Impact of Interfacial Rheology on Droplet Dynamics

Droplet dispersions with adsorbed exotic surface active species (proteins, fatty alcohol, fatty acids, solid particulates, lipids, or polymers) find an immense number of applications in the field of engineering and bioscience. Interfacial rheology plays an essential role in the dynamics of many of these systems, yet little is understood about how these effects alter droplet dynamics. Most surfactants studied historically have been simple enough that the droplet dynamics can be described by Marangoni effects (surfactant concentration gradients), surface dilution, and adsorption/desorption kinetics without including the intrinsic surface rheology. One of the challenges in examining droplet systems with complex interfaces is that the intrinsic rheological effects are strongly coupled with surfactant transport effects (surface convection, diffusion, dilution and adsorption/desorption). The surface rheology can impact the ability of surfactant to transport along the surface, while surfactant transport can alter the surface rheology by changing the surface concentration. In this work, we develop axisymmetric boundary-integral simulations that allow us to quantitatively explore the combined effect of intrinsic surface rheology and surfactant transport on droplet dynamics in the Stokes flow limit. We assume that the droplet interface is predominantly viscous and that the Boussinesq Scriven constitutive relationship describes the properties of the viscous membrane. The key questions that we address in this work are:

- **How do viscous membranes impact droplet deformation, breakup and relaxation?**

  When a droplet is placed under external flow, it can either attain a stable shape under flow or stretch indefinitely above a critical flow rate and break apart. In this topic, we first discuss the breakup conditions for a droplet suspended in an unbounded immiscible fluid under a general linear flow field using perturbation theories for surface viscosity in the limit of small droplet deformation. We neglect the inhomogeneity in surfactant concentration and surface tension for this part. We find that the surface shear/dilational viscosity increases/decreases the critical capillary number for droplet breakup compared to a clean droplet at the same capillary number and droplet viscosity ratio value. In the second part of this topic, we solve the problem using boundary integral simulations for the case of axisymmetric extensional flow. Numerically solving this problem allows us to examine the effect of Marangoni stresses, pressure thickening/thinning surface viscosities, and stronger flows. We compare the droplet breakup results from our simulations to results from second-order perturbation theories. We present the physical mechanism behind our observations using traction arguments from interfacial viscosities. We conclude this topic by examining the combined role of surface viscosity and surfactant transport on the relaxation of an initially extended droplet in a quiescent external fluid.

- **How do viscous membranes alter droplet sedimentation?**

  When an initially deformed droplet sediment under gravity, it can either revert to a spherical shape or undergo instability where the droplet develops a long tail or cavity at its rear end. Here, we use numerical simulations to discuss how interfacial viscosity alters the breakup criterion and the formation of threads/cavities under gravity. We examine the combined influence of intrinsic surface viscosity and surfactant transport on droplet stability by assuming a linear dependence of surface tension on surfactant concentration and an exponential dependence of interfacial viscosities on surface pressure. We find that surface shear viscosity inhibits the tail/cavity growth at the droplet's rear end and increases the critical capillary number compared to a clean droplet. In contrast, surface dilational viscosity promotes tail/cavity growth and lowers the critical capillary number compared to a clean droplet.

- **How do viscous membranes affect droplet coalescence?**

  When two droplets approach under external flow, a thin film is formed between the two droplets. Here, we develop numerical simulations to model the full coalescence process from the collision of two droplets under uniaxial compressional flow to the point where the film approaches rupture. We investigate the role of interfacial viscosity on the film profiles and drainage time. We observe that both surface shear and dilational viscosity significantly delay the film drainage time relative to a clean droplet. Interestingly, we find that the film drainage behaviour of a droplet with surface viscosity is not altered by the relative ratio of shear to dilational viscosity but rather depends on the sum of shear and dilational Boussinesq numbers. This is in contrast to the effect of surface viscosity observed in the previous processes (droplet breakup and sedimentation), where surface shear viscosity increases the critical capillary number compared to a clean droplet, while surface dilatational viscosity has the opposite effect.