DYNAMICS OF COMPLEX FLUID-FLUID INTERFACES

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EXTENDED ABSTRACT

Surface rheological properties like surface shear viscosities, or surface dilatational moduli often play an important role in the stability and dynamic behavior of emulsions, foam, biological fluids, liquid jets, coatings flows, or immiscible polymer blends [1]. This is particularly true when the interfaces in these systems have a complex microstructure, for example, when the surface active components stabilizing the interface form a 2d gel phase, a 2d glass phase, or 2d (liquid) crystalline phase. Such 2d mesophases are typically formed when interfaces are stabilized by colloidal particles, proteins, protein aggregates, protein-polymer complexes, or amphiphilic polymers [1]. Applied deformations induce changes in the microstructure of the interface, and the resulting changes in surface rheological properties (such as surface shear thinning, shear thickening, or thixotropic behavior) affect the behavior of the multiphase system on a macroscopic scale. Most currently available constitutive models for the surface extra stress tensor either do not account for the strain (rate) dependence of surface rheological properties, or are appropriate only for infinitesimally small rates, where departures from linear behavior are very small [1]. In this paper we will discuss recent advances in the development of nonlinear constitutive equations for the stress-deformation behavior of fluid-fluid interfaces in the framework of nonequilibrium thermodynamics. We will focus on two frameworks: the classical irreversible thermodynamics (CIT) framework, and the general-equation-for-the-nonequilibrium-reversible-irreversible-coupling (GENERIC) framework. We will illustrate the construction of surface rheological constitutive equations within these two frameworks for a specific example: interfaces stabilized by anisotropic colloidal particles, in the dilute particle concentration regime. In both frameworks we construct models describing the effect of microstructural changes on the nonlinear response of an interface to a deformation through a dependence of the surface stress tensor on a set of scalar and a tensorial structural variables. We present the time evolution equations for these structural variables, and evaluate the ability of these types of models to describe the shear thinning behavior typically observed experimentally for such interfaces. We compare the models in both simple and oscillatory shear. We find that both frameworks allow us to construct nonlinear expressions for the surface extra stress tensor capable of describing shear thinning behavior, but the CIT model gives realistic predictions only for small departures from equilibrium, whereas the GENERIC framework allows us to create models valid also far from equilibrium. Besides giving more accurate predictions for the shear thinning behavior the GENERIC model also predicts the existence of in-plane normal stresses (normal to the direction of flow), and effect of which its existence has been hypothesized, but that has so far not been observed experimentally. These results show that microstructural models developed using nonequilibrium thermodynamic frameworks provide a valuable tool for the analysis of the highly nonlinear dynamics of multiphase systems with complex liquid-liquid interfaces.

REFERENCES

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