park et al. [75], elsewhere in this issue) suggest that at least for single droplets or systems with a limited number of droplets such implementations are now feasible, albeit time consuming.

On the experimental side, evaluation of the coefficients in the nonlinear constitutive models would be greatly facilitated if information on structure evolution during deformation is available. For that purpose there is a need to develop two-dimensional rheo-optics experiments [76]. For interfaces stabilized by (anisotropic) colloidal particles with sizes in excess of $1\,\mu$m, structural evolution during surface shear deformations can be evaluated using microscopy [77–81]. Interfaces stabilized by smaller particles could be examined using scanning angle reflectometry [82,83], and polymer or lipid stabilized interfaces by grazing incidence X-ray or neutron reflectivity measurements. To the authors knowledge none of these techniques have been combined with simultaneous surface shear measurements, and doing so would be quite a challenge. For dilatational measurements rheo-optics experiments could be performed in Langmuir troughs, in combination with reflectivity measurements. But again, such experiments are difficult to perform.

Mesoscopic simulations could be a valuable tool to analyze surface rheological data, whenever detailed experimental observations on structure evolution are not available. But the field of mesoscopic surface simulation of complex fluid-fluid interfaces is still a largely unexplored field. The mesoscopic nonequilibrium thermodynamics framework discussed elsewhere in this issue by Lervik and Kjelstrup [84], and Santamaria-Holek et al. [85], may prove to be a valuable tool to construct mesoscopic models for complex interfaces. In conclusion, to improve our understanding of the dynamics of complex deformable interfaces we need significant advances in both theoretical modeling, experimental characterization, and computational methods, and there is a particular need for the integration of these disciplines.

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