LOCALIZED SCALE COUPLING AND NEW EDUCATINAL PARADIGIMS IN MULTISCALE MATHEMATICS AND SCIENCE

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INTRODUCTION

One of the most challenging multi-scale simulation problems in the area of multi-phase materials is to develop effective computational techniques for the prediction of coalescence and related phenomena involving rupture of a thin liquid film due to the onset of instability driven by van der Waals or other micro-scale attractive forces. Accurate modeling of this process is critical to prediction of the outcome of milling processes for immiscible polymer blends, one of the most important routes to new advanced polymeric materials. In typical situations, the blend evolves into an “emulsion” of dispersed phase drops in a continuous matrix fluid.

Coalescence is then a critical factor in determining the size distribution of the dispersed phase, but is extremely difficult to predict from first principles. The thin film separating two drops may only achieve rupture at dimensions of approximately 10 nm while the drop sizes are 0(10 µm). It is essential to achieve very accurate solutions for the flow and for the interface shape at *both* the macroscale of the full drops, and within the thin film (where the destabilizing disjoining pressure due to van der Waals forces is proportional approximately to the inverse third power of the local film thickness, h^{-3}). Furthermore, the fluids of interest are polymeric (through Newtonian) and the classical continuum description begins to fail as the film thins – requiring incorporation of molecular effects, such as a *hybrid code* that incorporates a version of coarse grain molecular dynamics within the thin film coupled with a classical continuum description elsewhere in the flow domain. Finally, the presence of surface active additions, either surfactants (in the form of di-block copolymers) or surface-functionalized micro- or nano-scale particles, adds an additional level of complexity, requiring development of a distinct numerical method to predict the nonuniform concentration gradients of these additives that are responsible for Marangoni stresses at the interface. Again, the physical dimensions of these additives may become comparable to the thin film dimensions, requiring an additional layer of multi-scale modeling.

ACCOMPLISHMENTS

Our strategy in attacking this difficult class of multi-scale problems has been:

(1) to develop multi-scale numerical methods that achieve accurate solutions for the drop collision and coalescence problem, assuming that a classical continuum description remains relevant down to arbitrarily thin film dimensions. This is already a challenging numerical problem, and is somewhat unusual, given the fact that the boundary geometry is unknown and evolves with time.

(2) to develop more accurate descriptions of the physics as the thin film region approaches molecular dimensions, and the classical continuum description begins to break down

(3) to develop algorithms that incorporate these improved descriptions into the numerical framework for this class of problems.

In prior work, we have partially accomplished the first of these objectives. Specifically, we have developed an efficient automated mesh refinement technique that allows us to obtain accurate solutions via boundary-integral techniques for an axisymmetric collision of a pair of drops (with clean fluid interfaces) in a flow, including detailed resolution of the macro-scale flow on the scale of the overall drop radius and the microscale flow in the thin film regions. This method is based upon the classical continuum model of a pair of Newtonian fluids, with sharp interfaces (i.e. discontinuous change in material properties) that are completely characterized by interfacial tension, and with van der Waals forces approximated via an unretarded disjoining pressure approximation for a pair of flat, *unbounded* interfaces that are separated by the same distance as the local film thickness h. Although the numerical solutions based upon this model are *very accurate* (much more accurate than previous attempts to solve the same problem), they do not agree quantitatively with experimental data for coalescence in head-on collisions. Our belief is that this is due to a breakdown in the classical continuum description, as well as unaccounted effects of surface active materials. During the course of this project we made major progress in resolving these points.

1) **An improved theory for disjoining pressure:** We have completed and published work on an extended version of the disjoining pressure model for van der Waals forces. The classic theory, used by all previous investigators, is valid for a pair of parallel flat surfaces of infinite extent. In this simplest "unretarded" form, this model assumes that the disjoining pressure is:

$$\Pi = -\frac{A_H}{6\pi h^3}$$

where A_H is the Hamaker constant and *h* is the uniform film thickness (which is assumed to be the local film thickness when this formula is applied to non-parallel interfaces). We have extended this theory to incorporate corrections for the situation in which the interfaces are not parallel and also exhibit local curvature,

$$\Pi = -\frac{A_H}{24\pi h^3}\left(4 - 3h_x^2 + 3hh_{xx}\right)$$

This correction to the physical model is not difficult to incorporate into the numerical algorithm, but is very important for accurate predictions for this class of multiscale problems. A paper reporting this result was published.

"Disjoining Pressure for Non-Uniform Thin Films", Bing Dai, L. Gary Leal and Antonio Redondo, *Physical Review E* , **78**, 061602 (2008). (also reproduced in December 22, 2008 issue of Virtual Journal of Nanoscale Science & Technology)

2) **A computational algorithm for inclusion of surfactant effects:** A computational algorithm was developed using the Boundary Integral technique to simulate the effects of surface active additives in the axisymmetric ("head-on") drop collision, thin film drainage and rupture process. This involves a composite numerical scheme – with the BI-based scheme with mesh refinement for the viscous flow, and a finite-element formulation for the surfactant transport problem. The results, which include a new understanding of the mechanisms by which surfactants inhibit coalescence, were published in Physics of Fluids.

"The Mechanism of Surfactant Effects on Drop Coalescence", Bing Dai and L. Gary Leal, *Physics of Fluids,* **20**, pp.040804-1-13 (2008).

3) **Breakdown of the continuum hypothesis: Slip at Interfaces.** As the film thickness approaches molecular dimensions, continuum theory will break down in two ways: first, the no-slip conditions at the edges of the film will no longer apply; second, the Navier-Stokes equations will break down in the bulk fluid. Fundamental work has been done to understand the first of these effects, which will appear before the continuum approximation breaks down in the bulk fluid. In the present problem, the issue is the *finite width and very low viscosity of the interfacial region*, which can be a significant fraction of the width of the thin film, with a viscosity that is two orders of magnitude lower than the bulk fluids ("Apparent slip at a polymer-polymer interface", J.L. Goveas and G.F. Fredrickson, European Physical Journal B 2 pp 79-92 (1998)).

   In principle, there are several ways to incorporate this effect into simulations. In a coarse-grain MD formulation, it would appear "automatically" but this involves *hybrid calculations* as discussed below that have not yet been developed for this class of problems that involve finite domain size and relatively long-time phenomena. One might also think of the so-called *diffuse interface methods* based upon the Cahn-Hilliard theory, but systematic ways of including van der Waals forces, which are the source of film rupture, have not been developed for this type of formulation. Finally, an approximation of the effect can be incorporated into the classical sharp interface model as *"apparent" slip* (i.e. a discontinuity of the tangential velocity across the interfaces with a magnitude that depends on the shear-stress in the external fluid, and a slip coefficient that can be predicted from first principles via the molecular theory of Goveas and Fredrickson).

   From a physical point of view, it is known that this departure from the usual continuum assumptions ("no-slip") can have profound effects (cf. T.S. Lo et.al. "Interfacial slip in sheared polymer blends", Phys Rev E, Art. No. 040801, (2005); C.C. Park et.al., "Study of molecular weight effects on coalescence: Interface slip layer", J. Rheology, **47,** 911-942, (2003)).

   From a numerical perspective, the inclusion of slip in the continuum formulation adds additional scalar unknowns – either the shear stress at the interface, or the tangential velocity jump at the interface, *but necessitates a completely new strategy to solve the resulting Boundary Integral problem*. This is because the mathematical nature of the problem is fundamentally changed from an integral equation of the second kind to a coupled set of integral equations of "mixed" type. During the course of this project, we developed an effective multiscale algorithm for this new formulation. In fact, we anticipate that there are many applications beyond the thin-film/coalescence problem where such an algorithm will be extremely valuable. For example, there are an increasing number of *microscale flow problems* (involving MEMS applications, for example) that are basically viscous flows with significant slip at the boundaries – where the same basic reformulation of the classical BI numerical algorithm will find direct application. This algorithm was then applied to problems involving the dynamics of drops in flow including the coalescence problem.

   "Properties and Solution Strategies for Mixed Type Boundary Integral Equations in Creeping Flow Problems", A. Ramachandran, K. Tsiglifis and L. G. Leal, *Computers and Fluids*, **64,** 141-156 (2012)

"The Effect of Interfacial Slip on the Dynamics of a Drop in Flow: Part 1. Stretching, Relaxation and Breakup", A.Ramachandran, K. Tsiglifis, A. Roy and L. G. Leal, *Journal of Rheology* **56,** 45-97(2012)

"The Effect of Interfacial Slip on the Dynamics of a Drop in Flow: Part 2. Coalescence", A.Ramachandran, K. Tsiglifis, A. Roy and L. G. Leal, in preparation

4) Hybrid Techniques for Multi-scale Problems Involving a Thin Film of Molecular Dimensions Coupled to a Macroscopic Flow Domain:

The classical boundary integral formulations for interfacial dynamics described above incorporate the mesoscopic disjoining pressure as an approximation to account for the non-hydrodynamic forces, e.g., van der Waals forces, for studies of deformable drop coalescence in a viscous suspending fluid. The continuum calculations can be carried down to arbitrarily small scales with the investment of enough computer time. However, it seems unlikely that this approach can ever exactly represent the whole coalescence process since it appears that the latter involves thin films that reach "molecular" dimensions prior to rupture. One way to assess the accuracy of the continuum approach as the film width is reduced, is to compare it with theoretical results that incorporate the first level approximation of molecular effects within the thin film region.

During this project, we collaborated with researchers at LANL, primarily Dr. Antonio Redondo, to develop methods to couple the continuum hydrodynamics with coarse-grain molecular simulation to study the coalescence process. Other researchers have previously developed so called "hybrid" methods for problems involving local regions of molecular scale that couple full-blown molecular dynamics in the localized region and continuum mechanics elsewhere. However, the size of the fluid domain and the time scale for which we require results is much greater than in these previous studies and we need to use a more coarse-grain version of molecular dynamics. We proposed to use the coarse-grained rigid blob molecular simulations for soft matter recently developed by Redondo and coworkers for the near contact region between adjacent drops. The biggest advantage of rigid blob technique is that the length and time scales can be readily adjusted by the definitions of the blob, e.g., it could be a segment in a polymer chain or the whole chain. The coarse-grained rigid blob technique is capable of being extended to a mesoscopic boundary integral formulations for interfacial dynamics coupled with the mesoscopic disjoining pressure to account for the non-hydrodynamic forces. However, this approach still cannot exactly represent the whole coalescence process which will eventually touch down to molecular scales, e.g., no necessary conditions to determine the coalescence. We thus proposed to couple the continuum hydrodynamics with coarse-grain molecular simulation to study the coalescence process. The coarse-grained rigid blob molecular simulations for soft matter developed by Redondo was proposed to apply in the near contact region of adjacent drops. The biggest advantage of rigid blob technique is that the length and time scales can be readily adjusted by the definitions of the blob, e.g., it could be a segment in a polymer chain or the whole chain. The coarse-grained rigid blob technique is capable of being extended to a mesoscopic scale. Outside the thin gap, the system was described by the continuum fluid mechanics. The axi-symmetric boundary element formulation described previously will be applied to study the external hydrodynamics. A 'hand-shake' technique was employed to exchange the information between the BEM simulation and rigid-blob coarse-grained molecular simulation till both procedures reach convergence. The quantity of fluid squeezed out of the thin gap obtained by BEM simulation was passed to the coarse-grained simulation to update the number of blobs in the thin gap for the mass conservation. The stress in the thin gap calculated by coarse-grained technique returns to the BEM simulation for the total stress balance of drops. Lennard-Jones inter-blob potential was applied and the potential constants were calibrated by the measured viscosities of different fluids. This approach was not completed at the point where the grant expired and remains unpublished.

Addendum: Subsequent to this grant, but enabled by it, Prof. Leal, in collaboration with Drs. Redondo and Graham, continued to work on the development of true hybrid methods involving a coupling between MD at the highest level of resolution and continuum mechanics (Navier-Stokes) at the lowest level. This work continues. To date, three papers have been published and additional papers will appear in the near future.

. "A Test of Systematic Coarse-Graining of Molecular Dynamics Simulations I. Thermodynamic Properties", Chia-Chun Fu, Pandurang M. Kulkarni, M. Scott Shell and L. Gary Leal, *J. Chemical Physics*, **137,** 164106 (2012).

. "Multiscale Modeling with Smoothed Dissipative Particle Dynamics" , P.M. Kulkarni, C.-C. Fu, M.S. Shell and L.G. Leal . *J. Chemical Physics* **138,** 234105 (2013).

" A Test of Systematic Coarse-Graining of Molecular Dynamics Simulations: Transport Properties", C.-C. Fu, P.M. Kulkarni, M.S. Shell and L.G. Leal, *Journal of Chemical Physics* (2013). (in Press)