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Dynamic properties of interfaces in soft matter: Experiments and theory

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The dynamic properties of interfaces often play a crucial role in the macroscopic dynamics of multiphase soft condensed matter systems. These properties affect the dynamics of emulsions, of dispersions of vesicles, of biological fluids, of coatings, of free surface flows, of immiscible polymer blends, and of many other complex systems. The study of interfacial dynamic properties, surface rheology, is therefore a relevant discipline for many branches of physics, chemistry, engineering, and life sciences. In the past three to four decades a vast amount of literature has been produced dealing with the rheological properties of interfaces stabilized by low molecular weight surfactants, proteins, (bio)polymers, lipids, colloidal particles, and various mixtures of these surface active components. In this paper recent experiments are reviewed in the field of surface rheology, with particular emphasis on the models used to analyze surface rheological data. Most of the models currently used are straightforward generalizations of models developed for the analysis of rheological data of bulk phases. In general the limits on the validity of these generalizations are not discussed. Not much use is being made of recent advances in nonequilibrium thermodynamic formalisms for multiphase systems, to construct admissible models for the stress-deformation behavior of interfaces. These formalisms are ideally suited to construct thermodynamically admissible constitutive equations for rheological behavior that include the often relevant couplings to other fluxes in the interface (heat and mass), and couplings to the transfer of mass from the bulk phase to the interface. In this review recent advances in the application of classical irreversible thermodynamics, extended irreversible thermodynamics, rational thermodynamics, extended rational thermodynamics, and the general equation for the nonequilibrium reversible-irreversible coupling formalism to multiphase systems are also discussed, and shown how these formalisms can be used to generate a wide range of thermodynamically admissible constitutive models for the surface stress tensor. Some of the generalizations currently in use are shown to have only limited validity. The aim of this review is to stimulate new developments in the fields of experimental surface rheology and constitutive modeling of multiphase systems using nonequilibrium thermodynamic formalisms and to promote a closer integration of these disciplines.

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CONTENTS

I. INTRODUCTION

Dynamic properties of interfaces, such as the interfacial shear and dilatational viscosities, or the surface dilatational modulus, can have a significant effect on the overall dynamics of multiphase soft condensed matter systems (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007). These properties affect the dynamic behavior of vesicles, nanocapsules, and

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microcapsules (Sagis, 2008), and are therefore important parameters in the design of encapsulation and controlled release systems, for pharmaceutical, food, cosmetics, printing, or agricultural applications. They also influence the amplitude of surface waves in free surface flows (Swean and Beris, 1994; Chen, Chen, and Chen, 1997), and may therefore affect, for example, strand or film extrusion processes, or coating processes. They affect the stability of foam (Prud'homme, 1996) and emulsions (Bos and van Vliet, 2001; Murray, 2002; Fischer and Erni, 2007), and the breakup of liquid jets or droplets (Jones and Middelberg, 2003; Regev *et al.*, 2010). They play a significant role in droplet coalescence in immiscible polymer blends (van Hemelrijck *et al.*, 2005). They can also be an important factor in the wetting behavior of thin films on solid surfaces (Edwards and Oron, 1995), important, for example, in coating processes, but also in extrusion processes (Dhori and Slattery, 1997; Dhori *et al.*, 1997), and polymer melt rheology (Dhori, Giacomin, and Slattery, 1997). They may also influence the viscous fingering in immiscible displacements, important in enhanced oil recovery. In biological systems they affect, for example, the deformation of blood cells in arterial flows (Warburton, 1996), the dynamic behavior of lung alveoli (Saad, Neumann, and Acosta, 2010), and the stability of the tear film of the eye (Leiske *et al.*, 2010; Svitova and Lin, 2010). In medical applications these properties are an important factor in the dynamics of microbubbles applied as ultrasound contrast agents (Doinikov, Haac, and Dayton, 2009a, 2009b).

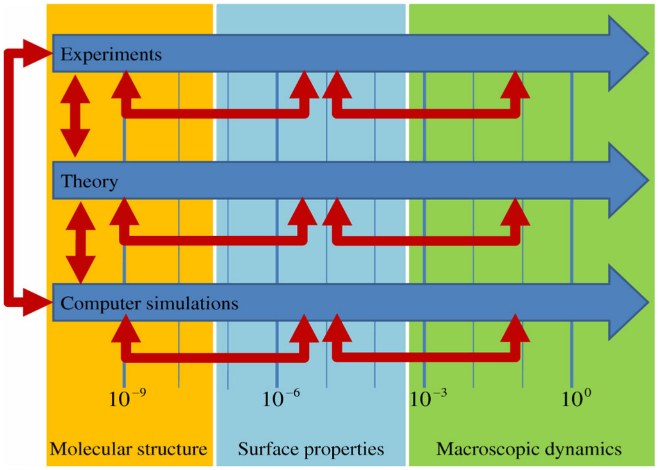

FIG. 1 (color online). Surface rheology plays a central role in understanding macroscopic dynamic behavior of multiphase soft condensed matter. When combined with experimental structure evaluation on the molecular scale, theoretical modeling (statistical physics, nonequilibrium thermodynamics), and computer simulations (for example, nonequilibrium molecular dynamics), surface rheology can be used to link information on the molecular scale of a system to its dynamics on the macroscopic scale.

In multiphase soft condensed matter systems with high surface area to volume ratios, such as emulsions, dispersions of vesicles, or dispersions of nanocapsules, microcapsules, or microbubbles, the macroscopic dynamics of the system are dominated by the dynamic behavior of the interfaces. The characteristic length scales of their interface are in the colloidal range, and therefore surface rheology plays a central role in understanding macroscopic dynamic behavior of the system (see Fig. 1). When combined with experimental structure evaluation on the molecular scale [neutron or grazing incidence x-ray reflectometry (Kaganer, Möhwald, and Dutta, 1999)], theoretical modeling (statistical physics, nonequilibrium thermodynamics) and computer simulations (for example, nonequilibrium molecular dynamics), surface rheology can be used to link information on the molecular scale of a system to its dynamics on the macroscopic scale (see Fig. 1).

Based on this, we conclude that the study of the stress-deformation behavior of interfaces is highly relevant for many disciplines, such as colloid and interface science, physical chemistry, biochemistry, biophysics, biology, polymer physics, pharmaceutical science, food science and engineering, process engineering, coating technology, nanotechnology, fluid mechanics, chemical physics, soft matter physics, medical sciences, mechanical engineering, agricultural engineering, or petroleum engineering.

In view of the above it is not surprising that in recent years a vast number of papers have been published on the dynamic properties of liquid-liquid and air-liquid interfaces with a wide variety of components adsorbed or spread at the interface: (mixtures of) low molecular weight (LMW) surfactants (Beneventi *et al.*, 2003; Liggieri, Ravera, and Ferrari, 2003; Wantke, Fruhner, and Örtegren, 2003; Stubenrauch and Miller, 2004; Liggieri *et al.*, 2005, 2006; Velázquez *et al.*, 2005; Andersen *et al.*, 2006; Gavranovic, Kurtz *et al.*, 2006; Kurtz, Lange, and Fuller, 2006; Aksenenko *et al.*, 2007; Grigoriev and Stubenrauch, 2007; Santini, Liggieri *et al.*, 2007; Santini, Ravera *et al.*, 2007; Fainerman, Petkov, and Miller, 2008; Fainerman *et al.*, 2008, 2009; Golemanov *et al.*, 2008; Kurtz *et al.*, 2008; L. Zhang *et al.*, 2008; Malcolm *et al.*, 2009; Razafindralambo *et al.*, 2009; Tadjoa, Cassagnau, and Chapel, 2009; Yin, Deng, and Esker, 2009; Zhang *et al.*, 2009; Fainerman, Aksenenko, Mys *et al.*, 2010; Fainerman, Aksenenko, Zholob *et al.*, 2010; Fainerman, Lylyk *et al.*, 2010), proteins (Petkov *et al.*, 2000; Bantchev and Schwartz, 2003; Borbás, Murray, and Kiss, 2003; Bos, Dunnewind, and van Vliet, 2003; Cascão Pereira *et al.*, 2003; Courty *et al.*, 2003; Rodríguez Patino *et al.*, 2003; Freer *et al.*, 2004; Ridout, Mackie, and Wilde, 2004; Cicuta and Terentjev, 2005; Maldonado-Valderrama, Fainerman, Cálvez-Ruiz *et al.*, 2005; Martin *et al.*, 2005; Roberts *et al.*, 2005a; Rodríguez Patino *et al.*, 2005, 2007; Vessely, Carpenter, and Schwartz, 2005; Ariola, Krishnan, and Vogler, 2006; Benjamins, Lyklema, and Lucassen-Reynders, 2006; Kolodziejczyk *et al.*, 2006; Wierenga *et al.*, 2006; Cicuta, 2007; Cox *et al.*, 2007; Dauphas *et al.*, 2007; Erni, Fischer, and Windhab, 2007; Juárez *et al.*, 2007; Noskov, Latnikova *et al.*, 2007; Ruíz-Henestrosa *et al.*, 2007a, 2007b; Erni *et al.*, 2008; Gao *et al.*, 2008; Hill *et al.*, 2008; Lakshmanan, Dhahathreyan, and Miller, 2008; Rossetti *et al.*, 2008; Ruíz-Henestrosa, Carrera Sánchez, and Rodríguez Patino, 2008; Alexandrov *et al.*, 2009; Day *et al.*, 2009; Maldonado-Valderama *et al.*, 2009; K. D. Martínez *et al.*, 2009; J. M. Martínez *et al.*, 2009; Murray, Dickinson, and Wang, 2009; Partanen *et al.*, 2009; Vézy *et al.*, 2009; Baldursdottir *et al.*, 2010; Berecz *et al.*, 2010; Blijdenstein, de Groot, and Stoyanov, 2010; Lee *et al.*, 2010; Mahmoudi *et al.*, 2010; Regev *et al.*, 2010), mixtures of proteins and polysaccharides (Baeza *et al.*, 2004a, 2006; Ganzevles *et al.*, 2006, 2007; Martínez *et al.*, 2007; Wooster and Augustin, 2007; Jourdain *et al.*, 2009; A. A. Perez *et al.*, 2009, 2010; Perez *et al.*, 2009a, 2009b; Piazza *et al.*, 2009; Miquelim, Lannes, and Mezzenga, 2010), mixtures of proteins and low molecular weight surfactants (Gunning *et al.*, 2004; Miller *et al.*, 2005; Alahverdjieva *et al.*, 2008; Kazakov *et al.*, 2008; Kotsmar, Krägel *et al.*, 2009; McAuley, Jones, and Kett, 2009; Pradines *et al.*, 2009), protein-lipid mixtures (Fang, Zou, and He, 2003; Carrera Sánchez and Rodríguez Patino, 2004; Golding and Sein, 2004; Ivanova *et al.*, 2004; Carrera Sánchez *et al.*, 2005; Roberts *et al.*, 2005b; Rouimi *et al.*, 2005; Cejudo Fernández *et al.*, 2006; Rodríguez Patino *et al.*, 2006a, 2006b; Álvarez Gómez and Rodríguez Patino, 2007a, 2007b; Lilbaek *et al.*, 2007; Álvarez Gómez *et al.*, 2008; Nishimura *et al.*, 2008; Reis *et al.*, 2008; Lucero Caro, Rodríguez Niño, and Rodríguez Patino, 2009; Rodríguez Niño, Lucero Caro, and Rodríguez Patino, 2009; Saad, Neumann, and Acosta, 2010; Svitova and Lin, 2010), lipids (Rodríguez Patino *et al.*, 2001; Yim and Fuller, 2003; Sosnowski, Pawelec, and Gradoń, 2006; Anton *et al.*, 2007; Vrânceanu *et al.*, 2007; Arriaga *et al.*, 2008; Krishnaswamy, Rathee, and Sood, 2008; López-Montero *et al.*, 2008; Lucero Caro, Rodríguez Niño, and Rodríguez Patino, 2008; Vrânceanu *et al.*, 2008; Walder, Levine, and Dennin, 2008; Doinikov, Haac, and Dayton, 2009a, 2009b; Saad *et al.*, 2009; Arriaga *et al.*, 2010; Leiske *et al.*, 2010; Lozano *et al.*, 2010), synthetic polymers or biopolymers (Rivillon *et al.*, 2002; Anseth *et al.*, 2003; Foreman *et al.*, 2003; Kim and Yu, 2003; Malzert *et al.*, 2003; Monroy *et al.*, 2003; Baeza *et al.*, 2004b; Cicuta and Hopkinson, 2004a; Lee *et al.*, 2004; Pérez-Orozco *et al.*, 2004; Babak, Desbrières, and Tikhonov, 2005; Gavranovic, Deutsch, and Fuller, 2005; Monroy *et al.*, 2005; Rippner Blomqvist, Wärnheim, and Claesson, 2005; Gavranovic, Smith *et al.*, 2006; Hilles, Maestro *et al.*, 2006; Hilles, Monroy *et al.*, 2006; Hilles, Sferrazza *et al.*, 2006; Kim *et al.*, 2006; Monteux *et al.*, 2006; Pérez *et al.*, 2006; Erni *et al.*, 2007; Mezdour *et al.*, 2007; Noskov, Biblin *et al.*, 2007; Babak *et al.*, 2008a, 2008b; Duerr-Auster, Gunde, and Windhab, 2008; Leiva *et al.*, 2008; Pérez *et al.*, 2008; Camino *et al.*, 2009; Dong *et al.*, 2009; Ertekin *et al.*, 2009; Georgieva *et al.*, 2009; Hilles *et al.*, 2009; Leick *et al.*, 2009; Maestro *et al.*, 2009; Marze, 2009; Miranda *et al.*, 2009; Spigone *et al.*, 2009; Castellani, Al-Assaf *et al.*, 2010; Castellani, Guibert *et al.*, 2010), mixtures of polymers and low molecular weight surfactants (Ritacco, Kurlat, and Langevin, 2003; Monteux, Fuller, and Bergeron, 2004; Rippner Blomqvist *et al.*, 2004; Klebanau *et al.*, 2005; Noskov, Loglio, and Miller, 2005; Picard and Davoust, 2006; Ritacco, Cagna, and Langevin, 2006; Nobre, Wong, and Darbello Zaniquelli, 2007; Wu *et al.*, 2007; Auguste *et al.*, 2008; Li *et al.*, 2008; Mezdour *et al.*, 2008; Xin *et al.*, 2008; H. Zhang *et al.*, 2008; Espinosa and Langevin, 2009), asphaltenes (Freer and Radke, 2004; Sztukowski and Yarranton, 2005; Hannisdal, Orr, and Sjöblom, 2007; Yarranton, Sztukowski, and Urrutia, 2007; Quintero *et al.*, 2009; Verruto, Le, and Kilpatrick, 2009; Zhaoxia *et al.*, 2010), and colloidal particles (Ravera *et al.*, 2006, 2008; Reynaert, Moldenaers, and Vermant, 2007; Wang *et al.*, 2008; Madivala, Fransaer, and Vermant, 2009; Dong *et al.*, 2010; Zang *et al.*, 2010). These references are mostly from the years 2003–2010. Many additional references to earlier work can be found in reviews on interfacial dynamic properties of interfaces stabilized by low molecular weight surfactants (Kovalchuk *et al.*, 2005; Ravera *et al.*, 2005), mixtures of proteins and hydrocolloids (Dickinson, 2003), protein-emulsifier mixtures (Wilde *et al.*, 2004), protein-surfactant mixtures (Rodríguez Patino, Rodríguez Niño, and Carrera Sánchez, 2007b; Rodríguez Patino, Carrera Sánchez, and Rodríguez Niño, 2008), and mixtures of polymers and surfactants (Goddard, 2002; Penfold, Thomas, and Taylor, 2006).

Surface rheology shares a lot of commonalities with the study of rheology of bulk phases, particularly when surface shear properties are determined. This is evidenced by the fact that many suppliers of commercial rheometers currently supply special geometries for the determination of surface shear viscosities and surface shear moduli, which can be fitted on their standard stress or strain controlled rheometers. With this development many of the standard tests applied to bulk phases (strain sweeps, frequency sweeps, step relaxation measurements, and creep experiments) can now also readily be applied to interfaces, and an increasing number of scientists in the field are taking advantage of these possibilities (see Tables I–VII).

But there are also significant differences between bulk and surface rheology. Whereas in the bulk phase we usually assume incompressibility of the material, this assumption does not hold for interfaces. Interfaces are in general easily compressed, and as a result a substantial part of surface rheology is devoted to the determination of surface dilatational properties (the resistance of the interface against in-plane all-sided compression). In comparison, only a small part of the rheological literature on bulk phase behavior focuses on the determination of the bulk viscosity or bulk modulus. Most of the work on rheology of bulk phases focuses on shear and elongational properties of incompressible fluids (Bird, Armstrong, and Hassager, 1987; Macosko, 1994; Larson, 1999). An additional difference with bulk rheology is that surface mass is not always conserved during deformation. When an interface is stretched the surface density decreases, and when soluble surface active materials are present in the bulk phase this decrease can partially be compensated by mass transfer from the bulk phase to the interface. As a result the momentum balance for the interface is in general coupled to the surface mass balance, and both balances have to be solved simultaneously. A considerable part of the experimental work in this field is focusing on the effects of subsurface mass transfer on surface dilatational properties.

In this paper we review recent experiments in the field of surface rheology, with particular emphasis on the models used to analyze the stress-deformation behavior of interfaces. We see that although many interesting and important contributions have been made to the field of surface rheology, recent advances in the theoretical modeling of stress-deformation behavior of interfaces are not yet used to their full potential. In many experimental studies the rheological parameters are not always unambiguously defined. This is

TABLE I. Surface dilatational and shear properties of interfaces with adsorbed (mixtures of) low molecular weight surfactants. Rheological models: BM = Boussinesq model, KV = Kelvin-Voigt, HL = Hooke's law, MM = Maxwell model, MMM = multimode Maxwell model, JM = Jeffreys model, 2VS = two Voigt elements in series, RP = reptation model, NLM = nonlinear model, ER = exponential relaxation model, and SER = stretched exponential relaxation. Methods: OBM = oscillating bubble method, BPT = bubble pressure tensiometry, SQELS = surface quasielastic light scattering, LT = Langmuir trough, CWA = capillary wave analysis, OR-ISR = oscillating rod interfacial stress rheometer, BCDR = biconical disk rheometer, DWRG = double-wall ring geometry, DNR = du Noüy ring rheometer, RT = ring trough, U = ultrasound, GFT = glass fiber technique, and PT = particle tracking.

Surface active material	Reference	Property	Model	Method
Sodium dodecyl sulfate (SDS)	Fainerman, Lylyk *et al.* (2010)	E_d	···	OBM
SDS/C_nEO_m mixtures	Fainerman, Aksenenko, Mys *et al.* (2010); Fainerman, Aksenenko, Zholob *et al.* (2010)	E_d	···	OBM
SDS/*n* dodecanol	Wantke, Fruhner, and Örtegren (2003)	E'_d, ε_d	KV	OBM
Sodium oleate and $C_{12}EO_6$	Beneventi *et al.* (2003)	E'_d	···	OBM
$C_{14}EO_8$	Fainerman, Petkov, and Miller (2008); Fainerman *et al.* (2008)	E'_d, ε_d	KV	OBM
n dodecanol	Liggieri, Ravera, and Ferrari (2003)	E_d	···	OBM
n-dodecyl-β-D-maltoside	Grigoriev and Stubenrauch (2007)	E'_d, ε_d	KV	CWA
n-dodecyl-β-D-maltoside /$C_{10}E_4$	Stubenrauch and Miller (2004); Santini, Ravera *et al.* (2007)	E'_d, ε_d	KV	OBM
Polyoxyethyleneglycol esters C_iE_f	Liggieri *et al.* (2005)	E'_d, ε_d	KV	OBM, BPT
Hexadecyl-1-*N*-L-tryptophan glycerol ether	Velázquez *et al.* (2005)	E'_d, ε_d	KV	LT, SQELS
$C_{10}E_8/C_{12}DMPO$	Liggieri *et al.* (2006)	E_d	···	OBM
Hexadecanol/eicosanol	Gavranovic, Kurtz *et al.* (2006); Kurtz, Lange, and Fuller (2006); Kurtz *et al.* (2008)	G'_s, G''_s	···	OR-ISR
F381/DMPB	Andersen *et al.* (2006)	E'_d, ε_d	KV	BPT
Span80	Santini, Liggieri *et al.* (2007))	E'_d, ε_d	KV	OBM, BPT
DMPO/$C_{14}DMPO$	Aksenenko *et al.* (2007)	E_d	···	OBM
Trisubstituted alkyl benzene sulfonates	L. Zhang *et al.* (2008)	E'_d, ε_d	KV	OBM
SLES, CAPB, LAc, MAc	Golemanov *et al.* (2008)	E_d	···	OBM
Gemini surfactant $C_{12}CO_2Na$-p-C_9SO_3Na	Zhang *et al.* (2009)	E'_d, ε_d	KV	LT
AFD_4-Zn^{II} peptide	Malcolm *et al.* (2009)	E_d	···	OBM
Triton surfactants	Fainerman *et al.* (2009)	E_d	···	OBM
Glucose octanoate, octyl glucuronate	Razafindralambo *et al.* (2009)	E'_d, E''_d	···	OBM
Silica alkoxides	Tadjoa, Cassagnau, and Chapel (2009)	G'_s, G''_s	···	DNR
Trisilanolisobutyl-POSS	Yin, Deng, and Esker (2009)	E'_d, ε_d	KV	SQELS

particularly true for surface dilatational rheology, which is often formulated in terms of the dynamic surface tension convention. This convention is popular among experimentalists, and although it is in principle correct, expressing the response of interfaces to dilation in terms of a dynamic surface tension has several disadvantages. We discuss these in more detail in the next section.

An additional problem is that data in surface dilation experiments are sometimes analyzed with incomplete momentum balances, in the sense that important contributions to this balance originating from surface shear stresses, surface inertial stresses, or viscous stresses exerted by the adjoining bulk phases are neglected without proper consideration of the magnitude of these contributions. As we see in the next section this may lead to an improper identification of the characteristics of the interface. For example, purely elastic interfaces may appear to be viscoelastic, when bulk viscous stresses are not properly accounted for.

A third issue is that most of the work we review here analyzes surface rheological data with *ad hoc* generalizations of models used for the analysis of rheological experiments on bulk phases. Any constitutive model for the surface stresses should be thermodynamically admissible, that is, it should not violate the second law of thermodynamics. But thermodynamic admissibility of these generalizations is in general not discussed. Since the original model was developed to describe the response of an incompressible material to a deformation, these generalizations are not guaranteed to correctly describe the behavior of highly compressible interfaces.

Finally, most of the work in this field focuses on the response of interfaces in the linear regime. A possible explanation for this observation is the limited availability of models to describe nonlinear rheological behavior of interfaces. When adsorbed or spread at interfaces, surface active species can form a wide range of surface phases. They can form 2D fluids, 2D dispersions and emulsions (phase-separated mixtures of surfactants), 2D soft gels, 2D glasses, 2D liquid crystalline phases, or 2D solid crystalline phases. Most of these phase states display nonlinear behavior, even at small deformations. Data in the linear regime are extremely useful, in particular, for investigating the structural properties of interfaces, close to equilibrium. But from a practical point of view it would be preferable to also investigate the nonlinear responses of interfaces, since most of the systems in which surface rheological parameters are important are produced or processed far from equilibrium, where responses are no longer linear.

Nonequilibrium thermodynamics (NET) is a discipline ideally suited for the development of thermodynamically admissible models, both near and far beyond equilibrium.

TABLE II. Surface dilatational and shear properties of interfaces with adsorbed proteins (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
α-lactalbumin	Gao *et al.* (2008)	E_d, G_s	⋯	OBM, DNR
β-lactoglobulin	Petkov *et al.* (2000)	E'_d, ε_d, G'_s, ε_s	KV	LT
β-lactoglobulin	Courty *et al.* (2003)	G_s	HL	GFT
β-lactoglobulin	Cicuta and Terentjev (2005)	E'_d, E''_d, G'_s, G''_s	⋯	LT
β-lactoglobulin	Kolodziejczyk *et al.* (2006)	E'_d, ε_d	KV	OBM
β-lactoglobulin	Maldonado-Valderama *et al.* (2009)	E_d, ε_d	KV	OBM
β-lactoglobulin	Lee *et al.* (2010)	ε_s	BM	PT
BSA	Cascão Pereira *et al.* (2003)	E'_d, E''_d	⋯	OBM
BSA	Lakshmanan, Dhahathreyan, and Miller (2008)	E'_d, ε_d	KV	OBM
BSA	Alexandrov *et al.* (2009)	E'_d, E''_d	⋯	BPT
BSA	Regev *et al.* (2010)	G'_s, G''_s	⋯	DWRG
BSA, ovalbumin, β-lactoglobulin, lysozyme	Borbás, Murray, and Kiss (2003)	G'_s, G''_s	⋯	BCDR
BSA, lysozyme, insulin	Baldursdottir *et al.* (2010)	G'_s, G''_s, ε_s	⋯	DNR
BSA/NDA complex	Juárez *et al.* (2007)	E'_d, E''_d	MM	OBM
β-casein	Bantchev and Schwartz (2003)	G'_s, G''_s	⋯	OR-ISR
β-casein	Maldonado-Valderrama, Fainerman, Cálvez-Ruiz *et al.* (2005)	E'_d, ε_d	KV	OBM
β-casein	Vessely, Carpenter, and Schwartz (2005)	G'_s, G''_s	⋯	OR-ISR
β-casein	Noskov, Latnikova *et al.* (2007)	E_d	⋯	LT
β-casein, lysozyme	Freer *et al.* (2004)	E'_d, G'_s	⋯	OBM, OR-ISR
β-casein/β-lactoglobulin	Ridout, Mackie, and Wilde (2004)	E'_d, G'_s	⋯	RT, DNR
β-casein, β-lactoglobulin	Cicuta (2007)	E_d, G_s, τ_d	SER	LT
β-casein, β-lactoglobulin, ovalbumin, glycinin	Martin *et al.* (2005)	σ_{ss}, σ_f	⋯	BCDR
β-casein, β-lactoglobulin, ovalbumin, BSA	Benjamins, Lyklema, and Lucassen-Reynders (2006)	E'_d, E''_d	KV	OBM
Caseinoglycomacropeptide	J. M. Martínez *et al.* (2009)	E'_d, E''_d	⋯	OBM
Na-caseinate	Partanen *et al.* (2009)	E_d	⋯	OBM
Na-caseinate, β-lactoglobulin	Murray, Dickinson, and Wang (2009)	E^*_d, ε_s	⋯	LT, BCDR
Soy proteins	Rodríguez Patino *et al.* (2003, 2005)	E'_d, E''_d	⋯	OBM
Soy proteins	Ruíz-Henestrosa *et al.* (2007a, 2007b)	E'_d, E''_d	⋯	OBM
Soy proteins and their hydrolysates	K. D. Martínez *et al.* (2009)	E'_d, E''_d	⋯	OBM
β-conglycinin	Ruíz-Henestrosa *et al.* (2007b)	E'_d, E''_d	⋯	OBM
Lysozyme	Erni, Fischer, and Windhab (2007); Erni *et al.* (2008)	G'_s, G''_s	MM	BCDR
Catalase, lysozyme	Roberts *et al.* (2005a)	G'_s, G''_s	⋯	DNR
Albumin, IgG, IgM, fibrinogen	Ariola, Krishnan, and Vogler (2006)	G'_s, G''_s	⋯	DNR
Ovalbumin	Wierenga *et al.* (2006)	Y_s, σ_{ss}	⋯	BCDR
Hydrophobins	Cox *et al.* (2007)	G'_s, G''_s	⋯	DNR
Hydrophobin HFBII, quillaja saponin, β-lactoglobulin, β-casein	Blijdenstein, de Groot, and Stoyanov (2010)	E_d, G'_s, G''_s	⋯	LT, BCDR
Hen egg yolk lipoprotein	Dauphas *et al.* (2007)	G'_s	⋯	DNR
Sun flower protein isolate	Rodríguez Patino *et al.* (2007)	E_d	⋯	OBM
Sunflower 2S albumins and lipid transfer protein	Berecz *et al.* (2010)	E_d	⋯	OBM
Saliva proteins	Rossetti *et al.* (2008)	G'_s, G''_s	⋯	DNR
Spider-silk protein	Vézy *et al.* (2009)	G'_s, G''_s	⋯	DNR
Wheat proteins	Hill *et al.* (2008)	E_d	⋯	OBM
Wheat protein isolate	Day *et al.* (2009)	E_d	⋯	LT
Whey protein isolates	Mahmoudi *et al.* (2010)	E'_d, ε_d	KV	OBM

NET can provide unambiguous definitions of surface rheological properties and a complete set of (coupled) balance equations for the bulk phases and interfaces of a multiphase system, consistent with the principles of conservation of mass, momentum, and energy. NET can also be used to construct (nonlinear) constitutive equations for the fluxes appearing in these balance equations, consistent with the second law of thermodynamics. These equations eliminate the need for using generalizations of bulk models to describe the behavior of interfaces.

Over the past decades NET formalisms have been a useful tool in the development of admissible models for the stress-deformation behavior of complex bulk phases, such as polymer melts, solutions of branched polymers, immiscible polymer blends, or nematic phases (Macosko, 1994; Larson, 1999; Öttinger, 2005). In recent years NET formalisms, such as classical irreversible thermodynamics, rational thermodynamics, or general equation for the nonequilibrium reversible-irreversible coupling (GENERIC), have been extended to deal with multiphase systems with complex

TABLE III. Surface dilatational and shear properties of interfaces with adsorbed mixtures of proteins and lipids, mixtures of proteins and LMW surfactants, or mixtures of proteins and polysaccharides (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
Protein/lipid systems				
Glycine/monostearine	Fang, Zou, and He (2003)	E'_d, E''_d	KV	LT
Casein/monoglycerides	Golding and Sein (2004)	G'_s, G''_s	$\cdots$	DNR
β-casein/monoglycerides	Carrera Sánchez and Rodríguez Patino (2004)	ε_s	$\cdots$	LT
β-casein/monoglycerides	Rodríguez Patino *et al.* (2006a)	E'_d, E''_d	$\cdots$	LT
β-casein/DOPC	Rodríguez Niño, Lucero Caro, and Rodríguez Patino (2009)	E'_d, E''_d	$\cdots$	LT
β-casein/DPPC	Lucero Caro, Rodríguez Niño, and Rodríguez Patino (2009)	E'_d, E''_d, ε_s	$\cdots$	RT, DNR
Caseinate, β-lactoglobulin/diglycerol esters	Álvarez Gómez and Rodríguez Patino (2007a, 2007b)	E'_d, E''_d	$\cdots$	OBM
Caseinate, β-lactoglobulin/diglycerol esters	Álvarez Gómez *et al.* (2008)	E'_d, E''_d	$\cdots$	OBM
Lung surfactants (proteins + phospholipids)	Ivanova *et al.* (2004)	E'_d, E''_d	MM	LT
Lung surfactants	Saad, Neumann, and Acosta (2010)	E_d	$\cdots$	OBM
Milk proteins/glycerides	Rouimi *et al.* (2005)	G'_s, G''_s	KV	DNR
Milk proteins, lipids, phospholipids	Carrera Sánchez *et al.* (2005)	E'_d, E''_d	$\cdots$	LT
Milk proteins, phospholipids	Lilbaek *et al.* (2007)	G'_s, ε_s	KV	DNR
β-lactoglobulin/monoglycerides	Rodríguez Patino *et al.* (2006b)	E'_d, E''_d	$\cdots$	LT
β-lactoglobulin/monoglycerides	Cejudo Fernández *et al.* (2006)	E'_d, E''_d	$\cdots$	LT
Catalase, lysozyme/DPPC, DPPG	Roberts *et al.* (2005b)	G'_s, G''_s	$\cdots$	DNR
Lysozyme/DPCC, cholesterol myristate	Nishimura *et al.* (2008)	G'_s, G''_s	$\cdots$	OR-ISR
Lysozyme/tear film lipids	Svitova and Lin (2010)	E_d, τ_d	ER	OBM
Lipase/monoglycerides	Reis *et al.* (2008)	E'_d, G'_s	$\cdots$	OBM, BCDR
Protein/LMW surfactant systems				
β-lactoglobulin, β-casein/Tween, SDS, CTAB, LPC-L	Gunning *et al.* (2004)	G'_s	$\cdots$	BCDR
β-lactoglobulin/C_{10}DMPO	Miller *et al.* (2005)	E^*_d	$\cdots$	OBM
β-lactoglobulin/SDS	Pradines *et al.* (2009)	E_d	$\cdots$	OBM
Lysozyme/C_{10}DMPO, SDS	Alahverdjieva *et al.* (2008)	E'_d, E''_d	$\cdots$	OBM
HSA/$C_{14}EO_8$	Kazakov *et al.* (2008)	E'_d, E''_d	$\cdots$	OBM
β-casein/C_{12}DMPO, DoTAB	Kotsmar, Kragel *et al.* (2009)	E'_d, E''_d	$\cdots$	OBM
Lactate dehydrogenase/Tween-20	McAuley, Jones, and Kett (2009)	G_s, ε_s	KV	DNR
Protein/polysaccharide systems				
β-lactoglobulin/PGA, xanthan, λ-carrageenan	Baeza *et al.* (2004a, 2006)	E'_d, E''_d	$\cdots$	LT
β-lactoglobulin/pectin	Ganzevles *et al.* (2006)	E_d, G_s	$\cdots$	OBM, BCDR
β-lactoglobulin/pullulan	Ganzevles *et al.* (2007)	E_d, G_s	$\cdots$	OBM, BCDR
Na-caseinate/dextran sulfate	Jourdain *et al.* (2009)	E_d, ε_d, G_s, ε_s	KV	OBM, BCDR
WPI-dextran conjugates	Wooster and Augustin (2007)	E_d, G'_s	$\cdots$	LT, DNR
WPI/Na-alginate, λ-carrageenan	A. A. Perez *et al.* (2009); Perez *et al.* (2010)	E'_d, E''_d	$\cdots$	OBM
WPC/hydroxypropyl-methyl cellulose	Perez *et al.* (2009a, 2009b)	E'_d, E''_d	$\cdots$	OBM
Soy protein hydrolysates/HPMC, locust bean gum, λ-carrageenan	Martínez *et al.* (2007)	E'_d, E''_d	$\cdots$	OBM
Soy proteins/high methoxyl pectin	Piazza *et al.* (2009)	E'_d, E''_d, G'_s, G''_s	$\cdots$	LT, BCDR
Egg albumin/κ-carrageenan, xanthan, guar gum	Miquelim, Lannes, and Mezzenga (2010)	E_d, G'_s, G''_s	$\cdots$	OBM, BCDR

interfaces (Öttinger, Bedeaux, and Venerus, 2009; Sagis, 2010a, 2010b). The second part of this review discusses the progress in this area of NET and shows how these frameworks can be used to construct thermodynamically admissible linear and nonlinear constitutive equations for the surface stress tensor. We also discuss constitutive equations for in-plane surface mass and surface heat transfer, and for transfer of mass, momentum, and energy across the interface, since far from equilibrium all modes of transport tend to be coupled, and it is no longer possible to discuss surface rheology without considering mass and energy transfer.

This review is organized in the following way. We first present a review of the conservation principles for multiphase systems with surface-excess variables associated with the interface. After a discussion of the mass, momentum, and energy balances of the interface, we define the surface rheological properties we focus on in the remainder of this paper. In Sec. III we review recent surface rheological experiments, focusing on the models used to analyze the experimental data. In Sec. IV we discuss the classical irreversible thermodynamics formalism for multiphase systems.

In Secs. V, VI, and VII we proceed with a discussion of recent advances in modeling multiphase systems with NET formalisms. As mentioned, there are several NET formalisms that can be used to model dynamics of interfaces in multiphase systems, and at present none of these formalisms have emerged as preferred by workers in the field (Lebon, Jou, and Casas-Vásquez, 2008). We therefore discuss five of the most frequently used formalisms and their advantages and disadvantages for modeling dynamic behavior of interfaces.

In Sec. V we review the extended irreversible thermodynamics formalism (EIT) and show how this formalism can be

TABLE IV. Surface dilatational and shear properties of interfaces with adsorbed lipids (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
Monopalmitin, monoolein	Rodríguez Patino *et al.* (2001)	E'_d, E''_d	$\cdots$	LT
Azobenzene-fatty acids	Yim and Fuller (2003)	G'_s, G''_s	$\cdots$	OR-ISR
DPPC	Arriaga *et al.* (2010)	E_d, ε_d	KV, MM	LT
DPPC, DPPC/CTAB	Sosnowski, Pawelec, and Gradoń (2006)	E'_d, ε_d, τ_d	MM	LT
DPPC, DPPE, DOPE, DOPC	Anton *et al.* (2007)	E'_d, E''_d, τ_d	MM	OBM
DPPC, DOPC, cholesterol	Vrânceanu *et al.* (2007, 2008)	E'_d, ε_d	KV	OBM
DPPC, DOPC	Lucero Caro, Rodríguez Niño, and Rodríguez Patino (2009)	E'_d, E''_d, G'_s, ε_s	$\cdots$	LT,RT, DNR
DPPC, *E. Coli* lipids	Arriaga *et al.* (2008)	E'_d, ε_d	NLM	LT
DPPC/DPPE-Biotynl + *F*-actin	Walder, Levine, and Dennin (2008)	G'_s, ε_s	MM	CT
DPPC/DPPG mixtures	Saad *et al.* (2009)	E_d	$\cdots$	OBM
DPPC/1414RAc mixtures	Lozano *et al.* (2010)	E'_d, E''_d	$\cdots$	LT
(DOPC, DOPE)/alamethicin	Krishnaswamy, Rathee, and Sood (2008)	G'_s, G''_s	MM	BCDR
E. Coli PLE	López-Montero *et al.* (2008)	E'_d, ε_d	MM	LT
DSPC:DSPE-PEG2000	Doinikov, Haac, and Dayton (2009a, 2009b)	E_d, ε_d	NLM	U
Meibomian (tear) lipids	Leiske *et al.* (2010)	G_s, ε^*_s	$\cdots$	OR-ISR
POPE, POPC	Anton *et al.* (2007)	E'_d, E''_d, τ_d	MM	OBM

used to develop linear and nonlinear viscoelastic models for the surface extra stress tensor. Also in this section we compare the results from the EIT formalism with those obtained using rational thermodynamics (RT) and review constitutive equations for the surface mass and surface energy flux vectors. We conclude this section with a discussion of constitutive equations for transport of momentum, mass, and energy across the interface. In Sec. VI we briefly review the extended rational thermodynamics formalism (ERT), and in Sec. VII we discuss recent advances in the development of GENERIC formulations for the dynamics of multiphase systems.

The aim of this review is to stimulate new developments in the fields of experimental surface rheology and constitutive modeling of multiphase systems using NET formalisms and to promote a closer integration of these disciplines.

II. CONSERVATION PRINCIPLES FOR MULTIPHASE SYSTEMS

A. Continuum models for interfaces

To describe the effects of interfacial stress-deformation behavior on the dynamics of complex multiphase systems, a model has to be introduced for the interface. A phase interface is formally defined as a three-dimensional region of finite thickness, separating two adjoining bulk phases. The local mass, momentum, energy, and entropy densities of the system change rapidly but continuously across this region, from their value in one bulk phase to their respective value in the other bulk phase.

This interfacial region can be modeled as a thin film of finite thickness, with its own material behavior and its own constitutive equations to describe that behavior (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007). The latter may deviate significantly from the constitutive equations describing behavior of the bulk phases. The behavior in the interface is often anisotropic, even when the adjoining bulk phases are isotropic phases. A problem with this type of model is that the direct experimental characterization of the material behavior in this thin region is difficult, and therefore it is hard to obtain data for the coefficients appearing in these models.

This type of model is popular for the description of stress-deformation behavior of membranes, the shells of polymer microcapsules, or other systems with interfacial regions of substantial thickness (Gordon *et al.*, 2004; Lulevich, Adrienko, and Vinogradova, 2004; Fery and Weinkamer, 2007). For thick interfacial regions the structure of the membrane or shell is assumed to be uniform in the direction perpendicular to the region, and material behavior is assumed to be given by the same constitutive equations as those used to describe bulk phase behavior of the film material. Such an approach is a reasonable approximation when contributions to the rheological behavior of the relatively narrow outer regions of the film are dominated by those of the interior of the film.

A more popular continuum model for phase interfaces is the Gibbs dividing surface (Gibbs, 1928), a two-dimensional surface placed sensibly within the interfacial region. Bulk properties are extrapolated up to the dividing surface, and the difference between the actual and extrapolated fields is accounted for by associating excess properties, such as a surface mass density, surface momentum, surface energy, or surface entropy with the dividing surface (Gibbs, 1928; Edwards, Brenner, and Wasan, 1991; Kralchevsky, Eriksson, and Ljunggren, 1994; Gatignol and Prud'homme, 2001; Lomholt and Miao, 2006; Slattery, Sagis, and Oh, 2007).

The excess properties of an interface can be related to the actual continuous fields in the interfacial region, using models for the microstructure of this region. These microstructural models have been, for example, used to derive expressions for surface tensions, interfacial bending rigidities, surface rheological parameters, and surface diffusion coefficients (Tolman, 1948; Kirkwood and Buff, 1949; Tolman, 1949a, 1949b; Buff, 1951, 1952, 1955, 1956, 1960a, 1960b; Hill, 1952; Buff and Stillinger Jr., 1956; Kondo, 1956; Buff and Saltsburg, 1957a, 1957b; Slattery, 1967; Melrose, 1968; Toxvaerd, 1972, 1976;Helfand and

TABLE V. Surface dilatational and shear properties of interfaces with adsorbed polymers (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
PVAc	Monroy *et al.* (2003)	E'_d, ε_d, τ_s,	KV, RP	LT
PVAc	Spigone *et al.* (2009)	E'_d, E''_d, G'_s, G''_s	⋯	LT, DNR, OR-ISR
PVAc, PVS, PODA	Hilles, Monroy *et al.* (2006)	E'_d, ε_d	NLM	LT
PVAc, P4HS	Cicuta and Hopkinson (2004a)	E'_d, ε_d	MM	SQELS
PVAc/P4HS blends	Rivillon *et al.* (2002)	E'_d, ε_d, $H(\tau)$	MM	LT, SQELS, CWA
P4HS	Monroy *et al.* (2005)	E'_d, ε_d, G'_s	KV	CWA
P4HS	Hilles *et al.* (2009)	ε_s	⋯	LT
PMMA	Maestro *et al.* (2009)	G'_s, G''_s	⋯	BCDR
PODA, PVS	Hilles, Maestro *et al.* (2006)	E'_d, ε_d, τ_d	NLM	LT
PEG-lipopolymers	Foreman *et al.* (2003)	G'_s, G''_s	MM	DNR
PEG2000	Malzert *et al.* (2003)	E'_d, E''_d, τ_s	MM	OBM
PEO-PPO triblock copolymers	Kim and Yu (2003)	E'_d, ε_d	KV	SQELS
PEO-PPO triblock copolymers	Rippner Blomqvist, Wärnheim, and Claesson (2005)	E'_d, E''_d, G'_s, G''_s	MM	RT, DNR
PEO-PPO triblock copolymers	Georgieva *et al.* (2009)	E'_d	KV	OBM
PCL-PEO-PCL triblock copolymers	Leiva *et al.* (2008)	E_d	⋯	LT
PFO-PEO-PFO triblock copolymers	Ertekin *et al.* (2009)	E_d	⋯	OBM
PS-PtBA block copolymers	Hilles, Sferrazza *et al.* (2006)	E'_d, ε_d, $H(\tau)$	MM	LT
AMPS-AM, AMPS-NIPAM copol.	Noskov, Biblin *et al.* (2007)	E'_d, E''_d	⋯	OBM
Siloxane-oxyalkylene copolymers	Anseth *et al.* (2003)	G'_s, G''_s	⋯	OR-ISR
PGA	Baeza *et al.* (2004b)	E'_d, E''_d	⋯	OBM
PGE	Duerr-Auster, Gunde, and Windhab (2008)	E'_d, E''_d, G'_s, G''_s	MM	OBM, BCDR
PGPR	Marze (2009)	E'_d, E''_d	⋯	OBM
PCL, eudragit RS	Babak *et al.* (2008a)	E'_d, E''_d	MMM	OBM
Chitosan sulfate, eudragit RS	Babak *et al.* (2008b)	E'_d, E''_d	MMM	OBM
Alkylated chitosan	Babak, Desbrières, and Tikhonov (2005)	E'_d, E''_d	MMM	OBM
Mesquite gum/chitosan	Pérez-Orozco *et al.* (2004)	η_s, J_s, τ_s	KV	BCDR
Acacia senegal gum, HM starch	Erni *et al.* (2007)	E^*_d, G'_s, G''_s, J_s	MM	OBM, BCDR
Acacia senegal, acacia seyal, beet pectin, gum ghatti	Castellani, Al-Assaf *et al.* (2010); Castellani, Guibert *et al.* (2010)	E_d	⋯	OBM
Hydroxypropylcellulose	Mezdour *et al.* (2007)	E'_d	KV	OBM
Hydroxypropylmethylcellulose	Pérez *et al.* (2006, 2008)	E'_d, E''_d	⋯	LT, OBM
Hydroxypropylmethylcellulose	Camino *et al.* (2009)	E'_d, E''_d	⋯	LT
Hydrophobically modified cellulose, alkyl polyoxyethyl sulfate	Dong *et al.* (2009)	E'_d, ε_d	KV	OBM
Gelatin	Leick *et al.* (2009)	E'_d, ε_d, G'_s, ε_s	KV	OBM, BCDR
Poly(1-alkylene-*co*-maleic acid)	Kim *et al.* (2006)	E'_d, ε_d	KV	SQELS
PDMDAAC	Noskov, Biblin *et al.* (2007)	E'_d, E''_d	⋯	OBM
Rotaxanes	Lee *et al.* (2004)	G'_s, G''_s	⋯	OR-ISR
Poly(tert-butyl metacrylate)	Gavranovic, Deutsch, and Fuller (2005); Gavranovic, Smith *et al.* (2006)	G'_s, G''_s, J_s	JM	OR-ISR
Poly(*N*-isopropylacrylamide)	Monteux *et al.* (2006)	G'_s, G''_s	⋯	OR-ISR
Poly(*n*-tetradecyl 4 vinylpyridinium-*co*-4-vinylpiridine) bromide	Miranda *et al.* (2009)	E_d, ε_d, τ_d	KV, ER	LT, SQELS

Sapse, 1975; Deemer and Slattery, 1978; Fischer and Methfessel, 1980; Boruvka, Rotenberg, and Neumann, 1986; Alts and Hutter, 1988; Helfand, Bhattacharjee, and Fredrickson, 1989; Kralchevsky and Ivanov, 1990; Blokhuis and Bedeaux, 1991; Edwards, Brenner, and Wasan, 1991; Blokhuis and Bedeaux, 1992, 1994; Mavrovouniotis and Brenner, 1993; Romero-Rochin and Varea, 1993; Kralchevsky, Eriksson, and Ljunggren, 1994; Groenewold and Bedeaux, 1995; Sagis and Bedeaux, 1996; Groenewold, 1997; Sagis, 2001a, 2001b; Lomholt and Miao, 2006). These models can be used for numerical computations of surface-excess parameters, and when combined with experiments, can provide additional information on the structure of complex interfaces.

B. Conservation of mass, momentum, and energy

The incorporation of excess properties in the conservation laws for mass, momentum, energy, and entropy results in a set of balance equations for the time evolution of the surface mass density, surface momentum, surface energy and surface entropy of the interface (Edwards, Brenner, and Wasan, 1991; Kralchevsky, Eriksson, and Ljunggren, 1994; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007). These differential balance equations act as boundary conditions for the differential equations of the bulk fields of the system. In this section we briefly review the specific forms of these interfacial balances and show how they are derived using generalizations of the well-known conservation laws to

TABLE VI. Surface dilatational and shear properties of interfaces with adsorbed polymers and low molecular weight surfactants (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
Sulfonated poly-acrylamide/CTAB	Ritacco, Kurlat, and Langevin (2003)	E_d', ε_d	KV	BPT
PEO-PPO triblock copolymer/β-lg	Rippner Blomqvist *et al.* (2004)	E_d', ε_d, G_s', G_s''	KV	RT, DNR
Polystyrene sulfonate/C_{12}TAB	Monteux, Fuller, and Bergeron (2004)	E_d', E_d'', G_s', G_s'', J_s	2VS	OBM, OR-ISR
Polystyrene sulfonate/DTAB	Noskov, Loglio, and Miller (2005)	E_d', E_d''	···	LT
Polystyrene sulfonate/DODAB	Klebanau *et al.* (2005)	E_d', ε_d	KV	LT
PAM-PAMPS copolymer/DTAB	Ritacco, Cagna, and Langevin (2006)	E_d', E_d''	KV	OBM
DNA/DOGS	Picard and Davoust (2006)	E_d', ε_d	KV	CWA
Gelatin/cationic gemini surfactant	Wu *et al.* (2007)	E_d'	KV	LT
λ-carrageenan/DTAB	Nobre, Wong, and Darbello Zaniquelli (2007)	E_d'	KV	OBM
Hydroxypropyl-methyl cellulose/C_nTAB	Li *et al.* (2008)	E_d', ε_d	KV	LT
PEG/DPPC	Auguste *et al.* (2008)	G_s', G_s''	···	OR-ISR
HPAM/CTAB	H. Zhang *et al.* (2008)	E_d'	KV	LT
PVP/sodium oleate	Xin *et al.* (2008)	E_d'	KV	LT
Hydroxypropyl cellulose/Lecithin	Mezdour *et al.* (2008)	E_d'	KV	OBM
DNA/DTAB, CMC/DTAB, PAMPS/DTAB	Espinosa and Langevin (2009)	G_s', G_s'', τ_s	MM	BCDR

multiphase systems with excess variables associated with the interfaces.

We start with the principle of conservation of mass. When mass is associated with the interface, this conservation principle requires

$$\frac{d}{dt}\sum_I\left[\int_{\mathcal{R}_I}\rho_I dV + \sum_{J\neq I}\int_{\Sigma_{I,J}}\rho^s_{I,J}dA\right] = \frac{d}{dt}\left[\int_{\mathcal{R}}\rho dV + \int_{\Sigma}\rho^s dA\right] = 0, \tag{1}$$

where ρ_I is the total mass density in bulk phase I, $\mathcal{R}_I$ is the domain of bulk phase I, $\mathcal{R}$ is the union of all bulk phase domains $\mathcal{R}_I$, dV denotes a volume integration, $\rho^s_{I,J}$ is the total surface mass density on the interface $\Sigma_{I,J}$ (separating bulk phases $\mathcal{R}_I$ and $\mathcal{R}_J$), Σ is the union of all interfacial domains, and dA denotes an area integration. The second part of this equation represents a shorthand notation in which we have, for brevity, dropped all indices. The density fields appearing in this part should be interpreted as piecewise continuous functions on their respective domains. Evaluating the material derivative in Eq. (1) we find that at each point in bulk phase $\mathcal{R}$ (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007)

$$\frac{d_b\rho}{dt} + \rho\nabla\cdot\mathbf{v} = 0, \tag{2}$$

which is the familiar equation of continuity. In Eq. (2) d_b/dt denotes a bulk material derivative, ∇ is the 3D gradient operator, and $\mathbf{v}$ is the velocity field in the bulk phase. In addition we find that for each point on the interface Σ (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007)

$$\frac{d_s\rho^s}{dt} + \rho^s\nabla_s\cdot\mathbf{v}^s + [\![\rho(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi}]\!] = 0, \tag{3}$$

where $\mathbf{v}^s$ is the surface velocity, and ∇_s is the surface gradient operator (Slattery, Sagis, and Oh, 2007). Here the surface material derivative d_s/dt is defined by (Slattery, Sagis, and Oh, 2007)

$$\frac{d_s\psi^s}{dt} = \frac{\partial\psi^s}{\partial t} + (\nabla_s\psi^s)\cdot(\mathbf{v}^s-\mathbf{u}), \tag{4}$$

where $\mathbf{u}$ is the speed of displacement of the interface. Note that we have defined the surface material derivative in terms

TABLE VII. Surface dilatational and shear properties of interfaces with adsorbed asphaltenes, particles, or mixtures of particles and low molecular weight surfactants (a list of abbreviations for models and methods is given in Table I).

Surface active material	Reference	Property	Model	Method
Crude oil asphaltines	Freer and Radke (2004)	E_d', ε_d	MM	OBM,
Crude oil asphaltines	Sztukowski and Yarranton (2005); Yarranton, Sztukowski, and Urrutia (2007)	E_d', ε_d	KV	OBM
Crude oil asphaltines	Hannisdal, Orr, and Sjöblom (2007)	E_d', ε_d	KV	OBM
Crude oil asphaltines	Quintero *et al.* (2009)	E_d', E_d''	···	OBM
Crude oil asphaltines	Verruto, Le, and Kilpatrick (2009)	E_d, ε_d, G_s', G_s''	KV	OBM, BCDR
Petroleum sulfonates	Zhaoxia *et al.* (2010)	ε_s	BM	BCDR
Silica particles	Zang *et al.* (2010)	G_s', G_s''	NLM	BCDR
Silica particles/CTAB	Ravera *et al.* (2006, 2008)	E_d', ε_d	KV	OBM, BPT
Silica particles/CTAB	Wang *et al.* (2008)	E_d', ε_d	KV	LT
Silica particles/CTAB	Dong *et al.* (2010)	E_d', E_d''	···	OBM
Polystyrene particles/SDS	Reynaert, Moldenaers, and Vermant (2007)	G_s', G_s''	···	OR-ISR
Ellipsoidal polystyrene particles	Madivala, Fransaer, and Vermant (2009)	G_s', G_s''	MM	BCDR

of the intrinsic surface velocity $\dot{\mathbf{y}} = \mathbf{v}^s - \mathbf{u}$. Without loss of generality we could also express this derivative in terms of $\mathbf{v}^s$ (Edwards, Brenner, and Wasan, 1991). The velocity $\mathbf{v}^s$ is formally defined as

$$\mathbf{v}^s \equiv \frac{d_s \mathbf{p}^s(y^1, y^2, t)}{dt}, \tag{5}$$

where $\mathbf{r} = \mathbf{p}^s(y^1, y^2, t)$ is the parametrization of the interface, and y^α $(\alpha = 1, 2)$ are the surface coordinates. The spatial velocity $\mathbf{u}$ is formally defined as

$$\mathbf{u} \equiv \frac{\partial \mathbf{p}^s(y^1, y^2, t)}{\partial t}. \tag{6}$$

The boldface brackets in Eq. (3) are used to denote jump terms, and are defined as

$$\llbracket \psi \boldsymbol{\xi} \rrbracket = \psi^{(I)} \boldsymbol{\xi}^{(I,J)} + \psi^{(J)} \boldsymbol{\xi}^{(J,I)}, \tag{7}$$

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

Equation (3) is referred to as the overall jump mass balance for the dividing surface (Slattery, Sagis, and Oh, 2007). For every point on the surface it describes the time rate of change of the surface mass density as a result of in-plane convection and transfer of mass from the bulk phases to the interface. Note that when there is no mass transfer to or from the interface, $\mathbf{v} \cdot \boldsymbol{\xi} = \mathbf{v}^s \cdot \boldsymbol{\xi}$, and the term in boldface brackets is identical to zero.

The principle of conservation of mass requires for each individual species in a multicomponent mixture that the time rate of change of mass of that species is equal to the rate at which mass of this species is produced by homogeneous and heterogeneous chemical reactions. If we let $\rho_{(A)}$ be the bulk density of species A at each point in the bulk domain $\mathcal{R}$, $\rho^s_{(A)}$ the surface mass density of species A at each point on the dividing surface, $r_{(A)}$ the rate at which mass of species A is produced per unit volume by homogeneous reactions in the bulk phase, and $r^s_{(A)}$ the rate at which mass of species A is produced per unit area by heterogeneous reactions on the dividing surface, then we find that the principle of conservation of mass requires (Slattery, Sagis, and Oh, 2007)

$$\frac{d}{dt}\left[\int_{\mathcal{R}} \rho_{(A)} dV + \int_{\Sigma} \rho^s_{(A)} dA\right] = \int_{\mathcal{R}} r_{(A)} dV + \int_{\Sigma} r^s_{(A)} dA. \tag{8}$$

This allows us to conclude that at any point in the bulk phase the principle of conservation of mass requires for each species A in the multicomponent mixture (Slattery, Sagis, and Oh, 2007)

$$\frac{d_{(A)}\rho_{(A)}}{dt} + \rho_{(A)} \nabla \cdot \mathbf{v}_{(A)} - r_{(A)} = 0 \tag{9}$$

and at any point on the dividing surface

$$\frac{d_{(A)s}\rho^s_{(A)}}{dt} + \rho^s_{(A)} \nabla_s \cdot \mathbf{v}^s_{(A)} - r^s_{(A)} + \llbracket \rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}^s) \cdot \boldsymbol{\xi} \rrbracket = 0. \tag{10}$$

Here $\mathbf{v}_{(A)}$ is the velocity of species A in the bulk phase, $\mathbf{v}^s_{(A)}$ is the surface velocity of species A, and $d_{(A)s}/dt$ is a surface material derivative, given by Eq. (4), with $\mathbf{v}^s$ replaced by $\mathbf{v}^s_{(A)}$. Equation (9) is referred to as the species mass balance, whereas Eq. (10) is referred to as the jump species mass balance (Slattery, Sagis, and Oh, 2007). It is often more convenient to express these balances in terms of the mass fraction $\omega_{(A)} = \rho_{(A)}/\rho$ and surface mass fraction $\omega^s_{(A)} = \rho^s_{(A)}/\rho^s$. In terms of these variables Eq. (10) reduces to (Slattery, Sagis, and Oh, 2007)

$$\rho^s \frac{d_s \omega^s_{(A)}}{dt} + \nabla_s \cdot \mathbf{j}^s_{(A)} - r^s_{(A)} + \llbracket \mathbf{j}_{(A)} \cdot \boldsymbol{\xi} + \rho(\omega_{(A)} - \omega^s_{(A)})(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} \rrbracket = 0, \tag{11}$$

where $\mathbf{j}_{(A)} = \rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v})$ is the mass flux vector of species A in the bulk phase, and $\mathbf{j}^s_{(A)} = \rho^s_{(A)}(\mathbf{v}^s_{(A)} - \mathbf{v}^s)$ is the surface mass flux vector for species A on the interface. At any point on the dividing surface Eq. (11) describes the time rate of change of the surface mass fraction of component A as a result of surface diffusion, heterogeneous chemical reactions in the interface, diffusion of A from the bulk to the interface, and convection of A from the bulk to the interface.

For a multiphase system the principle of conservation of momentum implies that

$$\frac{d}{dt}\left[\int_{\mathcal{R}} \rho \mathbf{v} dV + \int_{\Sigma} \rho^s \mathbf{v}^s dA\right] = \int_{\mathcal{S}} \mathbf{T} \cdot \mathbf{n} dA + \int_{\mathcal{C}} \mathbf{T}^s \cdot \boldsymbol{\mu} dL + \int_{\mathcal{R}} \sum_{A=1}^{N} \rho_{(A)} \mathbf{b}_{(A)} dV + \int_{\Sigma} \sum_{A=1}^{N} \rho^s_{(A)} \mathbf{b}^s_{(A)} dA, \tag{12}$$

where $\mathbf{b}_{(A)}$ is the force per unit mass acting on species A in the bulk phases, and $\mathbf{b}^s_{(A)}$ is the force per unit mass acting on the material of species A in the dividing surfaces. The second order tensor $\mathbf{T}$ represents the stress tensor in the bulk phase, $\mathbf{T}^s$ is the surface stress tensor, $\mathcal{S}$ is the outer bounding surface of the system, $\mathcal{C}$ is the line of intersection of the surfaces $\mathcal{S}$ and Σ, $\mathbf{n}$ is the unit normal vector on $\mathcal{S}$, and $\boldsymbol{\mu}$ is the unit vector tangent to Σ, normal to $\mathcal{C}$, and outwardly directed with respect to this curve. Evaluating the material derivative in Eq. (12), and using the divergence and surface divergence theorems (Slattery, Sagis, and Oh, 2007), we obtain for the bulk phases of the system

$$\rho \frac{d_b \mathbf{v}}{dt} - \nabla \cdot \mathbf{T} - \sum_{A=1}^{N} \rho_{(A)} \mathbf{b}_{(A)} = 0, \tag{13}$$

and for each point on the interface we find (Slattery, Sagis, and Oh, 2007)

$$\rho^s \frac{d_s \mathbf{v}^s}{dt} - \nabla_s \cdot \mathbf{T}^s - \sum_{A=1}^{N} \rho^s_{(A)} \mathbf{b}^s_{(A)} + \llbracket \rho(\mathbf{v} - \mathbf{v}^s)(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} - \mathbf{T} \cdot \boldsymbol{\xi} \rrbracket = 0. \tag{14}$$

This expression, referred to as the jump momentum balance (Slattery, Sagis, and Oh, 2007), momentum interface balance (Gatignol and Prud'homme, 2001), or surface-excess linear momentum balance (Edwards, Brenner, and Wasan, 1991), describes the time rate of change of surface momentum as a result of in-plane surface stresses (surface tension gradients, and surface viscous stresses, incorporated in the term $\nabla_s \cdot \mathbf{T}^s$), applied force fields, and inertial, hydrostatic, and viscous stresses exerted on the interface by the adjoining bulk phases. It is basically an extended version of the Young-Laplace equation (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007).

Finally, the principle of conservation of energy requires for every multiphase system that in an inertial frame of reference the time rate of change of the sum of the internal and kinetic energy of a body is equal to the work performed by the stresses acting on the body, plus the work done by the body forces, plus the energy transmitted to the body through its boundaries, and the energy transmitted to the material in the interior of the body (Slattery, Sagis, and Oh, 2007):

$$\begin{aligned}\frac{d}{dt}\Big[\int_{\mathcal{R}} \rho\Big(\hat{U}+\frac{1}{2}v^2\Big)dV + \int_{\Sigma}\rho^s\Big(\hat{U}^s+\frac{1}{2}(v^s)^2\Big)dA\Big] &= \int_{\mathcal{S}} \mathbf{v}\cdot\mathbf{T}\cdot\mathbf{n}dA + \int_{\mathcal{C}}\mathbf{v}^s\cdot\mathbf{T}^s\cdot\boldsymbol{\mu}dL \\ &+ \int_{\mathcal{R}}\sum_{A=1}^{N}\rho_{(A)}\mathbf{v}_{(A)}\cdot\mathbf{b}_{(A)}dV + \int_{\Sigma}\sum_{A=1}^{N}\rho^s_{(A)}\mathbf{v}^s_{(A)}\cdot\mathbf{b}^s_{(A)}dA \\ &- \int_{\mathcal{S}}\mathbf{q}\cdot\mathbf{n}dA - \int_{\mathcal{C}}\mathbf{q}^s\cdot\boldsymbol{\mu}dL + \int_{\mathcal{R}}\rho\hat{Q}dV \\ &+ \int_{\Sigma}\rho^s\hat{Q}^s dA. \qquad (15)\end{aligned}$$

Here $\hat{U}$ is the internal energy per unit mass of the bulk phases, $\hat{U}^s$ is the internal energy per unit mass associated with the dividing surfaces, $v^2 = \mathbf{v}\cdot\mathbf{v}$, $\mathbf{q}$ is the energy flux vector, $\mathbf{q}^s$ is the surface energy flux vector, $\hat{Q}$ is the radiant energy transmission per unit mass transmitted to the material in the bulk phases, and $\hat{Q}^s$ is the surface radiant energy transmission to the material in the interfaces. Evaluating the material derivative in Eq. (15), using the divergence and surface divergence theorem, and Eqs. (13) and (14), we find that the differential energy balance for the bulk phases of the system is given by (Slattery, Sagis, and Oh, 2007)

$$\rho\frac{d_b\hat{U}}{dt} = \mathbf{T}:\nabla\mathbf{v} + \sum_{A=1}^{N}\mathbf{j}_{(A)}\cdot\mathbf{b}_{(A)} - \mathrm{div}\mathbf{q} + \rho\hat{Q}, \qquad (16)$$

and that the jump energy balance for the interface takes the form

$$\begin{aligned}\rho^s\frac{d_s\hat{U}^s}{dt} &= \mathbf{T}^s:\nabla_s\mathbf{v}^s + \sum_{A=1}^{N}\mathbf{j}^s_{(A)}\cdot\mathbf{b}^s_{(A)} - \mathrm{div}_s\mathbf{q}^s + \rho^s\hat{Q}^s \\ &- \Big[\!\!\Big[\rho\Big(\hat{U}-\hat{U}^s+\frac{1}{2}|\mathbf{v}-\mathbf{v}^s|^2\Big)(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi} \\ &- (\mathbf{v}-\mathbf{v}^s)\cdot\mathbf{T}\cdot\boldsymbol{\xi} + \mathbf{q}\cdot\boldsymbol{\xi}\Big]\!\!\Big]. \qquad (17)\end{aligned}$$

The colon in the first term on the right-hand sides of Eqs. (16) and (17) denotes a double contraction between the two tensor fields.

We see that the conservation principles for mass, momentum, and energy allow us to formulate a complete set of evolution equations for the mass densities, momentum densities, and energy densities of the bulk phases and interfaces of a multiphase system. These equations must be complemented by equations for the time evolution of the bulk and surface entropy of the system. Since the various NET formalisms use different expressions for these equations, we review the entropy balances when we discuss the individual formalisms.

C. Surface rheological properties

The set of differential equations for the surface mass density, surface momentum density, and surface energy need to be closed with a set of constitutive equations for the fluxes appearing in them: the surface stress tensor, the surface mass flux vectors, and the surface energy vector. Specifying a constitutive equation for the surface stress tensor leads to the introduction of surface viscosities (shear and dilatational) for interfaces with liquidlike behavior, and to the introduction of surface moduli (shear and dilatational) for interfaces with elastic or viscoelastic behavior. The determination of these properties is the main aim of the field of surface rheology.

In NET the stress generated in an interface by an applied deformation is usually expressed in terms of the surface extra stress tensor $\boldsymbol{\sigma}^s$ (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007). This symmetric tangential surface tensor (Slattery, Sagis, and Oh, 2007) is related to the total surface stress tensor $\mathbf{T}^s$ by (Slattery, Sagis, and Oh, 2007)

$$\boldsymbol{\sigma}^s = \mathbf{T}^s - \gamma\mathbf{P}, \qquad (18)$$

where γ is the surface tension, and $\mathbf{P}$ is the surface projection tensor (the 2D equivalent of the 3D unit tensor) (Slattery, Sagis, and Oh, 2007). When a surface is deformed in, for example, a Langmuir trough, the effect of the deformation is typically recorded using a Wilhelmy plate (Wilhelmy, 1863). Since this device is historically associated with the measurement of surface tensions, the stresses induced in a deformed interface are often expressed in terms of a dynamic surface tension γ_d. The dynamic surface tension convention can be obtained from the surface stress tensor convention by replacing (Sagis, 2010c)

$$\mathbf{T}^s = \gamma\mathbf{P} + \boldsymbol{\sigma}^s \rightarrow \gamma_d\mathbf{P}. \qquad (19)$$

Although the dynamic surface tension convention is in principle correct, Eq. (18) will be used in the remainder of this paper, since it clearly reminds us that in the deformed state we are measuring stresses, which may depend on direction, rather than surface tensions, which are isotropic in nature. Anisotropy in the stress response, particularly important for interfaces in a solid or liquid crystalline state, may easily be overlooked in the dynamic surface tension convention.

For simple liquidlike interfaces several constitutive relations have been proposed for the surface extra stress tensor. For interfaces with a purely viscous response the linear Boussinesq model describes that response as (Boussinesq, 1913a, 1913b, 1913c; Scriven, 1960)

$$\boldsymbol{\sigma}^s = (\varepsilon_d - \varepsilon_s)[\mathrm{tr}\mathbf{D}^s]\mathbf{P} + 2\varepsilon_s\mathbf{D}^s, \tag{20}$$

where ε_d is the surface dilatational viscosity (the 2D equivalent of the bulk viscosity coefficient), ε_s is the surface shear viscosity, and $\mathbf{D}^s$ is the surface rate of deformation tensor. We see that this model is basically the 2D equivalent of the Newtonian fluid; for this type of fluid the extra stress tensor in the bulk phase $\boldsymbol{\sigma}$ is given by $\boldsymbol{\sigma} = (\kappa - \frac{2}{3}\eta)[\mathrm{tr}\mathbf{D}]\mathbf{I} + 2\eta\mathbf{D}$, where η is the shear viscosity of the bulk phase, κ is the bulk viscosity coefficient, $\mathbf{D}$ is the rate of deformation tensor in the bulk phase, and $\mathbf{I}$ the 3D unit tensor.

The derivation of Eq. (20) and a formal definition of the parameters that appear in it will be given in Secs. IV and V. When looking at Tables I–VII we see that few interfaces actually show purely viscous behavior, so the usefulness of the linear Boussinesq model is rather limited.

The behavior of fluidlike interfaces in uniaxial or biaxial extensional flows is characterized by the surface elongational viscosity (Olson and Fuller, 2000; Leiske *et al.*, 2010) (the 2D equivalent of the elongational viscosity of bulk phases, an important parameter in describing the dynamics of viscoelastic fluids such as polymer solutions and polymer melts in contraction flows). The surface extensional viscosity is particularly important in coating processes and (film or sheet) extrusion processes. Surface elongational flow properties can, for example, be determined by subjecting monolayers to a contraction flow in a Langmuir trough (Olson and Fuller, 2000; Leiske *et al.*, 2010).

For interfaces with a purely elastic response to a deformation a generalization of Hooke's law, the surface Hooke model, is often used. In this model the surface extra stress tensor is given by (Barthès-Biesel and Rallison, 1981; Pieper, Rehage, and Barthès-Biesel, 1998)

$$\boldsymbol{\sigma}^s = (E_d - G_s)[\mathrm{tr}\mathbf{U}^s]\mathbf{P} + 2G_s\mathbf{U}^s, \tag{21}$$

where E_d is the surface dilatational modulus, G_s is the surface shear modulus, and $\mathbf{U}^s$ is the surface displacement tensor (related to $\mathbf{D}^s$ by $\dot{\mathbf{U}}^s = \mathbf{D}^s$). The surface dilatational modulus E_d is defined by

$$E_d \equiv A\left(\frac{\partial \gamma}{\partial A}\right), \tag{22}$$

where A is the interfacial area. E_d is equal to the inverse of the isothermal compressibility of the interface and represents the resistance of the interface against in-plane all-sided compression. It is basically the 2D equivalent of the bulk modulus K_b, defined by $K_b \equiv -V(\partial P/\partial V)$, where P denotes the thermodynamic pressure and V the volume. A surface property closely related to the surface dilatational modulus is the surface Young modulus Y_s, given by

$$Y_s \equiv \frac{\sigma^s_{xx}}{U^s_{xx}}. \tag{23}$$

We see that the surface Young modulus is defined as the resistance of the interface to a uniaxial compression (for example, performed in a Langmuir trough). From Eq. (21) we see that the surface Young modulus of a completely compressible interface is related to the surface dilatational and shear moduli by $Y_s = E_d + G_s$. Often Eq. (21) is also applied to compressible interfaces which are not purely elastic. For many of these interfaces $G_s \ll E_d$. For that reason it is often tacitly assumed that the modulus determined in Langmuir trough experiments is the dilatational modulus. But for components with a tendency to form highly elastic gels at the interface this may introduce significant errors in the determination of the dilatational modulus. For an ideal Hookean interface the surface dilatational and shear moduli are related to Y_s by (Pieper, Rehage, and Barthès-Biesel, 1998; Zhu and Zheng, 2008)

$$E_d = \frac{Y_s}{2(1 - \nu_s)}, \tag{24}$$

$$G_s = \frac{Y_s}{2(1 + \nu_s)}, \tag{25}$$

where ν_s is the surface Poisson ratio, defined by $\nu_s = -U^s_{yy}/U^s_{xx}$. For a completely compressible interface $\nu_s = 0$, and when this type of interface is subjected to a uniaxial compression, we find that for highly elastic surfaces $E_d = G_s = Y_s/2$. Neglecting the contribution of G_s to Y_s would in this case lead to an overestimation of the dilatational modulus by 100%, relative to its actual value.

For purely elastic interfaces E_d and G_s are real parameters. The vast majority of interfaces display viscoelastic behavior, and for those interfaces E_d and G_s are complex numbers. The real part of the moduli represents the storage of elastic energy in the interface, whereas the imaginary part represents the viscous dissipation of energy. Several models have been proposed in the literature for the surface extra stress tensor of viscoelastic interfaces (Edwards, Brenner, and Wasan, 1991; Gatignol and Prud'homme, 2001; Slattery, Sagis, and Oh, 2007), and these will be discussed in Sec. V, in the context of our discussion of the extended irreversible thermodynamics formalism. In addition to the complex moduli E^*_d and G^*_s, studies occasionally also determine the closely related creep compliances J_d or J_s, defined by $J_d(t) = U^s_{xx}(t)/\sigma^s_{xx}$, and $J_s(t) = U^s_{xy}(t)/\sigma^s_{xy}$. These parameters are determined by measuring the displacement as a function of time, driven by a fixed applied surface stress. They are closely related to $E_d(t)$ and $G_s(t)$: From Eq. (21) we obtain $J_d(t) = [E_d(t) + G_s(t)]^{-1}$, and $J_s(t) = G_s^{-1}(t)$.

The rheological parameters discussed above represent the response of interfaces to in-plane deformations. Interfaces can also be deformed by out-of-plane deformations, such as bending. The resistance against bending is usually characterized by the bending rigidities, appearing in the familiar Helfrich expansion for the surface free energy (Helfrich, 1973). These parameters are, for example, important in the dynamic behavior of membranes (Dimova *et al.*, 2006; Danov, Kralchevsky, and Stoyanov, 2010), phase-separated biopolymer systems (Scholten, Sagis, and van der Linden, 2004, 2005, 2006; Scholten *et al.*, 2006b), or vesicles (Smeulders, Blom, and Mellema, 1990, 1992; de Haas, Ruiter, and Mellema, 1995). In this review we focus predominantly on in-plane rheological properties and will not discuss the response of interfaces to out-of-plane deformations.

III. EXPERIMENTAL CHARACTERIZATION OF SURFACE RHEOLOGICAL PROPERTIES

A. Methods

Tables I–VII give an overview of the specific systems studied in recent years, the rheological properties that were determined, the rheological models that were used to analyze the data, and the method used to obtain the data.

From these tables we see that dilatational moduli are most frequently determined using oscillating bubble methods (OBM), in which a nearly spherical droplet is formed at the tip of a needle, and the interface of this droplet is deformed sinusoidally by injecting and withdrawing fluid into or from the interior of the droplet, using a motor syringe. The surface tension and real and imaginary parts of the dilatational modulus are obtained from image analysis of the droplet shape. A popular variation of the OBM is bubble pressure tensiometry (BPT), in which a droplet or bubble is deformed using a piezoelement and the surface tension and dilatational moduli are obtained from measurements of the Laplace pressure. Both techniques can be applied in steady state, or in unsteady state. In the latter mode the determination of the surface dilatational properties can be used to study the kinetics of adsorption of surface active materials, or conformational changes that occur after adsorption at an interface, such as those observed in proteins. An advantage of this method is its relative simplicity, and its flexibility. Using additional syringes, the interior and exterior phases can be replaced with different solutions, which allow researchers to study the displacement of one surface active component by another, or to study the effects of multilayer adsorption on surface rheological properties (Ganzevles *et al.*, 2006).

A limitation of the OBM and BPT methods is the limited strain and frequency range that can be applied, especially for devices where the deformation is imposed using a motor syringe. The maximum frequency that can be applied is typically less than 1 Hz. With respect to the strain range, it is difficult to perform measurements at low strains (i.e., strains less than 0.01). This means that for most complex interfaces the applied deformation may be in the nonlinear regime, which complicates interpretation of the data.

Although the basic principle of the method is fairly simple, accurate analysis is complicated by a number of factors. In OBM and BPT methods data for the dilatational modulus are in general obtained using the Young-Laplace equation:

$$P^{(2)} - P^{(1)} = 2\gamma_d H, \tag{26}$$

where $P^{(2)}$ is the pressure in the interior of the droplet, $P^{(1)}$ is the pressure in the outer phase, and H is the curvature of the interface ($=1/R$ for spherical droplets, where R is the droplet radius). The Young-Laplace equation is a simplified version of the momentum balance at the interface, given in Eq. (14). The complete form of the momentum balance contains additional contributions describing the effects of in-plane inertial stresses, surface tension gradients, and inertial and viscous stresses exerted on the interface by the adjoining bulk phases. Next we discuss criteria which can be used for determining whether these additional contributions to the Laplace equation are indeed negligible.

If the deformations of the interface are small and slow, we may neglect inertial terms in Eq. (14). For small oscillatory deformations of the droplet radius ($R = R_0 + \delta R e^{i\omega t}$), the inertial term scales with frequency as $\rho^s \omega^2 \delta R \boldsymbol{\xi}$. Inertial effects are therefore negligible when $\rho^s \omega^2 \delta R \boldsymbol{\xi} \ll 2\gamma H \boldsymbol{\xi}$, or $\omega \ll \sqrt{2\gamma/\rho^s R \delta R}$ (Sagis, 2010c). If we assume typical values for $\gamma \sim 10^{-2}$ N/m, $\rho^s \sim 10^{-6}$ kg/m^2, $R \sim 10^{-3}$ m, and $\delta R \sim 0.1R$, we arrive at an upper limit for the frequency of the order of 10^5 s^{-1}. In oscillating bubble experiments where the interface is deformed by using a motor syringe, the maximum frequency of operation is of the order of 1 Hz. In those experiments where oscillations are induced using piezoelements the upper limit is about 500 Hz. So for both modes inertial effects can safely be discarded. But dilatational properties can also be determined using ultrasound with frequencies up to 10 MHz, and then inertial effects can no longer be neglected (Doinikov, Haac, and Dayton, 2009a, 2009b).

If inertial effects are neglected and the interface is deformed uniformly, gradients in the surface tension may also be omitted, and we find that Eq. (14) reduces to (Sagis, 2010c)

$$\nabla_s \cdot \boldsymbol{\sigma}^s + 2\gamma H \boldsymbol{\xi} + [\![-P\boldsymbol{\xi} + \boldsymbol{\sigma} \cdot \boldsymbol{\xi}]\!] = 0. \tag{27}$$

If we express Eq. (27) in spherical coordinates, combine the r, θ, and ϕ components, and linearize the result we obtain (Slattery, Sagis, and Oh, 2007; Sagis, 2008, 2010c)

$$2(\gamma + \mathrm{tr}\boldsymbol{\sigma}^s)H + P^{(1)} - P^{(2)} + \sigma_{rr}^{(2)} - \sigma_{rr}^{(1)} = 0. \tag{28}$$

The magnitude of the viscous bulk stress σ_{rr} is of the order of $\eta\omega(\delta R/R)^3$, where η is the shear viscosity in the bulk phase. The viscous bulk stresses will be negligible when $\eta\omega(\delta R/R)^3 \ll 2H\,\mathrm{tr}\boldsymbol{\sigma}^s$. For a purely elastic interface $\mathrm{tr}\boldsymbol{\sigma}^s = 2E_d\,\mathrm{tr}\mathbf{U}^s \sim 2E_d(\delta R/R)^2$, and we find that for the viscous stresses of the bulk phases to be negligible we must have $\eta \ll 4E_d/\delta R\omega$. Assuming typical values for $E_d \sim 10^{-2}$ N/m, and $\delta R \sim 10^{-4}$ m, we find that $\eta \ll 400/\omega$ for viscous bulk stresses to be negligible. In the high frequency regime of bubble pressure methods (~ 500 Hz) the viscosity of the bulk phases would have to satisfy $\eta \ll 1$ Pa s.

Using Eq. (26) on a system where bulk stresses are not negligible may lead to a misinterpretation of the characteristics of the interface. Assume we are determining the dilatational properties of a purely elastic interface. The imaginary component of the dilatational modulus of this interface should be zero. When bulk stresses are not negligible, the dynamic surface tension measured by the oscillating bubble method is given by

$$\gamma_d = \gamma + \mathrm{tr}\boldsymbol{\sigma}^s + (2H)^{-1}(\sigma_{rr}^{(2)} - \sigma_{rr}^{(1)}). \tag{29}$$

If the adjoining fluids are highly viscous liquids, and the results are analyzed with $\gamma_d = \gamma + \mathrm{tr}\boldsymbol{\sigma}^s$ rather than Eq. (29), the effect of the bulk stresses would appear as a nonzero imaginary component of the complex dilatational modulus, and we would incorrectly identify the interface as being viscoelastic rather than purely elastic. For aqueous solutions of simple surfactants the additional bulk terms in Eq. (29) will be undetectable, but for highly viscous oil phases or concentrated polymer solutions, with viscosities ~1 Pa s or higher, these terms will affect the measured value of the dilatational modulus significantly.

As an alternative to OBM and BPT methods, various studies use Langmuir troughs (LT) to determine dilatational properties. In this device a flat interface is deformed by the steady or oscillatory motion of one or more barriers, and the resulting change in surface tension is monitored with a Whilhelmy plate. Just as the OBM and BPT devices, the Langmuir trough can be used to perform measurements on interfaces which are in equilibrium with the bulk phase, or interfaces which are still in an unsteady state. Most LT studies listed in Tables I–VII are performed on interfaces not yet in an equilibrium state, and the time evolution of the surface dilatational properties is often used to extract information on the adsorption processes of the surface active components. As mentioned, in Langmuir troughs it is actually the surface Young modulus Y_s that is determined, and when the contribution of G_s to the Young modulus is not negligible, Y_s may deviate significantly from E_d. This problem can be avoided by using two Wilhelmy plates, one mounted parallel to the direction of the barriers of the trough, and one perpendicular to this direction (Petkov *et al.*, 2000; Cicuta and Terentjev, 2005; Cicuta, 2007). By measuring both the xx and yy components of the surface extra stress tensor simultaneously, both E_d and G_s can be extracted.

Dilatational and shear properties of the interface can also be extracted from surface wave analysis, using surface quasielastic light scattering (SQELS), in which the thermal fluctuations of the interface are analyzed, or capillary wave analysis (CWA), in which surface waves are generated mechanically or by using electric fields. Recent reviews of these techniques are given by Buzza *et al.* (1998, 2002), Penfold (2001), Cicuta and Hopkinson (2004b), Monroy *et al.* (2007), and Danov, Kralchevsky, and Stoyanov (2010).

A relatively new development is the application of Fourier transfer (FT) rheometry to determine surface dilatational properties in the nonlinear regime (Hilles, Maestro *et al.*, 2006; Hilles, Monroy *et al.*, 2006; Monroy *et al.*, 2007; Arriaga *et al.*, 2008). In FT rheometry a large amplitude oscillatory deformation is applied and the stress response is analyzed in frequency space (Wilhelm, Maring, and Spiess, 1998; Wilhelm, Reinheimer, and Ortseifer, 1999). For isotropic materials only odd harmonics appear in the frequency spectrum, and the number and intensity of these harmonics is a measure for the departure from linearity. In anisotropic systems even harmonics may also appear (Sagis, Ramaekers, and van der Linden, 2001). The technique has so far been applied only to dilatational rheology in Langmuir troughs (Hilles, Maestro *et al.*, 2006; Hilles, Monroy *et al.*, 2006; Arriaga *et al.*, 2008), but could in principle also be applied to oscillating bubble methods. A problem encountered in studying the nonlinear response of interfaces using this type of method is the lack of suitable nonlinear models to analyze the frequency spectrum. NET is an excellent tool to construct such models.

The techniques discussed up to this point are primarily used to determine dilatational properties of interfaces. For the determination of surface shear properties there is also a wide range of experimental techniques available. For example, they can be determined using rheometers equipped with a biconical disk geometry (BCDR). Since the biconical disk can be used in conjunction with commercial rheometers, it allows for characterization of interfaces with a wide range of tests (steady shear, oscillatory shear, step shear, strain sweeps, and frequency sweeps). Surface rheological properties, such as the surface shear viscosity, surface storage modulus, or surface loss modulus, can be determined in steady state (allowing the surface to reach an equilibrium state prior to measurements), or in an unsteady state. The latter mode can again be used to study adsorption processes, conformational changes after adsorption, or 2D gelling processes.

In the BCDR the surface shear properties are determined by analyzing the measured torque data with linear models such as the Boussinesq model given in Eq. (20), or its viscoelastic generalizations (Oh and Slattery, 1978; Edwards, Brenner, and Wasan, 1991; Erni *et al.*, 2003, 2004; Slattery, Sagis, and Oh, 2007). In the nonlinear response regime, the surface viscosities and moduli are determined using the same linear constitutive equations, but are then interpreted as *apparent* viscosities or moduli that depend on the (rate of) deformation (an approach also used in the experimental evaluation of rheological properties of bulk fluids).

A drawback of BCDR setups is that the relatively high inertia of the motor unit and geometry makes them unsuitable for interfaces with relatively low surface shear properties, such as interfaces stabilized by low molecular weight surfactants. They are primarily used for the study of interfaces stabilized by proteins (Borbás, Murray, and Kiss, 2003; Martin *et al.*, 2005; Wierenga *et al.*, 2006; Erni, Fischer, and Windhab, 2007; Erni *et al.*, 2008; Murray, Dickinson, and Wang, 2009; Blijdenstein, de Groot, and Stoyanov, 2010), protein and low molecular weight surfactant mixtures (Gunning *et al.*, 2004), mixtures of proteins and polysaccharides (Ganzevles *et al.*, 2006, 2007; Jourdain *et al.*, 2009; Piazza *et al.*, 2009; Miquelim, Lannes, and Mezzenga, 2010), polymers (Erni *et al.*, 2007; Duerr-Auster, Gunde, and Windhab, 2008; Leick *et al.*, 2009; Maestro *et al.*, 2009), or colloidal particles (Madivala, Fransaer, and Vermant, 2009; Zang *et al.*, 2010).

The inertia problem can be somewhat alleviated by using a double-wall ring geometry (DWRG) (Regev *et al.*, 2010; Vandebril *et al.*, 2010), instead of a bi-cone. Another device that reduces the inertia problem is the oscillating rod interfacial shear rheometer (OR-ISR) (Brooks *et al.*, 1999), in which the interface is deformed using a thin magnetic needle, displaced by two magnetic coils.

Surface shear properties can also be determined using the du Nuöy ring (DNR) method. In this technique an oscillatory torque is applied on the interface using a thin ring placed in the interface. The technique of normalized resonance is used to extract data for the surface shear properties. For a more detailed review of methods suitable for measuring surface shear properties see a number of recent publications (Edwards, Brenner, and Wasan, 1991; Warburton, 1996; Slattery, Sagis, and Oh, 2007; Miller *et al.*, 2010).

B. Constitutive models

When examining Tables I–VII we see that in most cases the model used to analyze data from surface rheological experiments is not clearly defined. Most simply determine the real and complex parts of the dilatational or shear modulus, without choosing a particular model to analyze their results. In those publications where a model is specified the most common one used is the Kelvin-Voigt (KV) model (Petkov *et al.*, 2000; Fang, Zou, and He, 2003; Kim and Yu, 2003; Monroy *et al.*, 2003, 2005; Ritacco, Kurlat, and Langevin, 2003; Wantke, Fruhner, and Örtegren, 2003; Pérez-Orozco *et al.*, 2004; Rippner Blomqvist *et al.*, 2004; Stubenrauch and Miller, 2004; Klebanau *et al.*, 2005; Liggieri *et al.*, 2005; Maldonado-Valderrama, Fainerman, Cálvez-Ruiz *et al.*, 2005; Rouimi *et al.*, 2005; Sztukowski and Yarranton, 2005; Velázquez *et al.*, 2005; Andersen *et al.*, 2006; Benjamins, Lyklema, and Lucassen-Reynders, 2006; Kim *et al.*, 2006; Kolodziejczyk *et al.*, 2006; Picard and Davoust, 2006; Ravera *et al.*, 2006, 2008; Ritacco, Cagna, and Langevin, 2006; Grigoriev and Stubenrauch, 2007; Hannisdal, Orr, and Sjöblom, 2007; Lilbaek *et al.*, 2007; Mezdour *et al.*, 2007, 2008; Nobre, Wong, and Darbello Zaniquelli, 2007; Santini, Liggieri *et al.*, 2007; Santini, Ravera *et al.*, 2007; Vrânceanu *et al.*, 2007, 2008; Wu *et al.*, 2007; Yarranton, Sztukowski, and Urrutia, 2007; Fainerman, Petkov, and Miller, 2008; Fainerman *et al.*, 2008; Lakshmanan, Dhahathreyan, and Miller, 2008; Leiva *et al.*, 2008; Li *et al.*, 2008; Wang *et al.*, 2008; Xin *et al.*, 2008; H. Zhang *et al.*, 2008; L. Zhang *et al.*, 2008; Dong *et al.*, 2009; Georgieva *et al.*, 2009; Jourdain *et al.*, 2009; Maldonado-Valderama *et al.*, 2009; McAuley, Jones, and Kett, 2009; Miranda *et al.*, 2009; Verruto, Le, and Kilpatrick, 2009; Yin, Deng, and Esker, 2009; Zhang *et al.*, 2009; Arriaga *et al.*, 2010; Mahmoudi *et al.*, 2010). In terms of spring-and-dashpot models commonly used to model 3D rheological responses, the Kelvin-Voigt model represents a single spring connected in parallel with a single dashpot. The complex dilatational modulus is assumed to be given by

$$E_d^* = E_d + i\omega\varepsilon_d. \tag{30}$$

Often the choice for the KV model is not specifically stated, but whenever studies used an expression of the form of Eq. (30) for the dilatational modulus, we assumed the KV model was used.

Another model frequently used is the single-mode Maxwell model (Rivillon *et al.*, 2002; Foreman *et al.*, 2003; Malzert *et al.*, 2003; Cicuta and Hopkinson, 2004a; Freer and Radke, 2004; Ivanova *et al.*, 2004; Babak, Desbrières, and Tikhonov, 2005; Rippner Blomqvist, Wärnheim, and Claesson, 2005; Hilles, Sferrazza *et al.*, 2006; Sosnowski, Pawelec, and Gradoń, 2006; Anton *et al.*, 2007; Erni, Fischer, and Windhab, 2007; Erni *et al.*, 2007, 2008; Juárez *et al.*, 2007; Krishnaswamy, Rathee, and Sood, 2008; López-Montero *et al.*, 2008; Walder, Levine, and Dennin, 2008; Espinosa and Langevin, 2009; Madivala, Fransaer, and Vermant, 2009; Arriaga *et al.*, 2010). In this model the interfacial behavior is characterized by two parameters: an interfacial viscosity (or modulus) and a single relaxation time. The model is applied to both dilatational and surface shear experiments, and in both cases the expression for the stress is a simple generalization of the linear Maxwell model used for bulk phases (Bird, Armstrong, and Hassager, 1987). In Sec. V we discuss this model in more detail and address the validity of the variations of this model used in the literature.

A simple extension of the single-mode Maxwell model is the multimode Maxwell model (Babak, Desbrières, and Tikhonov, 2005; Babak *et al.*, 2008a, 2008b), which assumes that the stress-deformation behavior of the interface is characterized by a set of discrete relaxation times, rather than a single one. Variations of this model with a continuous spectrum of relaxation times have also been used for the modeling of the stress response of interfaces with adsorbed or spread polymers (Rivillon *et al.*, 2002; Hilles, Sferrazza *et al.*, 2006).

A familiar variation on the Maxwell model is the Jeffreys model (Bird, Armstrong, and Hassager, 1987), and this model has also been generalized for analysis of surface rheological data (Gavranovic, Deutsch, and Fuller, 2005; Gavranovic, Smith *et al.*, 2006). This model describes the response of the interface by three parameters: a viscosity (or modulus) and two characteristic times. These two times are a relaxation time and a "retardation" time (Bird, Armstrong, and Hassager, 1987). The Jeffreys model will also be discussed in more detail in Sec. V.

Other models, less frequently used for the analysis of surface rheological data, are the stretched exponential relaxation model (Hilles, Sferrazza *et al.*, 2006; Cicuta, 2007), a two-Voigt element model (Monteux, Fuller, and Bergeron, 2004), and an adaptation of the reptation model (Noskov, 1995; Rivillon *et al.*, 2002; Monroy *et al.*, 2003). Studies such as the latter show that with some adaptations microstructural models originally developed for analysis of bulk rheological data can also be applied to interfaces. Other examples of this type of microstructural modeling are the analysis of the sol-gel transition in polymer interfaces using percolation models (Monroy *et al.*, 2005; Tadjoa, Cassagnau, and Chapel, 2009), or the scaling analysis of the rheological response of polymer stabilized interfaces with 2D affine network models (Cicuta and Hopkinson, 2004a; Hilles, Monroy *et al.*, 2006).

Nonlinear behavior of interfaces has been studied for interfaces stabilized by lipids (Arriaga *et al.*, 2008), interfaces stabilized by polymers (Hilles, Maestro *et al.*, 2006; Hilles, Monroy *et al.*, 2006), and interfaces stabilized by nanoparticles (Zang *et al.*, 2010). Arriaga *et al.* (2008), Hilles, Maestro *et al.* (2006), and Hilles, Monroy *et al.* (2006) used an expansion of the surface stress of the form $\sigma^s = \sigma_1^s e^{i\omega t} + \sigma_2^s e^{2i\omega t} + \sigma_3^s e^{3i\omega t} + \cdots$ to analyze the response of the interface to an oscillating deformation. The amplitudes σ_i^s are obtained by Fourier transforming the response and analyzing the obtained frequency spectrum. For isotropic interfaces only odd powers are expected to appear in the response, since for this type of interface the surface stress tensor satisfies $\boldsymbol{\sigma}^s(-\mathbf{U}^s) = -\boldsymbol{\sigma}^s(\mathbf{U}^s)$. In their experiments Hilles, Maestro *et al.* (2006) and Hilles, Monroy *et al.* (2006) also found even harmonics in the spectrum, indicating that the polymer stabilized interfaces had an anisotropic response to the applied deformation. The departures from linearity that can be modeled with this type of model are rather limited. We discuss this in more detail at the end of Sec. IV, where we discuss the classical irreversible thermodynamics formalism.

Zang et al. (2010) modeled the behavior of interfaces stabilized by silica nanoparticles and showed that at concentrations above a few tens of $\mathrm{mg\,m^{-2}}$ the particles form soft solid layers. These layers were shown to have a yield stress with a power law dependence on the strain rate amplitude (Zang et al., 2010).

The models listed above associate the response of the interface to a deformation to in-plane dynamic processes. Especially in dilatational experiments with soluble surfactants, the response of the interface will also be affected by mass transfer between the interface and the adjoining bulk phases. This effect is most commonly described with the Lucassen–van den Tempel (LVDT) model (Lucassen and van den Tempel, 1972a, 1972b), which assumes that the stress-deformation behavior is controlled by the diffusion of surface active components from (or to) the bulk phase to (or from) the interface. The LVDT model [or variations thereof, see, e.g., Wantke et al. (2005)] is a frequently used model to analyze the response of interfaces to oscillatory deformations and used by many of the papers listed in Tables I–VII. For complex interfaces both in-plane dynamics, involving momentum as well as surface mass transfer (Marangoni effects), and mass transfer to the interface may affect the response of the interface (Muñoz et al., 2000; Liggieri, Ravera, and Ferrari, 2003; Liggieri et al., 2005; Maldonado-Valderrama, Fainerman, Aksenenko et al., 2005), and models have become available that incorporate both in-plane effects and transport processes perpendicular to the interface (Noskov and Loglio, 1998; Ravera et al., 2001; Palazollo et al., 2002; Noskov et al., 2003; Ivanov et al., 2005; Ravera, Ferrari, and Liggieri, 2006; Kotsmar, Pradines et al., 2009). NET formalisms are ideally suited to incorporate these couplings between fluxes, as we illustrate in the next sections.

IV. CLASSICAL IRREVERSIBLE THERMODYNAMICS OF MULTIPHASE SYSTEMS

In this section we review the classical irreversible thermodynamics formalism for multiphase systems. The original classical irreversible theromodynamics (CIT) formalism developed by Onsager (1931a, 1931b) [see also de Groot and Mazur (1962)] was extended to multiphase systems with excess properties associated with the interfaces, by Bedeaux, Albano, and Mazur (1975), Zielinska and Bedeaux (1982), Bedeaux (1986), Albano and Bedeaux (1987), and Bedeaux and Vlieger (2002). In the classical irreversible thermodynamics formalism we start with an expression for the time rate of change of the surface entropy per unit mass $\hat{S}^s$ of the form (Zielinska and Bedeaux, 1982; Kjelstrup and Bedeaux, 2008)

$$\rho^s \frac{d_s \hat{S}^s}{dt} = -\nabla_s \cdot \mathbf{j}_S^s + \hat{\mathcal{E}}^s - [\![\rho(\hat{S} - \hat{S}^s)(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} + \mathbf{j}_S \cdot \boldsymbol{\xi}]\!]. \tag{31}$$

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 $\hat{S}$ is the entropy per unit mass of the bulk phase.

We then 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 interface this assumption implies

$$\hat{S}^s = \hat{S}^s(\hat{U}^s, \hat{\mathcal{A}}, \omega^s_{(1)}, \ldots, \omega^s_{(N-1)}), \tag{32}$$

where $\hat{\mathcal{A}}$ is the area per unit mass ($= 1/\rho^s$). From Eq. (32) we find that the left-hand side of Eq. (31) can be given by

$$\rho^s \frac{d_s \hat{S}^s}{dt} = \frac{\rho^s}{T^s}\frac{d_s \hat{U}^s}{dt} - \frac{\gamma \rho^s}{T^s}\frac{d_s \hat{\mathcal{A}}}{dt} - \frac{\rho^s}{T^s}\sum_{A=1}^{N} \mu^s_{(A)} \frac{d_s \omega^s_{(A)}}{dt}, \tag{33}$$

where T^s is the surface temperature, and $\mu^s_{(A)}$ is the surface chemical potential per unit mass of species A. Subsequently, the surface material derivatives of $\hat{U}^s$, $\hat{\mathcal{A}}$, and $\omega^s_{(A)}$ are eliminated using the jump energy balance (17), the overall jump mass balance (3), and the species jump mass balance (11) (Zielinska and Bedeaux, 1982; Slattery, Sagis, and Oh, 2007). After elimination of the surface material derivatives in Eq. (33), the right-hand side of the resulting equation is set equal to the right-hand side of Eq. (31), 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 form (Zielinska and Bedeaux, 1982)

$$\hat{\mathcal{E}}^s = \sum_\alpha J^s_\alpha X^s_\alpha + \sum_\alpha [\![(J_\alpha \cdot \boldsymbol{\xi}) X_\alpha]\!] \geq 0, \tag{34}$$

where J_α and J^s_α represent the fluxes in the system, and X_α and X^s_α are their respective driving forces. Based on Eq. (34) and the Curie principle (de Groot and Mazur, 1962) coupled linear constitutive equations for the fluxes are constructed of the form (Zielinska and Bedeaux, 1982; Slattery, Sagis, and Oh, 2007)

$$J^s_\alpha = \sum_\beta L^s_{\alpha\beta} X^s_\beta, \tag{35}$$

$$J_\alpha \cdot \boldsymbol{\xi} = \sum_\beta L_{\alpha\beta} X_\beta. \tag{36}$$

These constitutive equations are simplified using the Onsager reciprocal relations, which require that the phenomenological coefficients $L^s_{\alpha\beta}$ satisfy (de Groot and Mazur, 1962; Zielinska and Bedeaux, 1982)

$$L^s_{\alpha\beta} = \pm L^s_{\beta\alpha}, \tag{37}$$

where a positive sign describes the case when α and β are both even (or both odd) under time reversal, and the negative sign must be used when α is even and β is odd (or vise versa) under reversal of time. For the surface extra stress tensor, the surface mass flux vector, and the surface energy flux vector, this analysis leads to the following functional dependencies (Zielinska and Bedeaux, 1982):

$$\boldsymbol{\sigma}^s = \boldsymbol{\sigma}^s(\mathbf{D}^s), \tag{38}$$

$$\mathbf{q}^s = \mathbf{q}^s(\mathbf{d}^s_{(A)}, \nabla_s \ln T^s), \tag{39}$$

$$\mathbf{j}^s_{(A)} = \mathbf{j}^s_{(A)}(\mathbf{d}^s_{(A)}, \nabla_s \ln T^s), \tag{40}$$

where the second order tangential surface tensor $\mathbf{D}^s$ denotes the surface rate of deformation tensor, defined as (Slattery, Sagis, and Oh, 2007)

$$\mathbf{D}^s = \tfrac{1}{2}(\mathbf{P}\cdot\nabla_s\mathbf{v}^s + [\nabla_s\mathbf{v}^s]^T\cdot\mathbf{P}), \tag{41}$$

and $\mathbf{d}^s_{(A)} = \nabla_s\mu^s_{(A)} - \mathbf{b}^s_{(A)}$. Upon expansion of Eq. (38) up to linear order in $\mathbf{D}^s$, we obtain the familiar Boussinesq model, given in Eq. (20). As seen in Tables I–VII hardly any of the systems analyzed form purely viscous interfaces, so the usefulness of the Boussinesq model for analysis of surface rheological data is rather limited. The functional dependencies in Eqs. (39) and (40) lead to the following linear constitutive equations for $\mathbf{q}^s$ and $\mathbf{j}^s_{(A)}$:

$$\mathbf{q}^s = \lambda^{s\prime}\nabla_s \ln T^s + \sum_{A=1}^{N}\alpha^s_{(A)}\mathbf{d}^s_{(A)}, \tag{42}$$

$$\mathbf{j}^s_{(A)} = \sum_{A=1}^{N} D^s_{(AB)}\mathbf{d}^s_{(B)} + \alpha^s_{(A)}\nabla_s \ln T^s. \tag{43}$$

A more detailed discussion of the parameters in these equations is given in the next section. Here we merely note that when the cross coupling terms in Eqs. (42) and (43), representing, respectively, the surface Dufour effect (heat conduction driven by concentration gradients) and surface Soret effect (thermal diffusion), are negligible, we obtain the 2D equivalent of Fick's law and Fourier's law.

In view of the above we see that the CIT formalism clearly has a number of limitations, with respect to modeling of interfacial behavior. Equation (32) expresses the local surface entropy $\hat{S}^s(t)$ in terms of the local variables, $\hat{U}^s(t)$, $\hat{\mathcal{A}}(t)$, and $\omega^s_{(A)}(t)$, in the current configuration of the system. Therefore, within the CIT formalism we cannot describe viscoelastic interfaces, in which the response of the interface also depends on the history of these variables. We also see that the linear constitutive relations derived here arise from a simple Taylor expansion of the functional dependencies (38)–(40). In principle we could extend the linear relation for the surface stress tensor into the nonlinear regime by including higher order terms in the expansion. For an oscillatory shear deformation of the form $D^s_{xy} = D^s_{xy0}e^{i\omega t}$ this would lead to a stress of the form $\sigma^s_{xy}(t) = \sigma^s_1 e^{i\omega t} + \sigma^s_2 e^{2i\omega t} + \sigma^s_3 e^{3i\omega t} + \cdots$, where the even harmonics are identical to zero for isotropic interfaces. But since such an expansion is based on an expansion of the stress around the zero surface deformation rate, it is expected to be valid only for small departures from linearity.

These shortcomings of the CIT formalism can somewhat be alleviated by including structural variables in Eq. (32) for the surface entropy (Prigogine and Mazur, 1953). Although this inclusion leads to nonlinear constitutive models, these models are also limited to small deviations from linear material behavior (Sagis, Ramaekers, and van der Linden, 2001; Bedeaux and Rubi, 2002).

V. EXTENDED IRREVERSIBLE THERMODYNAMICS OF MULTIPHASE SYSTEMS

As mentioned, few interfaces display linear viscous behavior. Viscoelastic behavior is far more common for interfaces, and for that reason we discuss viscoelastic behavior in more detail. This section will focus mainly on the EIT formalism (Jou, Casas-Vásquez, and Lebon, 1988, 2001; Sagis, 2010a), but we also compare the results obtained using EIT with those obtained from rational thermodynamics.

A. Expression for the entropy production

In the extended irreversible thermodynamics formalism (Jou, Casas-Vásquez, and Lebon, 1988, 2001; Sagis, 2010a) the condition of local equilibrium is relaxed, and the surface entropy per unit mass is allowed to depend not only on the state variables $\hat{U}^s$, $\hat{\mathcal{A}}$, and the surface mass fractions $\omega^s_{(A)}$, but also on the local fluxes (Sagis, 2010a): the symmetric traceless part of the surface extra stress tensor $\bar{\boldsymbol{\sigma}}^s$, the trace of the surface extra stress tensor $\mathrm{tr}\boldsymbol{\sigma}^s$, the surface energy flux vector $\mathbf{q}^s$, and the surface mass flux vectors $\mathbf{j}^s_{(A)}$:

$$\hat{S}^s = \hat{S}^s(\hat{U}^s, \hat{\mathcal{A}}, \omega^s_{(1)}, \ldots, \omega^s_{(N-1)}, \bar{\boldsymbol{\sigma}}^s, \mathrm{tr}\boldsymbol{\sigma}^s, \mathbf{q}^s, \mathbf{j}^s_{(1)}, \ldots, \mathbf{j}^s_{(N)}). \tag{44}$$

The symmetric traceless part of the extra stress tensor is given by $\bar{\boldsymbol{\sigma}}^s = \boldsymbol{\sigma}^s - \frac{1}{2}(\mathrm{tr}\boldsymbol{\sigma}^s)\mathbf{P}$. Using the chain rule, we find that the generalized surface Gibbs equation is given by

$$\begin{aligned}\frac{d_s\hat{S}^s}{dt} &= \frac{1}{T^s}\frac{d_s\hat{U}^s}{dt} - \frac{\gamma}{T^s}\frac{d_s\hat{\mathcal{A}}}{dt} - \frac{1}{T^s}\sum_{A=1}^{N}\mu^s_{(A)}\frac{d_s\omega^s_{(A)}}{dt}\\ &\quad + l_{\mathrm{tr}\sigma}\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt} + \mathbf{L}_\sigma : \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} + \mathbf{l}_q\cdot\frac{d_s\mathbf{q}^s}{dt}\\ &\quad + \sum_{A=1}^{N}\mathbf{l}_{(A)}\cdot\frac{d_s\mathbf{j}^s_{(A)}}{dt},\end{aligned} \tag{45}$$

where the second order tensor $\mathbf{L}_\sigma$, the scalar $l_{\mathrm{tr}\sigma}$, and the vectors $\mathbf{l}_q$ and $\mathbf{l}_{(A)}$ are given by (up to linear order in the fluxes) (Sagis, 2010a)

$$\mathbf{L}_\sigma = -\frac{\alpha_\sigma}{\rho^s T^s}\bar{\boldsymbol{\sigma}}^s, \tag{46}$$

$$l_{\mathrm{tr}\sigma} = -\frac{\alpha_{\mathrm{tr}\sigma}}{\rho^s T^s}\mathrm{tr}\boldsymbol{\sigma}^s, \tag{47}$$

$$\mathbf{l}_q = -\frac{\alpha_{qq}}{\rho^s T^s}\mathbf{q}^s - \sum_A \frac{\alpha_{q(A)}}{\rho^s T^s}\mathbf{j}^s_{(A)}, \tag{48}$$

$$\mathbf{l}_{(A)} = -\sum_B \frac{\alpha_{(AB)}}{\rho^s T^s}\mathbf{j}^s_{(B)} - \frac{\alpha_{q(A)}}{\rho^s T^s}\mathbf{q}^s, \tag{49}$$

where α_σ, $\alpha_{\mathrm{tr}\sigma}$, α_{qq}, $\alpha_{q(A)}$, and $\alpha_{(AB)}$ are scalar coefficients. Expressions for these coefficients will be discussed in Secs. V.B, V.H, and V.I.

Substituting the jump energy balance (17), the overall jump mass balance (3), the species jump mass balance (11), and Eqs. (46)–(49) into Eq. (45), and comparing the result with Eq. (31) we find that the rate of surface entropy production per unit mass $\hat{\mathcal{E}}^s$ satisfies (Sagis, 2010a)

$$
\begin{aligned}
\hat{\mathcal{E}}^s = {} & \frac{1}{T^s}\bar{\boldsymbol{\sigma}}^s : \left[\bar{\mathbf{D}}^s - \alpha_\sigma \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt}\right] + \frac{\mathrm{tr}\boldsymbol{\sigma}^s}{T^s}\left[\mathrm{tr}\mathbf{D}^s - \alpha_{\mathrm{tr}\sigma}\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right] - \frac{1}{T^s}\sum_{A=1}^{N}\mathbf{j}^s_{(A)}\cdot\left(\mathbf{d}^s_{(A)} + \sum_{B=1}^{N}\alpha_{(BA)}\frac{d_s\mathbf{j}^s_{(B)}}{dt} + \alpha_{q(A)}\frac{d_s\mathbf{q}^s}{dt}\right) \\
& - \frac{1}{(T^s)^2}\left(\mathbf{q}^s - \sum_{A=1}^{N}\mu^s_{(A)}\mathbf{j}^s_{(A)}\right)\cdot\nabla_s T^s - \frac{1}{T^s}\mathbf{q}^s\cdot\left(\alpha^s_{q(A)}\sum_{A}\frac{d_s\mathbf{j}^s_{(A)}}{dt} + \alpha_{qq}\frac{d_s\mathbf{q}^s}{dt}\right) \\
& - \frac{1}{T^s}\left[\!\left[\rho\left(\hat{U} - T^s\hat{S} - \sum_{A=1}^{N}\mu^s_{(A)}\omega_{(A)} + \frac{1}{2}|\mathbf{v}-\mathbf{v}^s|^2\right)(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi} + \mathbf{q}\cdot\boldsymbol{\xi} - (\mathbf{v}-\mathbf{v}^s)\cdot\mathbf{T}\cdot\boldsymbol{\xi}\right.\right. \\
& \left.\left. - \sum_{A=1}^{n}\mu^s_{(A)}\mathbf{j}_{(A)}\cdot\boldsymbol{\xi} - T^s\mathbf{j}_S\cdot\boldsymbol{\xi}\right]\!\right] \geq 0, \qquad (50)
\end{aligned}
$$

where $\bar{\mathbf{D}}^s$ is the symmetric traceless part of the surface rate of deformation tensor $\mathbf{D}^s$. With this particular form of the entropy production of the interface we now continue and construct constitutive equations for the surface extra stress tensor, the surface energy flux vector, and the surface mass flux vectors. We compare these constitutive equations with the expressions obtained using the classical irreversible thermodynamics formalism.

B. Equation for the surface extra stress tensor

Equation (50) suggests that we choose the following functional form for the surface extra stress tensor:

$$\bar{\boldsymbol{\sigma}}^s = \bar{\boldsymbol{\sigma}}^s\left(\bar{\mathbf{D}}^s, \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt}\right), \qquad (51)$$

and

$$\mathrm{tr}\boldsymbol{\sigma}^s = \mathrm{tr}\boldsymbol{\sigma}^s\left(\mathrm{tr}\mathbf{D}^s, \frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right). \qquad (52)$$

Arriving at Eqs. (51) and (52) we have invoked the Curie principle (de Groot and Mazur, 1962), which states that fluxes depend only on driving forces of equal tensorial order. When we limit ourselves to linear relations this implies the extra stress tensor cannot depend on $\mathbf{q}^s$ or $\mathbf{j}^s_{(A)}$. Expanding both functionals up to linear order in their arguments, we obtain

$$
\begin{aligned}
\bar{\boldsymbol{\sigma}}^s &= \left(\frac{\partial\bar{\boldsymbol{\sigma}}^s}{\partial\bar{\mathbf{D}}^s}\right):\bar{\mathbf{D}}^s + \frac{\partial\bar{\boldsymbol{\sigma}}^s}{\partial(d_s\bar{\boldsymbol{\sigma}}^s/dt)}:\frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} \\
&= 2\varepsilon_s\bar{\mathbf{D}}^s - \tau_s\frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt}, \qquad (53)
\end{aligned}
$$

and

$$
\begin{aligned}
\mathrm{tr}\boldsymbol{\sigma}^s &= \left(\frac{\partial\,\mathrm{tr}\boldsymbol{\sigma}^s}{\partial\,\mathrm{tr}\mathbf{D}^s}\right)\mathrm{tr}\mathbf{D}^s + \frac{\partial\,\mathrm{tr}\boldsymbol{\sigma}^s}{\partial\,\mathrm{tr}\mathbf{D}^s}\left(\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right) \\
&= 2\varepsilon_d\,\mathrm{tr}\mathbf{D}^s - \tau_d\left(\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right). \qquad (54)
\end{aligned}
$$

Arriving at these expressions we have defined (assuming isotropic interfaces)

$$2\varepsilon_s(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P}^{(4)} = \frac{\partial\bar{\boldsymbol{\sigma}}^s}{\partial\bar{\mathbf{D}}^s}, \qquad (55)$$

and

$$2\varepsilon_d(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)}) = \frac{\partial\,\mathrm{tr}\boldsymbol{\sigma}^s}{\partial\,\mathrm{tr}\mathbf{D}^s}, \qquad (56)$$

where ε_d is the surface dilatational viscosity, and ε_s is the surface shear viscosity. The tensor $\mathbf{P}^{(4)}$ is the fourth order isotropic tangential surface tensor given by (Sagis, 1998a, 1998b)

$$\mathbf{P}^{(4)} \equiv \tfrac{1}{2}(a_{\alpha\mu}a_{\beta\nu} + a_{\alpha\nu}a_{\beta\mu} - a_{\alpha\beta}a_{\mu\nu})\mathbf{a}^\alpha\mathbf{a}^\beta\mathbf{a}^\mu\mathbf{a}^\nu, \qquad (57)$$

where $a_{\alpha\beta}$ is the surface metric, and $\mathbf{a}^\alpha$ ($\alpha = 1, 2$) are the tangential dual basis vectors for the interface (Slattery, Sagis, and Oh, 2007). This fourth order tensor transforms any second order surface tensor into its symmetric traceless part (and therefore $\mathbf{P}^{(4)}:\bar{\mathbf{D}}^s = \bar{\mathbf{D}}^s$).

Equations (55) and (56) are the formal definitions of the surface shear and surface dilatational viscosities. Note that these viscosities depend only on the state variables T^s, $\hat{\mathcal{A}}$, and $\omega^s_{(A)}$, and not on the surface rate of deformation tensor. Through this dependence of the viscosities on composition and temperature, the jump momentum balance is coupled to the jump mass and jump energy balances. The parameters τ_s and τ_d are defined by

$$\tau_s(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P}^{(4)} = -\frac{\partial\bar{\boldsymbol{\sigma}}^s}{\partial(d_s\bar{\boldsymbol{\sigma}}^s/dt)}, \qquad (58)$$

and

$$\tau_d(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)}) = -\frac{\partial\,\mathrm{tr}\boldsymbol{\sigma}^s}{\partial(d_s\,\mathrm{tr}\boldsymbol{\sigma}^s/dt)}, \qquad (59)$$

where τ_s is the surface shear relaxation time, and τ_d is the surface dilatational relaxation time. Equations (53) and (54) are basically the surface rheological equivalent of the single relaxation time differential Maxwell model for the bulk extra stress tensor (Bird, Armstrong, and Hassager, 1987). They describe the small deformation limit of interfaces with linear viscoelastic stress-deformation behavior. Substituting Eqs. (53) and (54) into Eq. (50), and identifying $\alpha_{\mathrm{tr}\sigma} = \tau_d/2\varepsilon_d$, and $\alpha_\sigma = \tau_s/2\varepsilon_s$, we retrieve (focusing only on the viscous dissipation part of the rate of surface entropy production)

$$\frac{2\varepsilon_s}{T^s}\left[\bar{\mathbf{D}}^s - \frac{\tau_s}{2\varepsilon_s}\frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt}\right]^2 + \frac{2\varepsilon_d}{T^s}\left[\mathrm{tr}\mathbf{D}^s - \frac{\tau_d}{2\varepsilon_d}\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right]^2 \geq 0. \qquad (60)$$

From this quadratic expression we can conclude that $\varepsilon_s \geq 0$ and $\varepsilon_d \geq 0$.

When we use the fact that $\bar{\boldsymbol{\sigma}}^s = \boldsymbol{\sigma}^s - \frac{1}{2}\,\mathrm{tr}\boldsymbol{\sigma}^s\mathbf{P}$, and combine Eqs. (53) and (54), we obtain

$$\boldsymbol{\sigma}^s = 2\varepsilon_s \mathbf{D}^s + (\varepsilon_d - \varepsilon_s)[\mathrm{tr}\mathbf{D}^s]\mathbf{P} - \tau_s \frac{d_s \boldsymbol{\sigma}^s}{dt} - \frac{1}{2}(\tau_d - \tau_s)\mathbf{P}\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt} + \frac{1}{2}\tau_s\,\mathrm{tr}\boldsymbol{\sigma}^s \frac{d_s\mathbf{P}}{dt}. \qquad (61)$$

We see that for interfaces with infinitely fast relaxation (τ_s, $\tau_d \to 0$) we retrieve the linear Boussinesq model (Boussinesq, 1913a, 1913b, 1913c; Scriven, 1960; Slattery, Sagis, and Oh, 2007), which we also obtained using the CIT formalism.

More importantly Eq. (61) shows that straightforward generalizations of the 3D linear Maxwell model to interfaces may lead to oversimplified models with limited validity. A popular generalization frequently used in the literature for the analysis of data from Langmuir trough experiments is of the form (in terms of the nomenclature used in this paper) (Ivanova *et al.*, 2004; Sosnowski, Pawelec, and Gradoń, 2006)

$$\sigma^s_{xx} = -\tau_d \frac{\partial \sigma^s_{xx}}{\partial t} + \varepsilon_d D^s_{xx}. \qquad (62)$$

Variations of this model are also used to analyze data from oscillating bubble experiments (Anton *et al.*, 2007; Juárez *et al.*, 2007). For a uniaxial compression in a Langmuir trough Eq. (61) reduces to

$$\sigma^s_{xx} = (\varepsilon_d + \varepsilon_s)D^s_{xx} - \frac{1}{2}(\tau_d + \tau_s)\frac{d_s\sigma^s_{xx}}{dt} - \frac{1}{2}(\tau_d - \tau_s)\frac{d_s\sigma^s_{yy}}{dt}, \qquad (63)$$

and this reduces to Eq. (62) only when the surface shear properties are negligible ($\varepsilon_s \ll \varepsilon_d$, and $\tau_s \ll \tau_d$), and when

$$\tau_d \frac{d_s\sigma^s_{yy}}{dt} \ll \sigma^s_{xx} - \varepsilon_d D^s_{xx} + \frac{1}{2}\tau_d \frac{d_s\sigma^s_{xx}}{dt}. \qquad (64)$$

If this condition is not satisfied, the *xx* and *yy* components of the surface extra stress tensor do not decouple, and Eq. (62) should not be used. Witten *et al.* (2010) showed that for elastic monolayers these components will in general not decouple. This shows we must be careful when applying straightforward generalizations of 3D models to describe the behavior of 2D interfaces. Equation (61) shows that for the determination of dilatational properties using Langmuir troughs, the two Wilhelmy plate method described by Petkov *et al.* (2000), Cicuta and Terentjev (2005), and Cicuta (2007) is preferred over the single Wilhelmy plate method. When two Wilhelmy plates are used, one oriented parallel to the barriers and one perpendicular, σ_{xx} and σ_{yy} can be measured simultaneously. Combining the expressions for both components we find

$$\sigma^s_{xx} - \sigma^s_{yy} = 2\varepsilon_s D^s_{xx} - \tau_s \frac{d_s(\sigma^s_{xx} - \sigma^s_{yy})}{dt}, \qquad (65)$$

and

$$\sigma^s_{xx} + \sigma^s_{yy} = 2\varepsilon_d D^s_{xx} - \tau_d \frac{d_s(\sigma^s_{xx} + \sigma^s_{yy})}{dt}, \qquad (66)$$

and from these expressions both surface shear and dilatational properties of the interface can be determined.

In surface shear experiments on flat interfaces Eq. (61) reduces to

$$\sigma^s_{xy} = 2\varepsilon_s D^s_{xy} - \tau_s \frac{d_s\sigma^s_{xy}}{dt}, \qquad (67)$$

identical in structure to the Maxwell model for linear viscoelastic bulk phases. So in surface shear mode the generalizations of the Maxwell model to interfaces used in the literature (Tables I–VII) are of the correct form.

It is not surprising that the straightforward generalization of a 3D model to dilatational experiments can lead to incorrect equations, since the vast majority of models developed for bulk stress-deformation behavior were developed for incompressible materials and were therefore not designed to deal with compressible media. This example clearly illustrates the advantage of using a more formal approach to constructing constitutive equations, based on NET, over using straightforward generalizations of bulk models.

C. Integral models

In 3D rheology constitutive equations for the stress tensor are often presented in an integral form. The differential Maxwell-type models in Eqs. (53) and (54) can also easily be recast in such an integral form. Integrating these equations with respect to time we find

$$\bar{\boldsymbol{\sigma}}^s = \int_{-\infty}^{t} K^s(t-s)\bar{\mathbf{D}}^s(s)ds, \qquad (68)$$

and

$$\mathrm{tr}\boldsymbol{\sigma}^s = \int_{-\infty}^{t} C^s(t-s)\mathrm{tr}\mathbf{D}^s(s)ds, \qquad (69)$$

where s is an integration variable, $C^s(t-s)$ is the surface dilatational memory function, and $K^s(t-s)$ is the surface shear memory function. When the extra stress tensor is given by Eqs. (53) and (54) the memory functions in Eqs. (68) and (69) are given by the single exponential forms

$$K^s(t-s) = \frac{2\varepsilon_s}{\tau_s}\exp\left[-\frac{(t-s)}{\tau_s}\right], \qquad (70)$$

$$C^s(t-s) = \frac{2\varepsilon_d}{\tau_d}\exp\left[-\frac{(t-s)}{\tau_d}\right]. \qquad (71)$$

Equations (70) and (71) are the typical memory functions for a fluid with fading memory (Bird, Armstrong, and Hassager, 1987; Slattery, Sagis, and Oh, 2007) and allow us to derive expressions for the complex surface dilatational and surface shear viscosities, often used to analyze surface rheological data. These complex viscosities can be defined as $2\varepsilon^*_d(\omega) = \tilde{C}^s(p = i\omega)$, and $2\varepsilon^*_s(\omega) = \tilde{K}^s(p = i\omega)$, where $\tilde{C}^s(p)$ and $\tilde{K}^s(p)$ are the Laplace transforms of $C^s(t)$ and $K^s(t)$. Taking the Laplace transform of Eqs. (68) and (69), and substituting $p = i\omega$, where ω denotes the frequency, we find that $\varepsilon^*_d(\omega) = \varepsilon'_d - i\varepsilon''_d$, with

$$\varepsilon'_d = \frac{\varepsilon_d}{1 + \omega^2\tau_d^2}, \qquad \varepsilon''_d = \frac{\varepsilon_d\omega\tau_d}{1 + \omega^2\tau_d^2}, \qquad (72)$$

and $\varepsilon^*_s(\omega) = \varepsilon'_s - i\varepsilon''_s$, with

$$\varepsilon_s' = \frac{\varepsilon_s}{1+\omega^2\tau_s^2}, \qquad \varepsilon_s'' = \frac{\varepsilon_s\omega\tau_s}{1+\omega^2\tau_s^2}. \tag{73}$$

Alternatively, we can also express the linear viscoelastic surface rheological properties in terms of the complex dilatational modulus $E_d^*(\omega) = E_{d0} + i\omega\varepsilon_d^*$ and complex surface shear modulus $G_s(\omega) = i\omega\varepsilon_s^*(\omega)$. Here E_{d0} is the dilatational modulus at zero frequency, given by Eq. (22). When the memory functions $C^s(t)$ and $K^s(t)$ are given by Eqs. (70) and (71), the expressions for these complex moduli reduce to $E_d^*(\omega) = E_d' + iE_d''$, with

$$E_d' = E_{d0} + \frac{\varepsilon_d\omega^2\tau_d}{1+\omega^2\tau_d^2}, \qquad E_d'' = \frac{\varepsilon_d\omega}{1+\omega^2\tau_d^2}, \tag{74}$$

and $G_s^*(\omega) = G_s' + iG_s''$, with

$$G_s' = \frac{\varepsilon_s\omega^2\tau_s}{1+\omega^2\tau_s^2}, \qquad G_s'' = \frac{\varepsilon_s\omega}{1+\omega^2\tau_s^2}. \tag{75}$$

Looking at the low and high frequency limits of the last two expressions we find that for $\omega \to 0$, $G_s'(\omega) = \varepsilon_s\tau_s\omega^2$, and $G_s''(\omega) = \varepsilon_s\omega$. In the limit $\omega \to \infty$ we obtain $G_s'(\omega) = \varepsilon_s/\tau_s$, and $G_s''(\omega) = \varepsilon_s/\tau_s^2\omega$. Similar relations can also be obtained for the scaling of $E_d'(\omega)$ and $E_d''(\omega)$. These relations show that the scaling behavior with respect to frequency of the surface loss and storage moduli for a linear viscoelastic interface is similar to that of the storage and loss moduli of linear viscoelastic bulk phases. The scaling behavior in these expressions can be used to check if an interface does indeed behave as a linear viscoelastic material.

D. Kelvin-Voigt and Jeffreys model

As seen in Tables I–VII, the Kelvin-Voigt model is a frequently invoked model to describe the rheological response of interfaces. This model can be derived from Eqs. (68) and (69) by assuming the following form for the memory functions:

$$K^s(t-s) = 2\varepsilon_s\delta(t-s) + 2G_sH_v(t-s), \tag{76}$$

$$C^s(t-s) = 2\varepsilon_d\delta(t-s) + 2E_dH_v(t-s), \tag{77}$$

where $\delta(t-s)$ is the Dirac delta function, and $H_v(t-s)$ is the Heaviside function. Substituting these functions into Eqs. (68) and (69), we obtain

$$\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s + 2G_s\bar{\mathbf{U}}^s, \tag{78}$$

$$\mathrm{tr}\boldsymbol{\sigma}^s = 2\varepsilon_d\,\mathrm{tr}\mathbf{D}^s + 2E_d\,\mathrm{tr}\mathbf{U}^s, \tag{79}$$

and combining these two equations we find that

$$\begin{aligned}\boldsymbol{\sigma}^s = {} & (\varepsilon_d - \varepsilon_s)[\mathrm{tr}\mathbf{D}^s]\mathbf{P} + 2\varepsilon_s\mathbf{D}^s \\ & + (E_d - G_s)[\mathrm{tr}\mathbf{U}^s]\mathbf{P} + 2G_s\mathbf{U}^s.\end{aligned} \tag{80}$$

This model is identical to the one used by Petkov *et al.* (2000). Most use a more simple form of this model retaining only either the dilatational part of the expression or the part describing shear deformations.

The Jeffreys model for the surface extra stress tensor can be derived assuming memory functions of the form

$$K^s(t-s) = \frac{2\varepsilon_s\tau_{s2}}{\tau_{s1}}\delta(t-s) + \frac{2\varepsilon_s}{\tau_{s1}}\left(1-\frac{\tau_{s2}}{\tau_{s1}}\right)\exp\left[-\frac{(t-s)}{\tau_s}\right], \tag{81}$$

$$C^s(t-s) = \frac{2\varepsilon_d\tau_{d2}}{\tau_{d1}}\delta(t-s) + \frac{2\varepsilon_d}{\tau_{d1}}\left(1-\frac{\tau_{d2}}{\tau_{d1}}\right)\exp\left[-\frac{(t-s)}{\tau_d}\right], \tag{82}$$

where τ_{d1} and τ_{s1} are relaxation times, and τ_{d2} and τ_{s2} are retardation times. Equations (81) and (82) lead to the following constitutive equations for the surface stress tensor:

$$\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s - \tau_{s1}\frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} + 2\varepsilon_s\tau_{s2}\frac{d_s\bar{\mathbf{D}}^s}{dt}, \tag{83}$$

and

$$\mathrm{tr}\boldsymbol{\sigma}^s = 2\varepsilon_d\,\mathrm{tr}\mathbf{D}^s - \tau_{d1}\left(\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt}\right) + 2\varepsilon_d\tau_{d2}\left(\frac{d_s\,\mathrm{tr}\mathbf{D}^s}{dt}\right). \tag{84}$$

These two expressions are the generalization of the Jeffreys model to describe the rheology of viscoelastic interfaces. Gavranovic, Deutsch, and Fuller (2005) and Gavranovic, Smith *et al.* (2006) used the Jeffreys model to analyze the surface shear properties of interfaces stabilized by poly(tert-butyl metacrylate).

E. Multimode Maxwell model

Equations (70) and (71) describe the relaxation behavior of an interface with a single relaxation time. These expression can easily be generalized to interfaces with a relaxation behavior characterized by multiple relaxation times. To that extend we simply replace Eqs. (70) and (71) by

$$K^s(t-s) = \sum_{k=1}^{n}\frac{2\varepsilon_s^k}{\tau_s^k}\exp\left[-\frac{(t-s)}{\tau_s^k}\right], \tag{85}$$

$$C^s(t-s) = \sum_{k=1}^{n}\frac{2\varepsilon_d^k}{\tau_d^k}\exp\left[-\frac{(t-s)}{\tau_d^k}\right], \tag{86}$$

where τ_d^k and τ_s^k are the relaxation times for the kth dilatational and surface shear modes, and ε_d^k and ε_s^k are the contributions to the dilatational and surface shear viscosities associated with that same mode. With Eqs. (85) and (86) we can write (53) and (54) as

$$\bar{\boldsymbol{\sigma}}^s = \sum_{k=1}^{n}\bar{\boldsymbol{\sigma}}_k^s, \qquad \mathrm{tr}\boldsymbol{\sigma}^s = \sum_{k=1}^{n}\mathrm{tr}\boldsymbol{\sigma}_k^s, \tag{87}$$

$$\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}_k^s}{dt} + \frac{1}{\tau_d^k}\mathrm{tr}\boldsymbol{\sigma}_k^s = \frac{2\varepsilon_d^k}{\tau_d^k}\mathrm{tr}\mathbf{D}^s, \tag{88}$$

and

$$\frac{d_s\bar{\boldsymbol{\sigma}}_k^s}{dt} + \frac{1}{\tau_s^k}\bar{\boldsymbol{\sigma}}_k^s = \frac{2\varepsilon_s^k}{\tau_s^k}\bar{\mathbf{D}}^s. \tag{89}$$

These expressions are the surface rheological equivalent of the generalized Maxwell model (Bird, Armstrong, and Hassager, 1987) for linear viscoelastic bulk phases. For an interface with this type of behavior the surface entropy production rate takes the form (again focusing only on viscous dissipation)

$$\sum_{k=1}^{n}\frac{2\varepsilon_s^k}{T^s}\left[\bar{\mathbf{D}}^s - \frac{\tau_s^k}{2\varepsilon_s^k}\frac{d_s\bar{\boldsymbol{\sigma}}_k^s}{dt}\right]^2 + \sum_{k=1}^{n}\frac{2\varepsilon_d^k}{T^s}\left[\mathrm{tr}\mathbf{D}^s - \frac{\tau_d^k}{\varepsilon_d^k}\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}_k^s}{dt}\right]^2 \geq 0, \tag{90}$$

which means that Eqs. (88) and (89) are thermodynamically admissible models for the stress tensor as long as $\varepsilon_d^k \geq 0$ and $\varepsilon_s^k \geq 0$ for all k.

The multimode Maxwell model has been used to model dilatational properties of interfaces stabilized by polymers, such as alkylated chitosan (Babak, Desbrières, and Tikhonov, 2005), chitosan sulfate (Babak *et al.*, 2008b), Eudragit RS (Babak *et al.*, 2008a, 2008b), and poly(ε-caprolactone) (Babak *et al.*, 2008a). The response of all these interfaces displayed two distinct modes.

F. Comparison with the rational thermodynamics formalism

The rational thermodynamics formalism takes a somewhat different approach to introduce viscoelasticity. In the RT formalism the assumption of local equilibrium is relaxed by assuming that the entropy depends not only on the state variables $\hat{U}^s$, $\hat{\mathcal{A}}$, and $\omega_{(A)}^s$ in the current configuration, but also on the history of these variables, i.e., the values of these variables in all past configurations of the surface (Coleman and Noll, 1961; Coleman, 1964a, 1964b):

$$\hat{S}^s = \Lambda_{s=0}^{\infty}[T^s(t-s), \hat{\mathcal{A}}(t-s), \omega_{(1)}^s(t-s), \ldots, \omega_{(N-1)}^s(t-s)], \tag{91}$$

where the limits $s = 0$ and $s = \infty$ on the functional Λ denote that $\hat{S}^s$ depends on the variables T^s, $\hat{\mathcal{A}}$, and $\omega_{(A)}^s$ in all past configurations leading up to the current configuration at time t. A constitutive assumption such as Eq. (91) leads to a functional dependence for the surface extra stress tensor of the form (Slattery, Sagis, and Oh, 2007)

$$\mathrm{tr}\boldsymbol{\sigma}^s = \mathrm{tr}\boldsymbol{\sigma}^s|_{s=0}^{\infty}[\mathrm{tr}\mathbf{D}^s(t-s)], \tag{92}$$

and

$$\bar{\boldsymbol{\sigma}}^s = \bar{\boldsymbol{\sigma}}^s|_{s=0}^{\infty}[\bar{\mathbf{D}}^s(t-s)]. \tag{93}$$

Expanding the functionals in Eqs. (92) and (93) in their respective arguments we find

$$\bar{\boldsymbol{\sigma}}^s = \delta\bar{\boldsymbol{\sigma}}^s|_{s=0}^{\infty}[\bar{\mathbf{D}}^s(t-s)], \tag{94}$$

where the right-hand side of this equation denotes the partial first Fréchet derivative of $\bar{\boldsymbol{\sigma}}^s$ with respect to $\bar{\mathbf{D}}^s$. We also obtain

$$\mathrm{tr}\boldsymbol{\sigma}^s = \delta\,\mathrm{tr}\boldsymbol{\sigma}^s|_{s=0}^{\infty}[\mathrm{tr}\mathbf{D}^s(t-s)], \tag{95}$$

where the right-hand side of this equation is the partial first Fréchet derivative of $\mathrm{tr}\boldsymbol{\sigma}^s$ with respect to $\mathrm{tr}\mathbf{D}^s(t-s)$. Both of these partial Fréchet derivatives have an integral representation (Coleman and Noll, 1961), which is identical to Eqs. (68) and (69). So at least for linear constitutive models the RT and EIT formalisms lead to the same result for the constitutive equation for the surface extra stress tensor.

G. Frame invariant nonlinear differential models

The differential models for the symmetric traceless part of the surface extra stress tensor $\bar{\boldsymbol{\sigma}}^s$ we introduced in the previous sections are all specified in terms of the surface material derivative. This material derivative of a surface tensor is not an invariant derivative in the sense that is not invariant under orthogonal changes of the frame of observation. We can alleviate this problem by replacing the surface material derivative in Eq. (53) by a frame invariant derivative, such as the surface corotational derivative:

$$\tau_s\overset{\triangledown}{\delta}\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s, \tag{96}$$

where the surface corotational derivative is defined as

$$\overset{\triangledown}{\delta}\bar{\boldsymbol{\sigma}}^s = \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} - \boldsymbol{\Omega}^s\cdot\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s\cdot\boldsymbol{\Omega}^s, \tag{97}$$

and the surface vorticity tensor

$$\boldsymbol{\Omega}^s = \tfrac{1}{2}(\mathbf{P}\cdot\nabla_s\mathbf{v}^s - [\nabla_s\mathbf{v}^s]^T\cdot\mathbf{P}). \tag{98}$$

We can make such a replacement without loss of generality, since for every symmetric surface tensor $\mathbf{A}^s{:}\boldsymbol{\Omega}^s = 0$, and Eq. (60) is still valid. Alternatively, we can use the upper convected derivative, defined by

$$\overset{\square}{\delta}\bar{\boldsymbol{\sigma}}^s = \frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} - ([\nabla_s\mathbf{v}^s]^T\cdot\mathbf{P})\cdot\bar{\boldsymbol{\sigma}}^s - \bar{\boldsymbol{\sigma}}^s\cdot(\mathbf{P}\cdot\nabla_s\mathbf{v}^s), \tag{99}$$

and replace Eq. (96) by

$$\tau_s\overset{\square}{\delta}\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s. \tag{100}$$

This is the surface rheological equivalent of the upper convected Maxwell model. We see that we can construct thermodynamically admissible models for the surface stress tensor which take on a form similar to those for viscoelastic bulk phases. We can exploit this analogy and construct various other models, such as the multimode surface Giesekus model. To construct this model we replace Eq. (100) by (Giesekus, 1982; Sagis, 2010a)

$$\tau_s\overset{\square}{\delta}\bar{\boldsymbol{\sigma}}^s + \mathbf{B}^s\cdot\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s, \tag{101}$$

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

$$\mathbf{B}^s = \mathbf{P} + \alpha_s(\mathbf{C}^s - \mathbf{P}) = (1-\alpha_s)\mathbf{P} + \alpha_s\mathbf{C}^s \tag{102}$$

and $\mathbf{C}^s$ is a positive definite configuration tensor, related to the surface extra stress tensor by

$$\boldsymbol{\sigma}^s = \frac{\varepsilon_s}{\tau_s}(\mathbf{C}^s - \mathbf{P}). \tag{103}$$

The parameter α_s is referred to as the surface mobility parameter. Substituting Eqs. (102) and (103) into Eq. (101) we obtain

$$\tau_s\overset{\square}{\delta}\bar{\boldsymbol{\sigma}}^s + \bar{\boldsymbol{\sigma}}^s + \frac{\alpha_s\tau_s}{\varepsilon_s}\bar{\boldsymbol{\sigma}}^s\cdot\bar{\boldsymbol{\sigma}}^s = 2\varepsilon_s\bar{\mathbf{D}}^s. \tag{104}$$

The multimode generalization of this model is given by

$$\tau_s^k \overset{\square}{\delta} \bar{\boldsymbol{\sigma}}_k^s + \bar{\boldsymbol{\sigma}}_k^s + \frac{\alpha_s^k \tau_s^k}{\varepsilon_s^k} \bar{\boldsymbol{\sigma}}_k^s \cdot \bar{\boldsymbol{\sigma}}_k^s = 2\varepsilon_s^k \bar{\mathbf{D}}^s. \tag{105}$$

Substituting Eq. (104) into Eq. (50) we find that

$$\frac{1}{2\varepsilon_s T^s} \operatorname{tr}(\bar{\boldsymbol{\sigma}}^s \cdot \mathbf{B}^s \cdot \bar{\boldsymbol{\sigma}}^s) \geq 0, \tag{106}$$

which implies that $\mathbf{B}^s$ is a positive semidefinite tensor. From its definition in Eq. (102) we see that for Eq. (104) or its multimode generalization (105) to be thermodynamically admissible, we must have $0 \leq \alpha_s^k \leq 1$. In a similar manner we can generalize Eq. (54) for the trace of $\boldsymbol{\sigma}^s$ to the dilatational Giesekus model:

$$\tau_d^k \left(\frac{d_s \operatorname{tr}\boldsymbol{\sigma}_s^k}{dt} \right) + \operatorname{tr}\boldsymbol{\sigma}_k^s + \frac{\alpha_d^k \tau_d^k}{\varepsilon_d^k} (\operatorname{tr}\boldsymbol{\sigma}_k^s)^2 = 2\varepsilon_d^k \operatorname{tr}\mathbf{D}^s \tag{107}$$

with $0 \leq \alpha_d^k \leq 1$. The multimode Giesekus model has been successfully employed in modeling the behavior of polymer melts and solutions. To my knowledge it has not yet been employed to describe the stress-deformation behavior of viscoelastic interfaces, stabilized by flexible polymers.

The analysis in this section shows that NET can be used to construct a wide range of nonlinear models for the stress-deformation behavior of interfaces. We could easily extend the analysis here to derive the surface rheological equivalents of the Oldroyd B model or Gordon-Schowalter model (Bird, Armstrong, and Hassager, 1987). Examples of such generalizations, and their application to the modeling of the deformation of capsules or blood cells in a flow field, can be found in the papers by Barthès-Biesel and co-workers (Barthès-Biesel and Rallison, 1981; Barthès-Biesel, 1991, 1998; Barthès-Biesel, Diaz, and Dhenin, 2002; Lac, Morel, and Barthès-Biesel, 2007). They used 2D generalizations of the Mooney-Rivlin and Skalak models to incorporate the effects of surface rheology on the deformation of the capsules.

A common characteristic of this type of nonlinear rheological model is that the deformation dependence of the stress tensor is expressed purely in terms of the (rate of) deformation tensor and its invariants. In bulk rheology these models have lost some of their popularity, and they are gradually being replaced by models that describe the nonlinear response of materials by incorporating scalar and tensorial structural variables in the constitutive equations. The expression for the stress tensor is then combined with one or more kinetic equations, which describe the time evolution of the structural variables, as a result of the applied deformation. For example, in a polymer solution these variables describe the local density, stretching, and orientation of polymer segments. For nematic phases they describe domain size and orientation, as a function of the applied deformation. The kinetic equations that describe the time evolution of these variables allow us to link rheological phenomena such as shear thinning, shear thickening, thixotropy, or rheopexy directly to the microstructure of the system. In addition they allow us to model phenomena such as shear banding and shear induced phase separation. These models clearly provide more insight in the nonlinear rheological behavior than the classical models, based solely on the rate of deformation tensor.

This approach can also be extended to the modeling of nonlinear stress-deformation behavior of interfaces. We discuss this issue in more detail in Sec. VII, where we discuss the GENERIC formalism. In Sec. VII we present a simple example of a surface rheological model that includes structural variables and give an example of the kinetic equations that describe the time evolution of these variables in an arbitrary flow field.

H. Expression for the surface mass flux vector

A major difference between surface rheology and rheology of bulk phases is that in surface rheology the total mass of an interface need not be conserved. When an interface is uniformly stretched or compressed, the change in surface concentration induced by the deformation may drive mass transfer of surface active species from the bulk to the interface or vise versa. Applied deformations may also cause a nonuniform surface concentration field in the interface. The nonuniform concentration field will induce surface diffusion along the interface and exchange of mass with the adjoining bulk phases. Since the rheological properties of the interface are depending on the local surface concentrations [see Eqs. (55)–(59)], the jump momentum balance (14) and jump species mass balance (11) are in general coupled and need to be solved simultaneously. To solve the latter equation, constitutive equations for the surface mass flux vector and the flux of mass from the bulk phase to the interface are needed. The effects of subsurface mass transfer on the dilatational properties are in general incorporated using the Lucassen–van den Tempel model (Lucassen and van den Tempel, 1972a, 1972b), which describes the subsurface transfer as Fickian diffusion. Surface diffusion is in general not accounted for, since its effects are assumed to be small in surface rheological experiments. During processing of multiphase systems such as emulsions or coatings, these systems are subjected to large deformations, and inhomogeneous surface concentration fields with considerable concentration gradients may develop.

In this section we discuss constitutive equations for the surface mass flux vector, within the framework of extended irreversible thermodynamics. The mass transfer from the adjoining bulk phases to the interface will be discussed in Sec. V.J. In our description of the in-plane mass transfer we not only include diffusion driven by concentration gradients (ordinary surface diffusion), but also diffusion driven by thermal gradients (the surface Soret effect), and driven by gradients in surface tension.

To construct a constitutive equation for the surface mass flux vectors we again use the jump entropy inequality (50) as a guide. This inequality suggests we adopt the following functional form for these vectors:

$$\mathbf{j}_{(A)}^s = \mathbf{j}_{(A)}^s \left(\mathbf{d}_{(1)}^s, \ldots, \mathbf{d}_{(N)}^s, \nabla_s \ln T^s, \frac{d_s \mathbf{j}_{(1)}^s}{dt}, \ldots, \frac{d_s \mathbf{j}_{(N)}^s}{dt}, \frac{d_s \mathbf{q}^s}{dt} \right). \tag{108}$$

Here we again invoked the Curie principle (de Groot and Mazur, 1962): The vectorial flux $\mathbf{j}_{(A)}^s$ may depend only on vectorial driving forces, and dependencies on the scalar driving force $\operatorname{tr}\mathbf{D}^s$ and tensorial driving force $\bar{\mathbf{D}}^s$ are excluded.

Expanding the functional in Eq. (108) up to linear order in its arguments, we obtain

$$\mathbf{j}^s_{(A)} = \sum_{B\neq A} D^s_{(AB)}\mathbf{d}^s_{(B)} + \alpha^s_{(A)}\nabla_s \ln T^s + \sum_{B\neq A}\tau_{(AB)}\frac{d_s\mathbf{j}^s_{(B)}}{dt} - \frac{\tau^T_{(A)}\alpha^s_{(A)}}{\lambda^{s\prime}}\frac{d_s\mathbf{q}^s}{dt}. \tag{109}$$

In arriving at this result we have defined (again assuming isotropic interfaces)

$$D^s_{(AB)}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial \mathbf{j}^s_{(A)}}{\partial \mathbf{d}^s_{(B)}}, \tag{110}$$

$$\alpha^s_{(A)}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial \mathbf{j}^s_{(A)}}{\partial \nabla_s \ln T^s}, \tag{111}$$

$$\tau_{(AB)}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial \mathbf{j}^s_{(A)}}{\partial (d_s\mathbf{j}^s_{(B)}/dt)}, \tag{112}$$

and

$$-\frac{\tau^T_{(A)}\alpha^s_{(A)}}{\lambda^{s\prime}}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial \mathbf{j}^s_{(A)}}{\partial (d_s\mathbf{q}^s/dt)}, \tag{113}$$

where $D^s_{(AB)}$ is related to the surface diffusion coefficient of species A, $\alpha^s_{(A)}$ is related to the thermal diffusion coefficient of A, $\lambda^{s\prime} = -\lambda^s T^s$, where λ^s is the thermal conductivity of the interface, $\tau_{(AB)}$ is the relaxation time for the surface diffusion of A driven by gradients in the surface chemical potential, and $\tau^T_{(A)}$ is the relaxation time for thermal surface diffusion of A.

When the contributions from thermal diffusion to the total diffusive flux can be neglected, Eq. (109) reduces to

$$\mathbf{j}^s_{(A)} = \sum_{B\neq A} D^s_{(AB)}\mathbf{d}^s_{(B)} + \sum_{B\neq A}\tau_{(AB)}\frac{d_s\mathbf{j}^s_{(B)}}{dt}. \tag{114}$$

And for diffusion in a binary mixture this reduces to the even simpler result

$$\tau_{(AB)}\frac{d_s\mathbf{j}^s_{(A)}}{dt} + \mathbf{j}^s_{(A)} = -D^s_{(AB)}\mathbf{d}^s_{(A)}. \tag{115}$$

For a binary mixture we can easily identify the coefficients $\alpha_{(AB)}$ and $\alpha_{q(A)}$ appearing in Eq. (50). By combining this equation with (109) we obtain $\alpha_{(AB)} = -\tau_{(AB)}/D^s_{(AB)}$, and $\alpha_{q(A)} = -\tau^T_{(A)}\alpha^s_{(A)}/\lambda^{s\prime}D^s_{(AB)}$. With this expression for the coefficients $\alpha_{(AB)}$, we find that for an isothermal nondeformed interface the rate of entropy production is given by

$$\frac{D^s_{(AB)}}{T^s}\left[\mathbf{d}^s_{(A)} + \frac{\tau_{(AB)}}{D^s_{(AB)}}\frac{d_s\mathbf{j}^s_{(A)}}{dt}\right]^2 \geq 0, \tag{116}$$

which allows us to conclude that $D^s_{(AB)} \geq 0$.

The first term in Eq. (115) describes relaxation effects in surface diffusion. These effects may be important in surface diffusion in polymer stabilized interfaces, which are likely to exhibit non-Fickian behavior. When $\tau_{(AB)} \ll 1$, and the effects of diffusion driven by external force fields can be neglected, Eq. (115) reduces to

$$\mathbf{j}^s_{(A)} = -D^s_{(AB)}\nabla_s\mu^s_{(A)}. \tag{117}$$

Using the fact that $\mu^s_{(A)} = \mu^s_{(A)}(T^s, \gamma, \omega^s_{(B)})$, we can rewrite this expression as

$$\mathbf{j}^s_{(A)} = -D^s_{(AB)}\left(\frac{\partial\mu^s_{(A)}}{\partial\omega^s_{(B)}}\nabla_s\omega^s_{(B)} + \frac{\partial\mu^s_{(A)}}{\partial\gamma}\nabla_s\gamma + \frac{\partial\mu^s_{(A)}}{\partial T^s}\nabla_s T^s\right). \tag{118}$$

The first term on the right-hand side of Eq. (118) represents ordinary surface diffusion (diffusion driven by gradients in the surface concentration), whereas the second term describes the diffusion driven by gradients in the surface tension. When the latter is negligible and the interface is isothermal we retrieve the surface equivalent of Fick's law of diffusion. We see that NET formalisms such as the EIT formalism provide us with efficient tools to incorporate all relevant modes of surface diffusion into the constitutive equation for the surface mass flux vector.

I. Expression for the surface energy flux vector

For the surface energy flux vector $\mathbf{q}^s$ the jump entropy inequality (50) suggests the following functional form (again applying the Curie principle):

$$\mathbf{q}^s = \mathbf{q}^s\left(\mathbf{d}^s_{(1)}, \ldots, \mathbf{d}^s_{(N)}, \nabla_s \ln T^s, \frac{d_s\mathbf{j}^s_{(1)}}{dt}, \ldots, \frac{d_s\mathbf{j}^s_{(N)}}{dt}, \frac{d_s\mathbf{q}^s}{dt}\right). \tag{119}$$

The first order expansion of this functional in terms of its arguments is given by

$$\mathbf{q}^s = \sum_{A=1}^{N}\alpha^s_{(A)}\mathbf{d}^s_{(A)} + \lambda^{s\prime}\nabla_s \ln T^s - \sum_{A=1}^{N}\sum_{B=1}^{N}\frac{\tau^T_{(A)}\alpha^s_{(A)}}{D^s_{(AB)}}\frac{d_s\mathbf{j}^s_{(A)}}{dt} - \tau_\lambda\frac{d_s\mathbf{q}^s}{dt}. \tag{120}$$

In arriving at this result we have defined

$$\alpha^s_{(A)}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial\mathbf{q}^s}{\partial\mathbf{d}^s_{(A)}}, \tag{121}$$

$$\lambda^{s\prime}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv \frac{\partial\mathbf{q}^s}{\partial\nabla_s \ln T^s}, \tag{122}$$

$$\sum_{B=1}^{N}\frac{\tau^T_{(A)}\alpha^s_{(A)}}{D^s_{(AB)}}(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv -\frac{\partial\mathbf{q}^s}{\partial(d_s\mathbf{j}^s_{(A)}/dt)}, \tag{123}$$

and

$$\tau_\lambda(T^s, \hat{\mathcal{A}}, \omega^s_{(A)}, \ldots, \omega^s_{(N-1)})\mathbf{P} \equiv -\frac{\partial\mathbf{q}^s}{\partial(d_s\mathbf{q}^s/dt)}. \tag{124}$$

When we are willing to neglect the surface Dufour effect, Eq. (120) reduces to

$$\tau_\lambda \frac{d_s \mathbf{q}^s}{dt} + \mathbf{q}^s = -\lambda^s \nabla_s T^s, \tag{125}$$

where $\lambda^s = -\lambda^{s\prime}/T^s$ is the surface thermal conductivity of the interface. When comparing Eq. (50) with Eq. (120) we can identify the coefficient α_{qq} appearing in Eq. (50) as $\alpha_{qq} = \tau_\lambda/\lambda^{s\prime} = -\tau_\lambda/\lambda^s T^s$. With this expression and Eq. (125) the rate of entropy production of a nondeformed interface with uniform composition reduces to

$$\frac{\lambda^s}{(T^s)^2}\left[\nabla_s T^s + \frac{\tau_\lambda}{\lambda^s}\frac{d_s \mathbf{q}^s}{dt}\right]^2 \geq 0, \tag{126}$$

which allows us to conclude that $\lambda^s \geq 0$.

Equation (125) is basically the surface equivalent of the Maxwell-Cattaneo equation (Jou, Casas-Vásquez, and Lebon, 1988, 2001) for the bulk energy flux vector. When substituted into the energy balance of the interface Eq. (125) produces a hyperbolic differential equation that predicts a finite speed of propagation of thermal signals. This type of equation has extensively been applied to the modeling of second sound in 3D solids, at low temperatures. For most multiphase soft condensed matter systems the relaxation effects are expected to be small. For systems in which $\tau_\lambda \ll 1$ Eq. (125) reduces to

$$\mathbf{q}^s = -\lambda^s \nabla_s T^s, \tag{127}$$

which is the surface equivalent of Fourier's law of thermal conduction. Again we see that NET formalisms provide us with a simple tool to construct constitutive equations, beyond the simple linear laws such as Fourier's law, that include anomalous contributions, such as relaxation terms or the Dufour effect.

J. Transfer of momentum, mass, and energy to and from the interface

The expression for the rate of surface entropy production in Eq. (50) can also be used to construct constitutive equations for the transfer of momentum, mass, and energy from the adjoining bulk phases to the interface. The construction of these constitutive equations is completely identical to the construction of the expressions for the surface stress tensor, the surface mass flux vector, and the surface energy flux vector: We construct linear relations for the fluxes of momentum, mass, and energy from the adjoining bulk phases to the interface in terms of the driving forces for these fluxes. Subsequently we substitute these linear relations into Eq. (50) to determine the restrictions this expression puts on the coefficients in these constitutive equations.

In Sec. IV we established the fact that the rate of surface entropy production is basically a bilinear form coupling the fluxes present in the system to their respective driving forces [see Eq. (34)]. Consider the boldface bracket term in Eq. (50). The third contribution to this term, equal to $(\mathbf{v} - \mathbf{v}^s) \cdot \mathbf{T} \cdot \boldsymbol{\xi}$, suggests that the main driving force for the transfer of momentum from the bulk phase to the interface is the velocity difference $(\mathbf{v} - \mathbf{v}^s)$. Analogous to Eq. (38) in Sec. IV, or Eq. (51) in Sec. V.B, this suggests we express the extra stress tensor for the adjoining bulk phases, $\boldsymbol{\sigma}^{(I)} = \mathbf{T}^{(I)} + P^{(I)}\mathbf{I}$ $(I = 1, 2)$, evaluated at the interface, as

$$\boldsymbol{\sigma}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = \boldsymbol{\sigma}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)}([\mathbf{v} - \mathbf{v}^s]). \tag{128}$$

Expanding this functional up to linear order in its argument, we find

$$\boldsymbol{\sigma}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = \rho^{(I)}\mathbf{v}^{(I)}(\mathbf{v}^{(I)} - \mathbf{v}^s) \cdot \boldsymbol{\xi}^{(I,J)} - \boldsymbol{\zeta}^{(I)} \cdot \left(\mathbf{v}^s - \mathbf{v}^{(I)}\frac{T^s}{T^{(I)}}\right), \tag{129}$$

where $\boldsymbol{\zeta}^{(I)}$ is the friction tensor for transfer of momentum between bulk phase I and the interface. The first term on the right-hand side of Eq. (129) represents convective transport of momentum to the interface (i.e., the inertial stresses exerted on the interface by the adjoining bulk phases). The second term describes the viscous stresses exerted on the interface by the adjoining bulk phases. Equation (129) is more than just a constitutive equation for the bulk stresses evaluated at the interface. It also ensures connectivity between the bulk and interfacial domains.

In a similar manner, Eq. (50) suggests that the main driving forces for mass transfer from the bulk phases to the interface are the differences in chemical potential between bulk phase and interface, the difference in temperature between bulk and interface, and the velocity difference between bulk and interface. Therefore, we express the bulk mass flux vector of species A for the adjoining phase I $(I = 1, 2)$ as

$$\begin{aligned}\mathbf{j}_{(A)}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = {} & -\Lambda_{(A)}^{(I)}\left(\frac{\check{\mu}_A^{(I)}}{T^{(I)}} - \frac{\check{\mu}_{(A)}^s}{T^s}\right) - \Lambda_{(A)}^{T(I)}(T^{(I)} - T^s) \\ & - \rho_{(A)}^{(I)}(\mathbf{v}^{(I)} - \mathbf{v}^s) \cdot \boldsymbol{\xi}^{(I,J)},\end{aligned} \tag{130}$$

where $\Lambda_{(A)}^{(I)}$ is the coefficient for mass transfer to and from the interface, driven by differences in the chemical potential of the bulk phase and the interface, and $\Lambda_{(A)}^{T(I)}$ is the coefficient for mass transfer driven by differences in the temperature of the bulk phase and interface. $T^{(I)}$ is the bulk temperature, $\check{\mu}_{(A)} = \mu_{(A)} - \frac{1}{2}\mathbf{v}^2$ is the velocity modified chemical potential of species A in the bulk phase, and $\check{\mu}_{(A)}^s = \mu_{(A)}^s - \frac{1}{2}\mathbf{v}^{s2}$ is the surface velocity modified surface chemical potential of species A in the interface. The last term in Eq. (130) represents convective transport of species A from the bulk phase to the interface. An expression such as Eq. (130) allows us to construct a wide range of models for transport of material from the bulk phase to the interface, by choosing an appropriate expression for the chemical potentials. These models include as a limiting case also simple "Fickian" behavior, which forms the basis for the LVDT model (Lucassen and van den Tempel, 1972a, 1972b).

Finally, Eq. (50) suggests we express the bulk energy flux vectors as $(I = 1, 2)$

$$\begin{aligned}\mathbf{q}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)} = {} & -\frac{T^{(I)} - T^s}{R_K^{(I)}} - \sum_{A=1}^{N-1} \Lambda_{(A)}^{T(I)} T T^s \left(\frac{\check{\mu}_A^{(I)}}{T^{(I)}} - \frac{\check{\mu}_{(A)}^s}{T^s}\right) \\ & - \rho^{(I)}\left[\hat{U}^{(I)} + \frac{1}{2}(\mathbf{v}^{(I)})^2\right](\mathbf{v}^{(I)} - \mathbf{v}^s) \cdot \boldsymbol{\xi}^{(I,J)} \\ & + \mathbf{v}^{(I)} \cdot \boldsymbol{\sigma}^{(I)} \cdot \boldsymbol{\xi}^{(I,J)}.\end{aligned} \tag{131}$$

The coefficient $R_K^{(I)}$ is the Kapitza coefficient, representing the resistance for transfer of energy between the bulk and the interface, driven by differences in temperature. The second term represents energy transfer to the interface associated with mass transfer, the third term describes convective transport of internal and kinetic energy to the interface, and the last term incorporates the effects of viscous heating of the interface by the bulk phases.

With Eqs. (129)–(131) the rate of surface entropy production takes the form (focusing only on the boldface bracket terms)

$$\left[\!\left[\frac{(T^s-T)^2}{TT^sR_K}\right]\!\right] + \left[\!\left[\left(\frac{\mathbf{v}}{T}-\frac{\mathbf{v}^s}{T^s}\right)\cdot T^s\boldsymbol{\zeta}\cdot\left(\frac{\mathbf{v}}{T}-\frac{\mathbf{v}^s}{T^s}\right)\right]\!\right] + \left[\!\left[\sum_{A=1}^{N-1}\Lambda_{(A)}\left(\frac{\check{\mu}_A}{T}-\frac{\check{\mu}^s_{(A)}}{T^s}\right)^2\right]\!\right] + \left[\!\left[\sum_{A=1}^{N-1}2\Lambda^T_{(A)}(T-T^s)\left(\frac{\check{\mu}_A}{T}-\frac{\check{\mu}^s_{(A)}}{T^s}\right)\right]\!\right] \geq 0. \tag{132}$$

From this quadratic expression we conclude that R_K and $\Lambda_{(A)}$ are positive scalars, and the friction tensor $\boldsymbol{\zeta}$ is a positive semidefinite second order tensor.

K. Comparison of EIT with other formalisms

In the preceding sections we have seen that by assuming a functional dependence for the surface entropy of the form of Eq. (44), we are able to derive constitutive equations for interfaces with viscoelastic material behavior. We can construct linear differential and integral models for the surface stress tensor of linear viscoelastic interfaces, as well as nonlinear models, such as the surface Giesekus model. Although Eq. (44) relaxes the assumption of local equilibrium, which is the basis for the CIT formalism, the additional variables in this expression are still local variables. For that reason the models derived here are not expected to be accurate when modeling interfaces with long range order. Another shortcoming of the EIT formalism is that all surface fluxes are expressed in terms of surface driving forces. There is no explicit connection to the bulk phases, something we would expect if the bulk phases are ordered phases themselves. In the next sections we show how such a connection can be constructed within the extended rational thermodynamics and the GENERIC formalisms.

VI. EXTENDED RATIONAL THERMODYNAMICS OF MULTIPHASE SYSTEMS

In the previous section we discussed how the EIT formalism can be used to construct constitutive models for the surface extra stress tensor, the surface energy flux vector, and the surface mass flux vectors. A common characteristic of these models is that the surface fluxes are expressed purely in terms of surface gradients, and there is no direct connection to the stresses in the bulk phase. For systems where the adjoining bulk phases are also complex phases we would expect such a coupling. For example, when the interface is separating a nematic phase from an isotropic phase, and the interface itself also is a nematic, we expect the orientation of rodlike particles in the bulk to affect the orientation of particles in the interface, and vise versa (Rey, 2000a, 2000b). In the ERT formalism (Liu and Müller, 1983; Liu, 1985) such a connection can be included in a relatively straightforward way. In ERT the fluxes are treated as conserved quantities, an approach inspired by results from kinetic theory (Liu and Müller, 1983; Liu, 1985; Jou, Casas-Vásquez, and Lebon, 1988). The time evolution of the extra stress tensor of the bulk phase is assumed to obey a balance equation of the form

$$\rho\frac{d\bar{\boldsymbol{\sigma}}}{dt} = -\nabla\cdot\mathbf{J}_\sigma + \mathbf{S}_\sigma, \tag{133}$$

where $\mathbf{J}_\sigma$ is a third order tensor field denoting the flux of stress, and $\mathbf{S}_\sigma$ is a source term. When applying this approach to a multiphase system we need to specify similar balance equations for the symmetric part of the surface extra stress tensor and its trace. These equations take the form

$$\rho^s\frac{d_s\bar{\boldsymbol{\sigma}}^s}{dt} = -\nabla_s\cdot\mathbf{J}^s_\sigma + \mathbf{S}^s_\sigma - [\![\rho(\bar{\boldsymbol{\sigma}}-\bar{\boldsymbol{\sigma}}^s)(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi} + \mathbf{J}_\sigma\cdot\boldsymbol{\xi}]\!], \tag{134}$$

$$\rho^s\frac{d_s\,\mathrm{tr}\boldsymbol{\sigma}^s}{dt} = -\nabla_s\cdot\mathbf{j}^s_{\mathrm{tr}\sigma} + S^s_{\mathrm{tr}\sigma} - [\![\rho(\mathrm{tr}\boldsymbol{\sigma}-\mathrm{tr}\boldsymbol{\sigma}^s)(\mathbf{v}-\mathbf{v}^s)\cdot\boldsymbol{\xi} + \mathbf{j}_{\mathrm{tr}\sigma}\cdot\boldsymbol{\xi}]\!]. \tag{135}$$

The constitutive equations for the fluxes $\mathbf{J}^s_\sigma$, $\mathbf{j}^s_{\mathrm{tr}\sigma}$, $\mathbf{J}_\sigma$, and $\mathbf{j}_{\mathrm{tr}\sigma}$ and the source terms $\mathbf{S}^s_\sigma$, $S^s_{\mathrm{tr}\sigma}$, $\mathbf{S}_\sigma$, and $S_{\mathrm{tr}\sigma}$ can be derived in the same way we constructed constitutive equations in Sec. V. First we derive an expression for the surface rate of entropy production, and then we use this expression to determine the functional forms for the new fluxes and source terms (again invoking the Curie principle). The final step is to expand the functions in their respective arguments. Up to linear order in the driving forces we obtain

$$\mathbf{J}^s_\sigma = \alpha_3\nabla_s\bar{\boldsymbol{\sigma}}^s, \tag{136}$$

$$\mathbf{j}^s_{\mathrm{tr}\sigma} = \alpha_4\nabla_s[\mathrm{tr}\boldsymbol{\sigma}^s], \tag{137}$$

$$\mathbf{S}^s_\sigma = -\frac{1}{\tau_s}\bar{\boldsymbol{\sigma}}^s + \frac{2\varepsilon_s}{\tau_s}\bar{\mathbf{D}}^s, \tag{138}$$

$$S^s_{\mathrm{tr}\sigma} = -\frac{1}{\tau_d}\mathrm{tr}\boldsymbol{\sigma}^s + \frac{\varepsilon_d}{\tau_d}\mathrm{tr}[\mathbf{D}^s], \tag{139}$$

$$\mathbf{J}^{(I)}_\sigma\cdot\boldsymbol{\xi}^{(I,J)} = k^{(I)}_\sigma(\bar{\boldsymbol{\sigma}}^{(I)}-\bar{\boldsymbol{\sigma}}^s) - \rho^{(I)}\bar{\boldsymbol{\sigma}}^{(I)}(\mathbf{v}^{(I)}-\mathbf{v}^s)\cdot\boldsymbol{\xi}^{(I,J)}, \tag{140}$$

and

$$\mathbf{j}^{(I)}_{\mathrm{tr}\sigma}\cdot\boldsymbol{\xi}^{(I,J)} = k^{(I)}_{\mathrm{tr}\sigma}(\mathrm{tr}\boldsymbol{\sigma}^{(I)}-\mathrm{tr}\boldsymbol{\sigma}^s) - \rho^{(I)}\,\mathrm{tr}\boldsymbol{\sigma}^{(I)}(\mathbf{v}^{(I)}-\mathbf{v}^s)\cdot\boldsymbol{\xi}^{(I,J)}. \tag{141}$$

Here α_3, α_4, $k^{(I)}_\sigma$, and $k^{(I)}_{\mathrm{tr}\sigma}$ are scalar coefficients. Equations (134)–(141) give us a set of linear diffusion-relaxation equations for the surface extra stress tensor, given by

$$\rho^s \frac{d_s \bar{\boldsymbol{\sigma}}^s}{dt} + \frac{1}{\tau_s}\bar{\boldsymbol{\sigma}}^s = -\nabla_s \cdot (\alpha_3 \nabla_s \bar{\boldsymbol{\sigma}}^s) + \frac{2\varepsilon_s}{\tau_s}\bar{\mathbf{D}}^s + [\![\rho \bar{\boldsymbol{\sigma}}^s(\mathbf{v} - \mathbf{v}^s)\cdot \boldsymbol{\xi} - k_\sigma(\bar{\boldsymbol{\sigma}} - \bar{\boldsymbol{\sigma}}^s)]\!], \tag{142}$$

and

$$\rho^s \frac{d_s\, \mathrm{tr}\boldsymbol{\sigma}^s}{dt} + \frac{1}{\tau_d}\,\mathrm{tr}\boldsymbol{\sigma}^s = -\nabla_s \cdot (\alpha_4 \nabla_s[\mathrm{tr}\boldsymbol{\sigma}^s]) + \frac{\varepsilon_d}{\tau_d}\,\mathrm{tr}[\mathbf{D}^s] + [\![\rho\, \mathrm{tr}\boldsymbol{\sigma}^s(\mathbf{v} - \mathbf{v}^s)\cdot \boldsymbol{\xi} - k_{\mathrm{tr}\sigma}(\mathrm{tr}\boldsymbol{\sigma} - \mathrm{tr}\boldsymbol{\sigma}^s)]\!]. \tag{143}$$

We see that when we neglect contributions from gradients in the surface stresses, these equations are similar to those derived using the EIT formalism [see Eqs. (53) and (54)]. The main difference between these expressions is the additional jump term present in Eqs. (142) and (143). These introduce an explicit coupling of the surface stress with the stress fields in the adjoining bulk phases.

Expressions similar to Eqs. (142) and (143) can also be derived for the surface energy flux vectors and surface mass flux vectors, but for brevity we will not discuss these here. The ERT formalism is not often used for the development of constitutive equations for bulk phases or interfaces. The assumption that the fluxes of the system may be treated as conserved variables is often cited as a weakness of this formalism, since there is no sound physical basis for that assumption. But the fact that it provides a relatively simple way to connect the surface fluxes to the bulk fluxes makes it an appealing formalism to describe complex multiphase systems. The RT, CIT, and EIT formalisms cannot provide such connections. In the next section we show that the coupling between bulk and surface stress fields can also be obtained without treating the fluxes as conserved variables. In the context of the GENERIC formalism this connection can be constructed through the incorporation of structural bulk and surface variables in the description of the system.

VII. GENERIC FORMALISM FOR MULTIPHASE SYSTEMS

The GENERIC formalism is a formulation of nonequilibrium thermodynamics, which describes the dynamics of a system in terms of two brackets: a Poisson bracket, describing the reversible part of the dynamics, and a dissipative bracket, representing the irreversible part of the dynamics (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 2005). Constraints are imposed on both types of brackets which restrict their specific form.

One of the strengths of the GENERIC formalism is its modular character (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 2005), which means that it is relatively easy to incorporate nonlinear dependencies on structural variables in the description of a system. These are scalar or tensorial variables describing the microstructure of the material. Structural variables can also be included in the classical irreversible thermodynamics or rational thermodynamics formalism, using the internal variables theory (Prigogine and Mazur, 1953), but this inclusion leads to constitutive models which typically are valid only for small deviations from linear material behavior (Sagis, Ramaekers, and van der Linden, 2001; Bedeaux and Rubi, 2002).

The GENERIC formalism also allows us to construct constitutive equations for the material behavior of the interface that couple this behavior directly to the behavior of the adjoining bulk phases. In the ERT formalism we discussed in the previous section such a coupling is introduced by treating the fluxes as conserved variables. As we see in this section, the GENERIC formalism introduces this coupling in a far more natural way, without treating fluxes as conserved variables.

The GENERIC formulation has been applied mainly to isolated single phase systems (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 2005), where only bulk contributions to the two-bracket formulation are needed to describe the dynamics of the system. Recently, Öttinger, Bedeaux, and Venerus (2009) introduced a GENERIC formalism for multiphase systems, in the context of bubble growth by exsolution of a dissolved component from an oversaturated solution. This formalism includes interfacial contributions to the Poisson and dissipative brackets and is valid for systems with invicid interfaces (Öttinger, Bedeaux, and Venerus, 2009). In their development Öttinger, Bedeaux, and Venerus (2009) assumed that mass does not accumulate at the interface and that the surface mass density is negligible. Therefore, they do not consider the effects of surface rheology, surface diffusion, or surface heat conduction. For the system they are considering this is a more than reasonable assumption. But for many practical multiphase systems, stabilized by (mixtures) of surface active components these effects may not be negligible. For those systems a generalization of the approach of Öttinger, Bedeaux, and Venerus (2009) is needed that incorporates these effects. Such generalizations were recently introduced (Sagis, 2010b, 2010d) and will be discussed in the remainder of this section.

A. GENERIC for systems with viscous interfaces

In the GENERIC formalism the dynamics of a multiphase system are described by a single compact equation of the form

$$\frac{dA}{dt} = \{A, E\} + [A, S], \tag{144}$$

where the Poisson bracket $\{A, E\}$ represents the reversible part of the dynamics of the system; it is defined by (Grmela and Öttinger, 1997; Öttinger and Grmela, 1997; Öttinger, 2005)

$$\{A, E\} \equiv \frac{\delta A(\mathbf{x})}{\delta \mathbf{x}} \cdot \mathbf{L} \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}}. \tag{145}$$

In this expression $E(\mathbf{x})$ is the Hamiltonian of the system, $\mathbf{x}$ is the vector of independent system variables, and $\mathbf{L}$ is an antisymmetric matrix. The derivatives in this expression are to be interpreted as functional derivatives. The arbitrary observable A is defined as

$$A = \int_{\mathcal{R}} a dV, \tag{146}$$

where a denotes the density of A. The Poisson bracket has the properties

$$\{A, B\} = -\{B, A\}, \tag{147}$$

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0. \tag{148}$$

The last identity is referred to as the Jacobi identity. These two identities restrict the reversible part of the dynamics of the system.

The bracket $[A, S]$ represents the dissipative part of the dynamics of the system, and is given by

$$[A, S] \equiv \frac{\delta A(\mathbf{x})}{\delta \mathbf{x}} \cdot \mathbf{M} \cdot \frac{\delta S(\mathbf{x})}{\delta \mathbf{x}}, \tag{149}$$

where $\mathbf{M}$ is a symmetric positive semidefinite matrix, and $S(\mathbf{x})$ is the total entropy of the system. The dissipative bracket has the following properties:

$$[A, B] = [B, A], \tag{150}$$

$$[A, A] \geq 0. \tag{151}$$

The last expression (together with the degeneracy property of the total entropy, $\{S, A\} = 0$) ensures that the entropy production of the system is positive:

$$\frac{dS}{dt} = [S, S] \geq 0. \tag{152}$$

For multiphase systems the Hamiltonian of the system and the entropy are given by

$$E = \int_{\mathcal{R}} \left(\frac{\mathbf{m}^2}{2\rho} + \bar{U}(\mathbf{r}) \right) dV + \int_{\Sigma} \left(\frac{(\mathbf{m}^s)^2}{2\rho^s} + \bar{U}^s(\mathbf{r}) \right) dA, \tag{153}$$

$$S = \int_{\mathcal{R}} \bar{S}(\rho, \bar{U}, \rho_{(A)}, \ldots, \rho_{(N-1)}) dV + \int_{\Sigma} \bar{S}^s(\rho^s, \bar{U}^s, \rho^s_{(A)}, \ldots, \rho^s_{(N-1)}) dA. \tag{154}$$

Here $\bar{U}$ and $\bar{S}$ are the internal energy and entropy per unit volume in the bulk phase, respectively, and $\bar{U}^s$ and $\bar{S}^s$ are the internal energy and entropy per unit area of the interface. The vector $\mathbf{m} = \rho \mathbf{v}$ is the momentum density in the bulk phase, and $\mathbf{m}^s = \rho^s \mathbf{v}^s$ is the momentum density in the interface Σ. For systems with viscous interfaces an appropriate choice for the system variables would be (Sagis, 2010d)

$$\mathbf{x} = (\rho, \mathbf{m}, \bar{U}, \rho_{(1)}, \ldots, \rho_{(N-1)}), \tag{155}$$

$$\mathbf{x}^s = (\rho^s, \mathbf{m}^s, \bar{U}^s, \rho^s_{(1)}, \ldots, \rho^s_{(N-1)}). \tag{156}$$

The choice of independent system variables is an important step in constructing a GENERIC model for a multiphase system. Variables describing the state of the interface can be divided into two classes: variables insensitive to the precise location of the dividing surface [macroscopically relevant variables (Öttinger, Bedeaux, and Venerus, 2009)] and variables that change significantly upon changing the location of the dividing surface [macroscopically ambiguous variables (Öttinger, Bedeaux, and Venerus, 2009)]. The latter type of variable may even vanish for specific choices of the location of the dividing surface. Any macroscopic description of the dynamics of a multiphase system should be invariant under the choice of the location of the dividing surface and should therefore be based on macroscopically relevant variables. Except $\bar{U}^s$, all variables in the set $\mathbf{x}^s$ are, in fact, macroscopically ambiguous variables. With that in mind the set $\mathbf{x}^{s\prime} = (\rho^s, \mathbf{v}^s, \hat{U}^s, \omega^s_{(1)}, \ldots, \omega^s_{(N-1)})$ would be a more appropriate choice for the independent variables for the interface. However, the set $\mathbf{x}^s$ generates a slightly simpler form of the Poisson and dissipative brackets (Sagis, 2010b, 2010d). When developing a GENERIC formulation with this set of independent variables, the resulting set of balance and constitutive equations can easily be transformed to the set $\mathbf{x}^{s\prime}$, assuring that the final form of the model is expressed in macroscopically relevant variables. For a more detailed discussion of the choice of appropriate interfacial variables, in the context of gauge invariance, see Öttinger, Bedeaux, and Venerus (2009).

For multiphase systems the Poisson and dissipative brackets will have contributions from both the bulk phase variables and the surface variables, and Eq. (144) takes the following form (Sagis, 2010b, 2010d):

$$\frac{dA}{dt} = \{A, E\}^b + \{A, E\}^j + \{A, E\}^s + [A, S]^b + [A, S]^j + [A, S]^s, \tag{157}$$

where $\{A, B\}^b$ and $[A, B]^b$ are the contributions from the bulk phase variables to the Poisson and dissipative brackets, $\{A, B\}^s$ and $[A, B]^s$ are the contributions to the Poisson and dissipative brackets from the interfacial variables in Eq. (156), and $\{A, B\}^j$ and $[A, B]^j$ are contributions to the Poisson and dissipative brackets involving transport of mass, momentum, and energy from the bulk phases to the interfaces.

For the specific form of these brackets see Sagis (2010d). In view of the length of the expressions we will not repeat them here. With the specific form used by Sagis (2010d) we obtained a complete set of balance equations for the bulk and interfacial variables defined in Eqs. (155) and (156): We obtained the equation of continuity, the momentum balance for a Newtonian fluid, the energy balance, and the species mass balances. For the interfacial variables we obtained the overall jump mass balance, the jump momentum balance for a linear viscous surface fluid (Boussinesq model), the jump energy balance, and the jump species mass balances for each of the components adsorbed at the interface. The energy and species mass balances include contributions from heat transfer driven by concentration gradients (Dufour effect) and contributions from mass transfer driven by temperature gradients (Soret effect). The set of balance equations developed by Sagis (2010d) is completely equivalent with the set of equations derived by the RT and CIT formalisms. The strength of the GENERIC formulations in Öttinger, Bedeaux, and Venerus (2009) and Sagis (2010d) is that they can easily be extended to systems with surfaces displaying highly nonlinear material behavior. We illustrate this in the next section.

B. Incorporation of structural variables in multiphase GENERIC

Generalizations of material behavior to the highly nonlinear regime are most easily constructed using scalar, vectorial, or tensorial structural variables, describing the response of the microstructure of the system to an applied deformation, temperature gradient, or concentration gradient. In the GENERIC formalism a dependence on the microstructure of the system can be introduced by including structural variables in the set of system variables, defined in Eqs. (155) and (156). Sagis (2010b) recently developed a model for a multiphase system in which the microstructure of the bulk and interfaces are described by both a scalar and a tensorial structural parameter:

$$\mathbf{x}^T = (\rho, \mathbf{m}, \bar{U}, \rho_{(1)}, \ldots, \rho_{(N-1)}, \bar{\Gamma}, \bar{\mathbf{C}}), \tag{158}$$

$$\mathbf{x}^{sT} = (\rho^s, \mathbf{m}^s, \bar{U}^s, \rho^s_{(1)}, \ldots, \rho^s_{(N-1)}, \bar{\Gamma}^s, \bar{\mathbf{C}}^s). \tag{159}$$

The scalar parameter $\bar{\Gamma}$ can be a local polymer segment density, or a local particle density, and the symmetric tensorial density $\bar{\mathbf{C}}$ can be a segment or particle orientation tensor. The scalar parameter $\bar{\Gamma}^s$ can be a local surface density of segments or particles adsorbed at an interface, and the symmetric tangential surface tensor $\bar{\mathbf{C}}^s$ can be an orientation tensor for these segments or particles in the interface.

These structural variables generate additional terms in the brackets in Eq. (157) describing reversible and irreversible processes for these variables. Sagis (2010b) included diffusive and relaxation processes. Again, for brevity we will not repeat the detailed form of the Poisson and dissipative brackets and merely present the main results of Sagis (2010b). For the choice of independent surface variables given in Eqs. (158) and (159) the expression for the surface extra stress tensor reduces to

$$\boldsymbol{\sigma}^s_{\text{tot}} = (\varepsilon_d - \varepsilon_s)[\text{div}_s \mathbf{v}^s]\mathbf{P} + 2\varepsilon_s \mathbf{D}^s + 2\bar{\mathbf{C}}^s \cdot \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s} + \mathbf{G}^s \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s}, \tag{160}$$

where $\mathbf{G}^s$ is a second order surface tensor describing the coupling of the scalar field $\bar{\Gamma}^s$ with the velocity gradient field, and $\bar{F}^s_c$ is the contribution of the microstructure of the interface to the surface Helmholtz free energy. The time evolution equations for the scalar and tensorial structural parameters are given by

$$\rho^s \frac{d_s \hat{\Gamma}^s}{dt} - \mathbf{G}^s : \nabla_s \mathbf{v}^s + \frac{R^s_1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} - \nabla_s \cdot \left[\mathbf{D}^s_\Gamma \cdot \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\Gamma}^s} \right) \right] + \left[\!\left[\rho(\hat{\Gamma} - \hat{\Gamma}^s)(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} - \left[\mathbf{D}_\Gamma \cdot \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\Gamma}} \right) \right] \cdot \boldsymbol{\xi} \right]\!\right] = 0, \tag{161}$$

$$\overset{\square}{\delta} \bar{\mathbf{C}}^s + \mathbf{R}^s_2 : \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s} \right) - \nabla_s \cdot \left[\mathbf{D}^s_C \odot^3 \nabla_s \left(\frac{1}{T^s} \frac{\partial \bar{F}^s_c}{\partial \bar{\mathbf{C}}^s} \right) \right] + \left[\!\left[\bar{\mathbf{C}}(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} - \left[\mathbf{D}_C \odot^3 \nabla \left(\frac{1}{T} \frac{\partial \bar{F}_c}{\partial \bar{\mathbf{C}}} \right) \right] \cdot \boldsymbol{\xi} \right]\!\right] = 0. \tag{162}$$

Here $\hat{\Gamma}^s = \bar{\Gamma}^s/\rho^s$, R^s_1 is a scalar describing the relaxation of $\bar{\Gamma}^s$, $\mathbf{D}^s_\Gamma$ is a second order diffusion tensor related to surface diffusion processes for $\bar{\Gamma}^s$, and $\mathbf{D}_\Gamma$ quantifies diffusion of $\bar{\Gamma}$ in the bulk phase. $\mathbf{R}^s_2$ is a fourth order tensor describing relaxation processes for the tensor $\bar{\mathbf{C}}^s$, and $\mathbf{D}^s_C$ is a sixth order tensor field quantifying the contributions of diffusion processes to the time rate of change of $\bar{\mathbf{C}}^s$. Diffusion processes for $\bar{\mathbf{C}}$ in the bulk phases are described by the sixth order tensor $\mathbf{D}_C$. The symbol $\odot^3$ denotes a threefold tensor contraction.

From Eqs. (161) and (162) a wide range of models can be generated by choosing specific forms for the scalar R^s_1, the tensors $\mathbf{G}^s$, $\mathbf{D}^s_\Gamma$, $\mathbf{D}_\Gamma$, $\mathbf{R}^s_2$, $\mathbf{D}^s_C$, and $\mathbf{D}_C$, and the microstructural contributions to the Helmholtz free energy, $\bar{F}_c$, and $\bar{F}^s_c$.

We illustrate this procedure with a relatively simple example: an interface with adsorbed anisotropic colloidal particles (such as encountered in, for example, Pickering stabilized emulsions). In Pickering emulsions the particles tend to be closely packed at the interface and are often aggregated. In our example the particle concentration in the interface is assumed to be in the dilute regime, and the repulsive interactions between the particles are assumed to be sufficiently strong to prevent aggregation of the colloidal particles. Therefore, the interface can be considered a stable dilute 2D dispersion of anisotropic particles. Such an interface can be created in a Langmuir trough or a surface rheometer, by spreading colloidal particles at the interface. Methods are available to produce anisotropic colloidal particles with tunable particle-particle interactions [see, e.g., Zhang *et al.* (2011)].

When this interface is subjected to a deformation in an arbitrary flow field, the particles in the interface tend to align in the direction of the flow. This causes a reduction of the surface shear viscosity, similar to the shear thinning effect observed in dispersions of anisotropic particles in bulk fluids. The relevant scalar structural variable in this example is the surface density of the particles ρ^s_p, so $\bar{\Gamma}^s = \rho^s_p$, or $\hat{\Gamma}^s = \omega^s_p$, where $\omega^s_p = \rho^s_p/\rho^s$ is the surface mass fraction of particles. A suitable tensorial structural variable for this case is the surface particle orientation tensor $\mathbf{Q}^s$, defined by

$$\mathbf{Q}^s \equiv \langle \mathbf{n}^s \mathbf{n}^s - \tfrac{1}{2}\mathbf{P} \rangle_s, \tag{163}$$

where $\mathbf{n}^s$ is the unit vector characterizing the orientation of the particles in the interface, and $\langle \cdots \rangle_s$ denotes a local average over a portion of the interface. The tensor $\mathbf{Q}^s$ is a symmetric traceless tangential surface tensor. When the particles are also present in the adjacent bulk phases, the corresponding bulk structural variables are the bulk particle density ρ_p and the bulk particle orientation tensor $\mathbf{Q} = \langle \mathbf{n}\mathbf{n} - \tfrac{1}{3}\mathbf{I} \rangle_b$. Here $\mathbf{n}$ denotes the orientation of a particle in the bulk phase, and $\langle \cdots \rangle_b$ is a local average over a portion of the bulk phase.

Expanding the surface Helmholtz free energy up to second order in terms of these structural variables gives

$$\bar{F}^s_c = \bar{F}^{s0}_c + \tfrac{1}{2}\alpha^s_1 T^s (\rho^s_p)^2 + \tfrac{1}{2}\alpha^s_2 T^s \mathbf{Q}^s : \mathbf{Q}^s, \tag{164}$$

where $\bar{F}^{s0}_c$ is the Helmholtz free energy per unit area of the bare nondeformed interface. In a similar manner we expand the Helmholtz free energy of the bulk phases:

$$\bar{F}_c = \bar{F}_c^0 + \tfrac{1}{2}\alpha_1 T \rho_p^2 + \tfrac{1}{2}\alpha_2 T \mathbf{Q}{:}\mathbf{Q}. \tag{165}$$

When the coefficients α_1^s and α_2^s are constants, independent of position on the interface, Eq. (160) reduces to

$$\begin{aligned}\boldsymbol{\sigma}_{\text{tot}}^s = {}& (\varepsilon_d - \varepsilon_s)[\text{div}_s \mathbf{v}^s]\mathbf{P} + 2\varepsilon_s \mathbf{D}^s + g_1^s \mathbf{P} + g_2^s \mathbf{Q}^s \\ & + g_3^s (\mathbf{Q}^s)^{-1} + 2\alpha_2^s T^s \mathbf{Q}^s \cdot \mathbf{Q}^s,\end{aligned} \tag{166}$$

where we assumed (Öttinger, 2005)

$$\alpha_1^s \rho^s T^s \mathbf{G}^s = g_1^s \mathbf{P} + g_2^s \mathbf{Q}^s + g_3^s (\mathbf{Q}^s)^{-1}. \tag{167}$$

The coefficients g_i^s are functions of ρ_p^s and the invariants of $\mathbf{Q}^s$. We see that the expression for the configurational Helmholtz free energy of the interface in Eq. (164) predicts a stress response that depends on the orientation of the particles. To complete this model we need to provide the time evolution equations for the structural variables ρ_p^s and $\mathbf{Q}^s$. Starting from Eq. (161) we find that the scalar variable ρ_p^s satisfies

$$\begin{aligned}\rho^s \frac{d_s \omega_p^s}{dt} & - \mathbf{G}^s{:}\nabla_s \mathbf{v}^s - D_\omega^s \nabla_s^2 (\rho^s \omega_p^s) \\ & + [\![\rho(\omega_p - \omega_p^s)(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} - \mathbf{j}_p \cdot \boldsymbol{\xi}]\!] = 0,\end{aligned} \tag{168}$$

where we defined the flux $\mathbf{j}_p = D_\omega \nabla(\rho \omega_p)$. The second term in this expression describes the coupling of the surface particle density with the velocity gradient field. The third term represents an in-plane diffusive flux, driven by gradients in the surface particle density. Finally, the boldface bracket term describes exchange of particles between bulk phase and the interface, by convective and diffusive processes.

From Eq. (162) we obtain

$$\overset{\square}{\delta}\mathbf{Q}^s + R_2^s \mathbf{Q}^s - D_Q^s \nabla_s^2 \mathbf{Q}^s + [\![\mathbf{Q}(\mathbf{v} - \mathbf{v}^s) \cdot \boldsymbol{\xi} - \mathbf{j}_Q \cdot \boldsymbol{\xi}]\!] = 0, \tag{169}$$

where we defined the flux $\mathbf{j}_Q = D_Q \nabla \mathbf{Q}$. Arriving at these two equations we assumed

$$R_1^s = 0, \qquad \mathbf{R}_2^s = R_2^s (\alpha_2^s)^{-1} \mathbf{P}^{(4)}, \tag{170}$$

$$\mathbf{D}_\omega^s = D_\omega^s (\alpha_1^s)^{-1} \mathbf{P}, \qquad \mathbf{D}_\omega = D_\omega (\alpha_1)^{-1} \mathbf{I}, \tag{171}$$

$$\mathbf{D}_Q^s = D_Q^s (\alpha_2^s)^{-1} \mathbf{P}^{(6)}, \qquad \mathbf{D}_Q = D_Q (\alpha_2)^{-1} \mathbf{I}^{(6)}, \tag{172}$$

and we have assumed that the coefficients R_2^s, D_ω^s, and D_Q^s are independent of position on the interface. The tensors $\mathbf{P}^{(6)}$ and $\mathbf{I}^{(6)}$ are sixth order isotropic irreducible tensors [for their definition, see, e.g., Sagis (1998b)]. With Eqs. (166), (168), and (169) we have constructed a model for the surface stress tensor of this type of interface, which (depending on the values of the coefficients appearing in it) predicts shear thinning and thixotropic behavior. The coefficients in the model can be determined by comparing numerical solutions for these equations with experimental data. Since this model is based on a simple Taylor expansion, we expect this model to be valid only for small departures from equilibrium. For large deformations a more appropriate choice for $\bar{F}_c^s$ would be (Sarti and Marrucci, 1973; Öttinger, 2005; Sagis, 2010b)

$$\bar{F}_c^s = -k_B T^s \rho^s \omega_p^s [-\ln \omega_p^s + \tfrac{1}{2} \ln \det(2\mathbf{Q}^s + \mathbf{P})]. \tag{173}$$

Numerical solutions for the model in Eqs. (166), (168), and (169) are not yet available in the literature. Recently a similar model was constructed for the same system, but used the classical irreversible thermodynamics formalism (Sagis, 2011). In this model the expression for the surface extra stress tensor is given by

$$\begin{aligned}\boldsymbol{\sigma}^s = {}& K_2^s(\mathbf{Q}^s{:}\mathbf{D}^s)\mathbf{P} + K_3^s(\mathbf{Q}^s{:}\mathbf{D}^s)\mathbf{Q}^s + 2K_1^s \mathbf{D}^s \\ & + 2K_2^s[\mathbf{Q}^s \cdot \mathbf{D}^s + \mathbf{D}^s \cdot \mathbf{Q}^s] + 2K_3^s \mathbf{Q}^s \cdot \mathbf{D}^s \cdot \mathbf{Q}^s \\ & - K_3^s(\mathbf{D}^s \cdot \mathbf{Q}^s \cdot \mathbf{Q}^s + \mathbf{Q}^s \cdot \mathbf{Q}^s \cdot \mathbf{D}^s) \\ & - \tfrac{1}{2}K_3^s \mathbf{P}(\mathbf{Q}^s \cdot \mathbf{Q}^s){:}\mathbf{D}^s + \tfrac{1}{2}K_3^s(\mathbf{Q}^s{:}\mathbf{Q}^s)\mathbf{D}^s \\ & - 2\alpha_1^s L_1^s \mathbf{Q}^s - \phi_2^s(\mathbf{Q}^s{:}\mathbf{Q}^s)\mathbf{P} - 2\phi_1^s(\mathbf{Q}^s \cdot \mathbf{Q}^s),\end{aligned} \tag{174}$$

and the time rate of change of the surface orientation tensor is given by

$$\begin{aligned}\rho^s \frac{d_s \mathbf{Q}^s}{dt} = {}& -2\rho^s D_r^s \mathbf{Q}^s + 2\nu_1 \mathbf{Q}^s \cdot \mathbf{Q}^s + \nu_2[\mathbf{Q}^s{:}\mathbf{Q}^s]\mathbf{P} \\ & + L_2^s(\mathbf{Q}^s{:}\mathbf{D}^s)\mathbf{P} + L_3^s(\mathbf{Q}^s{:}\mathbf{D}^s)\mathbf{Q}^s + 2L_1^s \mathbf{D}^s \\ & + 2L_2^s[\mathbf{Q}^s \cdot \mathbf{D}^s + \mathbf{D}^s \cdot \mathbf{Q}^s] + 2L_3^s \mathbf{Q}^s \cdot \mathbf{D}^s \cdot \mathbf{Q}^s \\ & - L_3^s(\mathbf{D}^s \cdot \mathbf{Q}^s \cdot \mathbf{Q}^s + \mathbf{Q}^s \cdot \mathbf{Q}^s \cdot \mathbf{D}^s) \\ & - \frac{1}{2}L_3^s \mathbf{P}(\mathbf{Q}^s \cdot \mathbf{Q}^s){:}\mathbf{D}^s + \frac{1}{2}L_3^s(\mathbf{Q}^s{:}\mathbf{Q}^s)\mathbf{D}^s.\end{aligned} \tag{175}$$

The coefficients L_i^s, K_i^s, ϕ_i^s, and ν_i^s are constants, to be determined by comparison with experimental data. D_r^s denotes the surface rotational diffusion coefficient of the particles. Arriving at these expressions, two additional assumptions were made: The shear was assumed to be sufficiently low to avoid gradients in the particle concentration, and the deformation was assumed to be a pure in-plane shear flow (i.e., $\text{tr}\mathbf{D}^s = 0$). The first of these assumptions implies that the mass balance for the particles Eq. (168) is satisfied identically. Note that this model is based on a Taylor expansion of the surface free energy and the Onsager coefficients in terms of the surface orientation tensor (Sagis, 2011), and therefore it is valid only for low shear rates, where departures from the equilibrium structure are still relatively small.

In Fig. 2 we plotted the components Q_{xy}^s and Q_{xx}^s of the surface orientation tensor, as a function of time, for three different surface shear rates $\dot{\gamma}$ (0.05, 0.08, and 0.1 s^{-1}). This figure also shows the effective surface shear viscosity $\varepsilon_{\text{eff}}^s$, equal to $\sigma_{xy}^s/\dot{\gamma}$, as a function of time, for the same three shear rates. The curves were calculated using Eqs. (174) and (175), with parameters $K_1 = 1$ Ns/m, $K_3 = -4.0$ Ns/m, $\alpha = 8.0$ J/kg, $L_1^s/\rho^s = 10.0$, $L_2^s/\rho^s = 10.0$, $L_3^s/\rho^s = -5.0$, $\nu_3 = 2(\nu_1 + \nu_2)/\rho^s = -1.5\ \text{s}^{-1}$, $D_r^s = 1.0\ \text{s}^{-1}$, and $\rho^s = 2.0 \times 10^{-6}\ \text{kg/m}^2$. We clearly see an effect of the shear rate on the time evolution of the components of $\mathbf{Q}^s$ and the effective surface viscosity. An increase in shear rate results in increased orientation of the particles and in a reduction of the effective surface shear viscosity. Although this model is still limited to small shear rates, it is able to capture the

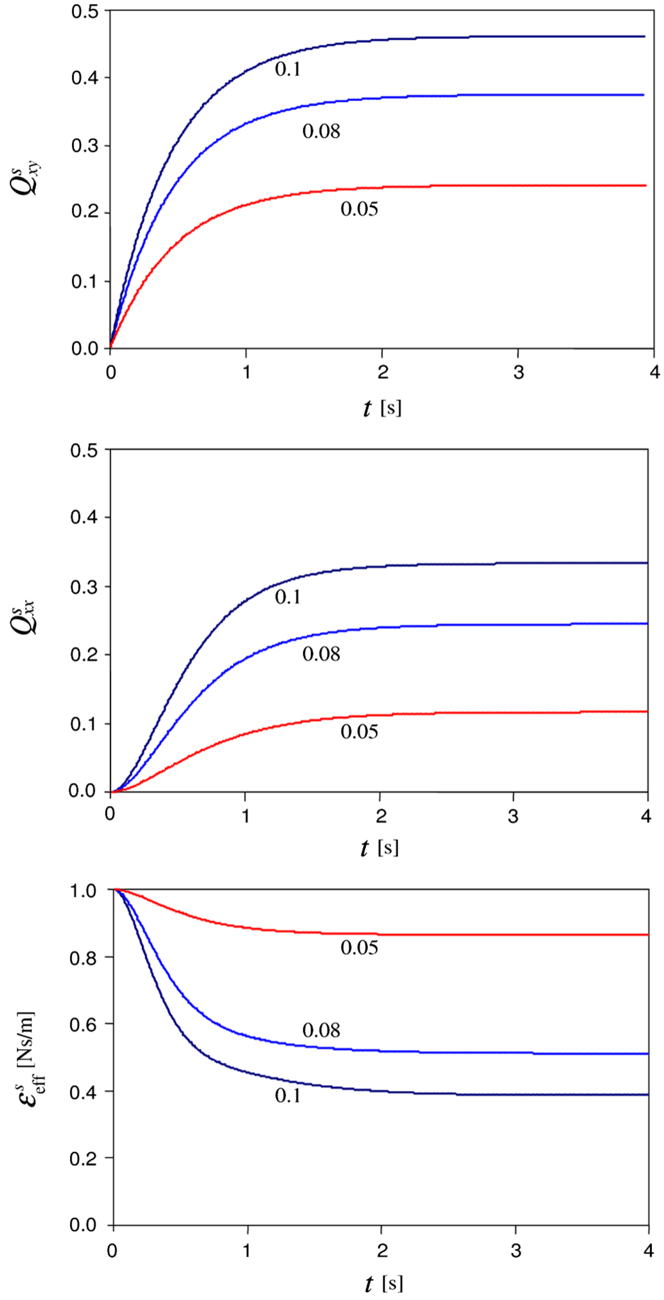

FIG. 2 (color online). Q^s_{xy}, Q^s_{xx}, and $\varepsilon^s_{\rm eff}$ as a function of time, for three different shear rates $\dot{\gamma}$: 0.1, 0.08, and 0.05 s^{-1}. Parameters: $K_1 = 1$ Ns/m, $K_3 = -4.0$ Ns/m, $\alpha = 8.0$ J/kg, $L^s_1/\rho^s = 10.0$, $L^s_2/\rho^s = 10.0$, $L^s_3/\rho^s = -5.0$, $\nu_3 = 2(\nu_1 + \nu_2)/\rho^s = -1.5\ \mathrm{s}^{-1}$, $D^s_r = 1.0\ \mathrm{s}^{-1}$, and $\rho^s = 2.0 \times 10^{-6}\ \mathrm{kg/m^2}$.

thixotropic and shear thinning behavior observed for this type of interface.

Thus far structural models have found only limited application in the analysis of surface rheological data. Rey (2000a, 2000b, 2000c) used structural variables to model the interfacial dynamics of nematic polymer-viscous fluid interfaces. Oh, Lagoudas, and Slattery (2005) used a structural model to describe the interfacial behavior in single wall carbon nanotubes. Successful applications of structural models in the modeling of nonlinear behavior of complex bulk phases are more numerous [for an overview, see, e.g., Öttinger (2005)]. We expect that this type of model will also prove to be valuable in the analysis of surface rheological data of complex interfaces, especially when the rheological techniques are combined with spectroscopic and scattering techniques that provide information on the structural changes occurring in the interface during deformation (van der Linden, Sagis, and Venema, 2003).

VIII. CONCLUSIONS

In this review we discussed recent advances in experimental and theoretical surface rheology, in an attempt to bridge the gap between these two fields. Experimental surface rheology is currently an active research field, and with the advent of nanotechnology the interest in characterization of surface rheological properties of complex phase interfaces is likely to increase even further. Although many interesting contributions to the field of experimental surface rheology have been made in recent years, the incorporation of novel developments in theoretical modeling of interfacial behavior, based on nonequilibrium thermodynamics, is still in an early stage. Data of surface rheological experiments are often analyzed with straightforward generalizations of constitutive models developed to describe behavior of incompressible bulk phases. We have seen here that such generalizations may lead to incorrect interpretation of data, particularly when applied to data from dilatational experiments. Data are also often analyzed with incomplete versions of the surface momentum balance, and contributions to this balance from inertial or viscous forces exerted on the interface by the bulk phases are often neglected without proper consideration of their magnitude.

The coupling of the rheological response with mass transfer between the interface and the adjoining bulk phases is in most cases based on simple Fickian diffusion models (Lucassen and van den Tempel, 1972a, 1972b). Complex surface active materials such as polymers, polymer-polysaccharide complexes, or colloidal particles can show significant deviations from Fickian behavior and consequently need more sophisticated models to describe their transfer to and from the interface.

Recent developments in the extension of NET formalisms (CIT, EIT, ERT, and GENERIC) to multiphase systems can be used to construct thermodynamically admissible constitutive models for the surface stress tensor, the surface mass flux vectors, the surface energy fluxes, and the fluxes of momentum, mass, and energy from the bulk phases to the interface, able to describe the response of interfaces in both the linear response regime and the highly nonlinear regime, far beyond equilibrium. The latter regime is particularly important during manufacture and processing of multiphase systems.

The nonlinear response regime is currently rarely studied, most likely as a result of the lack of appropriate models to describe this response. We have shown here that NET formalisms such as the EIT formalism can be used to construct a wide range of admissible nonlinear models, such as the Giesekus model discussed in Sec. V.G. Models of this type express the surface stress tensor purely in terms of the (rate of) deformation tensor and its invariants. In the rheology of bulk fluids these types of models have lost some popularity, in favor of structural models. Structural models describe the response of a material by including additional scalar, vectorial, or tensorial variables in the set of independent system variables, which leads to an expression for the stress tensor that depends directly on the microstructure through a dependence on these variables. The expression for the stress tensor is supplemented with one or more kinetic equations describing the time evolution of the structural variables as a result of the applied deformation. These types of models have proven to be successful in modeling nonlinear rheological responses, such as shear thinning, shear thickening, thixotropy, or rheopexy in a wide range of complex fluids, such as polymer solutions, polymer melts, solutions of wormlike micelles, biological fluids such as blood, immiscible blends, highly concentrated dispersions of colloidal particles, or liquid crystalline phases.

We have shown here that by using recent extensions of the GENERIC formalism (Öttinger, Bedeaux, and Venerus, 2009; Sagis, 2010b, 2010d), structural models can also be obtained for the surface rheology of interfaces, linking the nonlinear response of that interface directly to changes in its microstructure, resulting from an applied deformation. We envision that such models can make an important contribution to the extension of surface rheology into the nonlinear regime. They will be particularly useful for modeling interfaces with a complex microstructure, such as those stabilized by polymers, proteins, or colloidal particles. These surface active components can form interfaces with a wide range of microstructures, such as 2D gels, 2D (liquid) crystalline phases, 2D emulsions, or 2D composite structures. This type of modeling would also be useful in the description of (shear induced) phase separation or phase changes in the interface. These processes appear to play an important role in shape transitions of cells, such as those observed in sickle cell disease (Deuticke, 1968; Sheetz and Singer, 1974; Liebler, 1986), the creation of specific morphologies and functionalities in the shells of nanoparticles (Jackson, Myerson, and Stellacci, 2004; Li *et al.*, 2006), or the wetting properties of mixed monolayers at the air and water interface (Duprés *et al.*, 1999).

Progress in all branches of the field of surface rheology could be greatly accelerated if the experimental and theoretical branches of this field were integrated more closely. By combining the determination of surface rheological parameters with experimental structure evaluation techniques on the molecular scale (neutron or x-ray reflectometry, ellipsometry, and surface linear dichroism) and colloidal scale (Brewster angle microscopy, confocal scanning laser microscopy, and polarized light microscopy), with theoretical modeling (statistical physics and NET), and with numerical simulations on the molecular, microscale, and macroscale, a link can be established between properties of multiphase soft condensed matter systems on the molecular scale and the macroscopic dynamics of the system. This combination of disciplines, which is a multiscale multidisciplinary approach, is illustrated in Fig. 3.

This multiscale multidisciplinary approach also requires an effort in the field of numerical methods, an issue we have so far not addressed. On the molecular scale, methods such as nonequilibrium molecular dynamics could be used to explore the effect of molecular structure of surface active components on the microstructure of the interface. Such simulations could provide valuable input on the link between the interfacial microstructure and surface rheological properties.

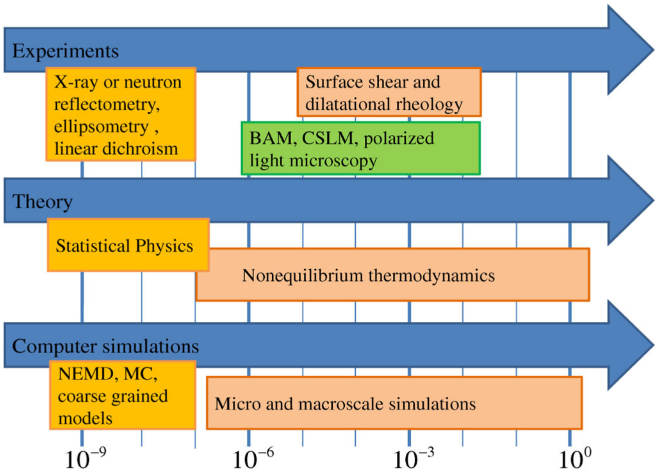

FIG. 3 (color online). A multiscale multidisciplinary approach to model dynamics of multiphase soft condensed matter systems, combining surface rheology with experimental structural evaluation on molecular and microscales, theoretical modeling, and numerical simulations.

On the macroscopic scale, currently available numerical methods have problems resolving interfaces in multiphase flows, and since most of the nonlinear models we have discussed here do not have analytical solutions, numerical schemes need to be developed that can handle the interfacial balance equations accurately.

A combined approach of experimental evaluation, theoretical modeling, and numerical simulation would not only benefit surface rheology, but also disciplines such as nanotechnology, biology, biophysics, coating technology, and all other disciplines dealing with multiphase systems in which interfacial rheological properties have an important contribution to the overall dynamics of that system.

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