Novel Analysis Methods for the Nonlinear Dilatational Rheology of Complex Fluid-Fluid Interfaces

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When fluid-fluid interfaces are stabilized by proteins, (anisotropic) colloidal particles, or polymers, the microstructure of the interface is often highly complex. These surface active components may form 2D gels, 2D glass phases, 2D (liquid) crystalline phases, or 2D dispersions. The response of complex interfaces to dilatational deformations is often nonlinear even at small deformations, as a result of structural rearrangements induced by the applied deformation. The data analysis commonly used by profile analyzing tensiometers (PAT) for the determination of surface dilatational properties cannot adequately describe highly nonlinear responses of complex interfaces [1]. Here we discuss how Lissajous curves and a generalized form of the Laplace equation can be used to obtain more meaningful measures for the dilatational properties of complex interfaces. As an example we present dilatational data, obtained with a PAT, for fluid-fluid interfaces stabilized by oligosaccharide-fatty acid esters, protein fibrils, and protein-polysaccharide complexes. At high deformation amplitudes the Lissajous curves of surface pressure versus deformation of these interfaces show remarkable asymmetries between the compression and extension part of the cycle. For example, air-water interfaces stabilized by oligosaccharide-fatty acid mono-esters display strain-thinning behavior in extension, and strain-hardening in compression. A possible explanation for this behavior is that during compression the interface is compressed to a 2D soft glassy state. Oil-water interfaces stabilized by semi-flexible protein fibrils display a highly elastic response upon compression, and a more viscous response upon extension. These interfaces may be undergoing an isotropic-to-nematic transition during compression. We analyze the Lissajous curves for these interfaces with a scheme recently introduced by Ewoldt et al. [2]. With this scheme we extract four dilatational moduli from the Lissajous curve: the moduli at minimum and maximum expansion, E_{dM}^{ex} and E_{dL}^{ex}, and the moduli at minimum and maximum compression, E_{dM}^{com} and E_{dL}^{com}. We also obtain the nonlinearity parameters $S^{ex} = (E_{dL}^{ex} - E_{dM}^{ex})/E_{dL}^{ex}$ and $S^{com} = (E_{dL}^{com} - E_{dM}^{com})/E_{dL}^{com}$. When these parameters are determined as a function of deformation amplitude, frequency, and droplet size, a quantification of the response of complex interfaces to dilatational deformations can be obtained, that gives insight in the microstructure of the interface. Using a generalized form of the laplace equation [1], we show that the effective transient surface tension of a deformed complex interface may contain contributions from deviatoric surface stresses or bending stresses.
Our results show that although a careful and extensive analysis of data is needed (based on Lissajous curves and a generalized form of the Laplace equation) it is feasible to explore the often exotic dilatational behavior of complex interfaces with PAT measurements.

Literature:

1. Sagis LMC, 2011. Dynamic properties of interfaces in soft matter: experiments and theory. Rev. Mod. Phys. **83:** 1367.
2. Ewoldt RH, Hosoi AE, McKinley GH, 2008. New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear. J. Rheol. **52:** 1427.