Molecular Simulations of Free Surface Flows:
The Initial Stages of Coalescence and Rupture

Abstract

Free surface flows are a class of problems in fluid mechanics in which the shape of the interface at the free boundary is unknown *a priori*, evolves in time and must be determined as part of the solution. Free surface flows can be found everywhere around us—from the motion of ocean waves, raindrop formation, waterfall mist, to something as mundane as a dripping faucet in our kitchens. More importantly, they are crucial to products and technological applications like inkjet printing, paints and coating processes, separation processes, spraying, determining the stability of foams and emulsions. Owing to the complex interfacial dynamics governed by forces of inertia, viscosity and surface tension, free surface flows are a fascinating, yet complex class of problems. These problems are made even more interesting when the phenomena involve finite-time singularities—particularly the phenomena of breakup and coalescence. While free surface flows have been historically studied using the equations of continuum mechanics, many of the phenomena such as drop or bubble coalescence are initiated at length and timescales much smaller than those described by the equations of continuum mechanics. With the growing interest in processes performed at such smaller scales, it is important to gain molecular level insights to free surface flows and reconcile them with the continuum description of these problems.

The goal of this thesis is to study two such problems. The first problem considered is of droplet coalescence. We reduce the required computational effort by only simulating those parts of the drops directly facing each other. Particle reservoirs, along with grand canonical MC steps (GCMC), are used to maintain the bulk densities of the drops at specified values. These GCMC steps also enable the drops to be both thermally and chemically equilibrated prior to coalescence, thereby eliminating any potential evaporative phenomena that may confound the analysis. We identify three distinct regimes of droplet coalescence, with three distinct scaling laws in time for bridge radius corresponding to each regime—an initial linear regime, identified as a molecular precursor before the dynamics transitions to the viscous and inertial regimes identified by previous continuum analyses. In doing so, we reconcile the discrepancies between the results of previous continuum and molecular studies. The second problem is that of retraction and rupture of thin liquid sheets. We use molecular dynamics simulations to study the rate of retraction and compare it with the well-known result from the Taylor-Culick theory. We also explore the role played by thermal fluctuations on the liquid surface caused by the motion of particles in driving the rupture of the sheets into filaments.