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Editorial

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Experiments, theory, and simulation

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A complex interface is defined as an interface in which the adsorbed species form mesophases, such as 2d gels, 2d glass phases, 2d dispersions, 2d (liquid) crystalline phases, or 2d composite structures. Such interfacial mesophases can be formed by, for example, proteins, protein aggregates, protein-polysaccharide complexes, amphiphilic polymers, mixtures of immiscible lipids, or amphiphilic colloidal particles [1]. Complex interfaces are found in emulsions for food and personal care applications, vesicles and microcapsules for controlled delivery purposes, biological systems such as red blood cells or lung alveoli, or protective biodegradable coatings. In recent years numerous articles have appeared focusing on the determination of dynamic properties of complex fluid-fluid interfaces, and on exploring the effects of those properties on the macroscopic behaviour of multiphase materials [1].

In contrast to complex interfaces, simple interfaces are those stabilised by low molecular weight surfactants, which do not order in mesophases. Their response to shear deformations tends to be linear even at relatively high deformation rates, and is predominantly viscous. Simple interfaces often have very low surface shear viscosities ($\ll 10^{-6}$ Ns/m). For multiphase materials with simple interfaces surface tension tends to be the only surface property with a discernable effect on the macroscopic dynamic behaviour of the material.

For materials with complex fluid-fluid interfaces, additional surface properties such as their surface shear and dilatational moduli, or bending rigidities, may affect their dynamic behaviour, and the effect of these properties may even dominate the effects of surface tension. For example, surface shear and dilatational moduli are an important factor in the stability of foam [2] and emulsions [1,3–6], they affect the

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amplitude of surface waves in free surface flows [7–9] (important in coating flows or film extrusion processes), they influence the breakup of liquid jets or droplets [10,11], and they affect the wetting behaviour of thin films on solid surfaces [12], or the dynamic behaviour of lung alveoli [13]. The dynamic behaviour of water-in-water emulsions, such as vesicles and phase-separated biopolymer solutions, is affected by the bending rigidity [1,14–20] and permeability [20,21] of their interfaces. In contrast to simple interfaces, the response of complex interfaces to a perturbation is often highly nonlinear. This nonlinear response is the result of changes in the structure of the interface. Examples of this behaviour are the shear thinning behaviour (a decrease in rheological properties for increasing (rate of) deformation) observed in interfaces stabilised by colloidal particles [22–28]. Similar strain thinning behaviour was also observed in interfaces stabilised by protein fibrils [29]. Some of these fibrils appear to have the ability to form liquid crystalline phases, after adsorption at the interface [29–33]. Above their isoelectric point they are negatively charged and can be cross-linked by divalent ions [34], so they also have the potential to form highly cross-linked isotropic elastic networks at interfaces. When interfaces, stabilised by either a liquid crystalline phase or an isotropic network of these fibrils, are deformed in a surface shear experiment, the fibrils tend to align with the direction of flow, reducing the surface shear properties.

The determination of surface properties of complex fluid-fluid interfaces (in particular the surface rheological ones), and the modelling of their effect on the dynamic behaviour of multiphase materials is the main focus of this issue. Javadi et al. [35] discuss recent advances in the characterisation of dilatational rheological properties of interfaces using bubble pressure, drop profile, and capillary pressure tensiometry. One of the issues raised by Javadi et al. [35] at the end of their contribution is the proper generalisation of the Young-Laplace equation typically used for the analysis of tensiometry experiments, to dynamic conditions. The contribution by Sagis [36] discusses how such generalisations can be derived within the framework of non-equilibrium thermodynamics.

In droplet or bubble based oscillatory tensiometry methods the surface dilatational modulus is usually expressed in terms of a dynamic surface tension, and the usefulness of this concept is discussed by Sagis [37], based on an analysis of the generalised surface momentum balance. This analysis shows that for complex interfaces the response to a deformation contains not only contributions from changes in surface tension, but may also include contributions from in-plane and out-of-plane deviatoric stresses, inertial stresses, and contributions from the bending rigidity of the interface. For establishing the dominant contributions in the response a testing protocol is suggested, which includes frequency, amplitude, and droplet radius variations.

In their contribution Rühs et al. [38] discuss how mass transfer can interfere with the determination of surface rheological properties, of interfaces stabilised by globular protein monomers, and protein fibrils. In a follow-up discussion Sagis et al. [39] discuss how deformations of elastic membranes can induce adsorption of globular proteins at the interface. Both papers are illustrations of the coupling of in-plane momentum transfer and mass transfer between the interface and the adjoining bulk phases, often observed in complex interfaces. Suggestions on how to deal with this coupling on an experimental as well as theoretical level are provided in both contributions.

The issue continues with a contribution by Fischer [40], with an overview of recent experiments on surface rheological characterisation of interfaces stabilised by mixtures of proteins and polysaccharides. In spite of their practical relevance (such mixtures are for example frequently encountered in food emulsions or foam) such interfaces have received relatively little attention in the literature.

In their contribution Verwijlen et al. [41] discuss a novel geometry that can be mounted on a rotational rheometer, and can be used to determine surface dilatational

properties. This geometry (a variation of the double-wall-ring geometry [11,42], originally developed for the determination of surface shear properties) subjects the interface to a mixed flow field, and can be used as an alternative to tensiometric methods. Advantages and limitations of this new geometry are discussed [41].

In their response to a deformation complex fluid-fluid interfaces share many commonalities with viscoelastic bulk phases. The surface shear and dilatational moduli are basically the 2d equivalents of the shear and bulk modulus of a three dimensional bulk phase. It is a well-known fact that in bulk phases shear deformations can generate normal stresses (the first and second normal stress difference). A recently developed constitutive model for the extra stress tensor of an interface stabilised by rod-like particles [43,44], predicts the existence of normal stresses also for interfaces subjected to shear deformations. These stresses are in-plane, perpendicular to the direction of flow. The existence of such normal stresses has so far not been confirmed by experiments, and the contribution by Sagis [45] suggests a possible experimental setup for measuring these stresses, combining a shear band device mounted in a Langmuir trough, with a nano-force transducer.

As we noted earlier in this paper, complex interfaces often have a highly nonlinear response to deformations, even at low deformation (rates). There are however very few constitutive equations available in the literature, capable of describing this nonlinear behavior properly [1]. In his contribution Sagis [46] discusses the derivation of such equations within the framework of nonequilibrium thermodynamics (NET). Several frameworks are reviewed (classical irreversible thermodynamics, extended irreversible thermodynamics, extended rational thermodynamics, and GENERIC) with respect to the type of constitutive models that can be constructed within these frameworks, and advantages and limitations of each of the frameworks are discussed. Emphasis is on the derivation of structural models, i.e. models in which the response of an interface to an applied deformation is linked directly to the time evolution of its microstructure (described by one or more structural variables, of a scalar, vectorial, or tensorial nature). Structural models have been used widely and successfully in modelling the nonlinear rheology of complex bulk phases, such as polymer melts and solutions, liquid crystalline phases, or biopolymer solutions [47–49]. For modelling interfacial behaviour only a few examples of such models currently exist [50–54].

The next two contributions in this issue discuss the use of mesoscopic nonequilibrium thermodynamics (MNET) to model transfer processes in complex multiphase materials. Santamaria et al. [55] discuss the use of MNET for modelling diffusion and adsorption processes in porous materials with narrow irregularly shaped pores. Lervik and Kjelstrup [56] apply MNET to modelling active transport of calcium ions through cell walls.

The contribution by Glavatskiy and Bedeaux [57] discusses the validity of the local equilibrium assumption for interfaces in multiphase materials, by comparing a macroscopic description of such materials that incorporates surface excess densities, with a local nonequilibrium square gradient model. They show that these two descriptions are consistent, which justifies treating the interface as a separate thermodynamic system in local equilibrium with its surroundings. This assumption forms the basis of many NET descriptions for multiphase materials.

The final three contributions to this issue discuss numerical methods to simulate the dynamics of multiphase materials with complex interfaces. Krüger et al. [58] discuss hybrid simulation methods that combine a lattice Boltzmann solver for the flow in the bulk phases with, for example, an immersed boundary method (applied to the simulation of vesicles and capsules), or a molecular dynamics algorithm (applied to the simulation of interfaces stabilised by nanoparticles). Park et al. [59] discuss simulations of the behaviour of droplets stabilised by insoluble surfactants in microfluidics devices, using a diffuse-interface method, in which the Navier-Stokes/Cahn-Hilliard

equations and a surfactant conservation equation are solved by a finite element method, along with a grid deformation method. The issue closes with a contribution by Gross and Reusken [60] who discuss simulations of multiphase problems based on sharp-interface methods, and illustrate these methods for rising droplets with a clean interface model, and spherical droplets in a Poisseuille flow with a Boussinesq-Scriven interface model.

To summarise, the collection of papers presented in this issue cover recent advances in the areas of experimental characterisation, theoretical modelling, and simulation of the dynamic behaviour of complex fluid-fluid interfaces. Some pertinent issues of this field have been addressed (such as how to deal with the highly nonlinear response of interfaces to an applied deformation, or the coupling of in-plane momentum transfer with mass transfer between the bulk phase and interface), and solutions for these were suggested. We believe the field of surface dynamics will greatly benefit from a closer integration of experiments, theory, and simulation work.

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