Simulations of Interfacial Dynamics of Complex Fluids Using Diffuse Interface Method with Adaptive Meshing

by

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Abstract

A diffuse-interface finite-element method has been applied to simulate the flow of two-component rheologically complex fluids. It treats the interfaces as having a finite thickness with a phase-field parameter varying continuously from one phase to the other. Adaptive meshing is applied to produce fine grid near the interface and coarse mesh in the bulk. It leads to accurate resolution of the interface at modest computational costs. An advantage of this method is that topological changes such as interfacial rupture and coalescence happen naturally under a short-range force resembling the van der Waals force. There is no need for manual intervention as in sharp-interface model to effect such event. Moreover, this energy-based formulation easily incorporates complex rheology as long as the free energy of the microstructures is known. The complex fluids considered in this thesis include viscoelastic fluids and nematic liquid crystals. Viscoelasticity is represented by the Oldroyd-B model, derived for a dilute polymer solution as linear elastic dumbbells suspended in a Newtonian solvent. The Leslie-Ericksen model is used for nematic liquid crystallen which features distortional elasticity and viscous anisotropy. The interfacial dynamics of such complex fluids are of both scientific and practical significance.

The thesis describes seven computational studies of physically interesting problems. The numerical simulations of monodisperse drop formation in microfluidic devices have reproduced scenarios of jet breakup and drop formation observed in experiments. Parametric studies have shown dripping and jetting regimes for increasing flow rates, and elucidated the effects of flow and rheological parameters on the drop formation process and the final drop size. A simple liquid drop model is used to study the neutrophil, the most common type of white blood cell, transit in pulmonary capillaries. The cell size, viscosity and rheological properties are found to determine the transit time. A compound drop model is also employed to account for the cell nucleus. The other four cases concern drop and bubble dynamics in nematic liquid crystals, as determined by the coupling among interfacial anchoring, bulk elasticity and anisotropic viscosity. In particular, the simulations reproduce unusual bubble shapes seen in experiments, and predict self-assembly of microdroplets in nematic media.
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Statement of Co-Authorship

This thesis contains seven co-authored and self-contained manuscripts that are either published in or submitted to peer-reviewed journals. Following is a list of contributions to the following areas:

- **Identification and design of research program**
  The identification and the design of the research program for this thesis has been decided by the author in collaboration with and supervised by Professor James J. Feng.

- **Performing the research**
  The research for this thesis has been performed entirely by the author. Discussion with group members and the supervisor took place at regular group meetings.

- **Data analyses**
  The data analyses for the current research has been performed by the author under the direct supervision of the thesis advisor, Professor James J. Feng.

- **Manuscript preparation**
  This thesis has been prepared and organized by the author under the direct supervision of Professor James J. Feng. The final version has incorporated comments and suggestions by the supervisory committee and the examining committee.
Chapter 1

Introduction

1.1 Interfacial dynamics

The interface separating two immiscible fluids such as water and oil plays a central role in the fluid dynamics of the mixture. This may be demonstrated by stirring an oil drop in a cup of water. With gentle stirring, the oil drop moves about on the water surface. Stronger stirring causes the oil drop to break up into many smaller droplets. After the stirring stops, the droplets gradually coalesce and in time reform a single oil drop. This simple process reveals three key interfacial phenomena: interfacial movement, breakup and coalescence. Interfacial dynamics refers to the motion and topological change of the interface subject to flows in the bulk phases or external forces due to electric and magnetic fields.

In equilibrium, the oil drop assumes a round shape because of surface tension or interfacial tension, which is a result of the cohesive forces between similar molecules in each component. This is illustrated by Fig. 1.1. The interior molecules have all the same kind of molecules around them. However, those on the surface also have the dissimilar molecules as neighbors, and this reduces the attractive force on them and puts those surface molecules in an unfavorable energy state. In other words, it takes work to move a molecule from the interior onto the interface because of the cohesive force. This interfacial energy can also be seen as a tension against the creation of interfacial area, and is known as the interfacial tension. If the interface is between a liquid and air, the tension is also called a surface tension. This interfacial force adds another dimension to the fluid dynamics and plays a significant role in many interfacial phenomena.

Many industrial process involve the control and manipulation of the interface. Familiar examples include coating, polymer coextrusion and foaming. Interfacial flows in microfluidic devices have recently gained much attention (Stone et al., 2004), with intriguing applications such as the generation of monodisperse single and double emulsions (Anna et al., 2003; Nisisako et al., 2003; Utada et al., 2005). The significance of the interfacial dynamics in microfluidics is easy to understand from a scaling standpoint. The small length-scale gives rise to large ratios of surface area to the bulk volume, and therefore highlights the role of interfacial effects. The next chapter contains further details on simple and compound drop formation in microfluidic devices.

To predict the behavior of the interface, one needs to solve the fluid dynamics of both fluids in the bulk, as well as the evolution of the interface. The interfacial tension gives rise to a normal force proportional to the curvature of the interface, which exerts its effects on the flow field. This makes interfacial flows a difficult task since the interfacial forces are nonlinear, even in the case of inertialess creeping flows. Besides the nonlinearity of the interfacial dynamics, the two fluids typically have mismatched densities, viscosities and other physical properties. These also contribute to the difficulty of analyzing interfacial
flows. Therefore, only a few theoretical solutions exist for interfacial flows; they are the
linear theory of the breakup of infinite cylindrical fluid threads (Rayleigh, 1879; Tomotika,
1935; Mikami & Mason, 1975), and a self-similarity theory (Eggers, 1997) that yields
scaling arguments. In recent years, computer simulation has emerged as an important
tool for studying interfacial dynamics. On the one hand, numerical simulations can reveal
fundamental physics of the process that is hard to obtain experimentally. On the other
hand, they may also provide guidelines for design and fabrication in both experiments
and industrial applications.

1.2 Complex fluids

Complex fluids are microstructured fluids. The evolution of the internal microstructures
affects the macrodynamics of the fluids and vice versa. Examples include polymeric
solutions and melts, liquid crystals, gels, suspensions, emulsions and micellar solutions
(Larson, 1999). These materials often have unique industrial applications as the mi-
crostructure can be manipulated by means of flow or other methods to achieve desired
mechanical, optical or other physical properties. One such application is polymer blends
(Utracki, 1990) made of incompatible components. Under certain flow conditions, the
dispersed phase is stretched into filaments. After solidification, these long polymeric
filaments turn into strong fibers and give the materials great strength. Another exam-
ple is polymer-dispersed liquid crystals (PDLC), in which liquid crystalline droplets are
dispersed in a polymer matrix before they are solidified. It shows great potential in
electro-optical applications (West, 1990); for example, one can control the opacity of a
PDLC glass by manipulating the electric field across it (Mucha, 2003).

Complex fluids often exhibit unique interfacial behavior. For example, a thread of
Newtonian liquid breaks up into drops via the well-known Rayleigh instability. A thread
of non-Newtonian polymer solution, on the other hand, develops the so-called bead-on-
a-string morphology (Oliveira et al., 2006), with a chain of droplets connected by a thin liquid string. The string persists for long times without breaking because the polymer lends the liquid a great resistance against breakup. In fact, this strong polymer stress plays key roles in many other situations, such as in partial coalescence (Yue et al., 2006a) and drop formation in microfluidics (Zhou et al., 2006). Liquid crystals are another class of complex fluids that show unusual interfacial dynamics. An anisotropic interfacial tension gives rise to non-spherical shapes for bubbles and drops dispersed in the liquid crystal (Zhou et al., 2007). These phenomena have motivated the research described in the following chapters.

1.3 Methodology

Recently, we have developed a finite-element based algorithm with adaptive meshing that is capable of simulating the flow of two-component systems of rheologically complex fluids (Yue et al., 2006b). The interfaces are treated as having a finite thickness with a phase-field parameter varying continuously from one phase to the other. Fluid properties such as density and viscosity, and flow quantities such as pressure may change steeply yet continuously across the interfaces. Therefore no discontinuity appears in the system. The phase-field parameter, which defines the position of the interfaces, is described by a mixing energy consisting of two components, one “hydro”-philic and the other “hydro”-phobic. An advantage of this method is that topological changes such as interfacial rupture and coalescence happen naturally under a short-range force resembling the van der Waals force. There is no need for manual intervention as in sharp-interface models to effect such events. Moreover, this energy-based formulation easily incorporates complex rheology as long as the free energy of the microstructures is known.

Our theoretical model has two major features: constitutive equations for complex rheology and the diffuse interface method for the interface. The numerical algorithm has two main components as well: a finite element formulation and an adaptive mesh generator. In the following subsections, we briefly describe these four items.

1.3.1 Constitutive equations

Newtonian fluids have a stress tensor that is proportional to the instantaneous strain rate tensor. Microstructured fluids have a much more complex behavior since the microstructural conformation evolves in the flow and the stress tensor generally depends on the strain history. Generally, the stress and strain-rate tensors are related by constitutive equations instead of an explicit functional form. This dissertation focuses on polymeric fluids and liquid crystals as two important classes of complex fluids. In the following, we briefly describe the Oldroyd-B model for polymer solutions and the Leslie-Ericksen model for nematic liquid crystals. More detailed derivations are available in the reference books cited.

The Oldroyd-B fluid model describes a dilute polymer solution as linear elastic dumbbells suspended in a Newtonian solvent. The elastic stress $\tau_d$ is given by the Maxwell
equation (Bird et al., 1987a)

\[ \tau_d + \lambda_H \tau_d^{(1)} = 2\mu_p D, \]  

(1.1)

where \( \lambda_H \) is the relaxation time that may range from microseconds to seconds, \( \mu_p \) is the polymer viscosity and \( D = [\nabla v + (\nabla v)^T]/2 \) is the strain-rate tensor. \( \mu_p/\lambda_H \) gives the elastic modulus for the dumbbells, and the subscript (1) denotes the upper convected derivative (Bird et al., 1987a):

\[ A^{(1)} = \frac{dA}{dt} - (\nabla v)^T \cdot A - A \cdot \nabla v, \]  

(1.2)

for a second-rank tensor \( A \), \( \nabla v \) being the velocity gradient tensor. The total stress \( \tau \) is the sum of the polymer elastic stress and the solvent viscous stress. In terms of \( \tau \), the Oldroyd-B constitutive equation reads:

\[ \tau + \lambda_H \tau^{(1)} = 2\mu (D + \lambda_2 D^{(1)}), \]  

(1.3)

where \( \lambda_H \) is the total viscosity, and \( \lambda_2 \) is the retardation time.

The Leslie-Ericksen theory treats the liquid crystal molecules as rigid rods whose average orientation may be spatially distorted in three basic ways: splay, bend and twist. If we take equal contributions from these three elastic modes, an elastic stress can be written out (de Gennes & Prost, 1993):

\[ \sigma^e = K \nabla n \cdot (\nabla n)^T \]  

(1.4)

where \( K \) is an elastic constant and \( n \) is the molecular orientation. In addition to the elastic stress, the liquid crystal also has an anisotropic viscous stress

\[ \sigma' = \alpha_1 D : nnnn + \alpha_2 Nn + \alpha_3 Nn + \alpha_4 D + \alpha_5 nn \cdot D + \alpha_6 D \cdot nn \]  

(1.5)

where \( \alpha_{1-6} \) are the Leslie viscous coefficients, and \( N = \frac{dn}{dt} - \Omega \cdot n \) is the rotation of liquid crystal molecules with respect to the background flow field with vorticity tensor \( \Omega \). In general, the molecules perpendicular to the flow direction cause greater viscous stress than do those parallel to it. The orientation field \( n \) evolves in the flow field according to a balance between elastic and viscous torques:

\[ K \nabla^2 n = \gamma_1 N + \gamma_2 D \cdot n. \]  

(1.6)

Where \( \gamma_1 = \alpha_3 - \alpha_2 \) and \( \gamma_2 = \alpha_3 + \alpha_2 \). Thus, the flow and stress are coupled through the orientation field \( n(x) \) and have to be solved together.

### 1.3.2 Diffuse interface method

A straightforward way of handling the moving interfaces is to have a mesh that has grid points on the interfaces, and deforms according to the flows on both sides of the boundary. This has been implemented in boundary integral and boundary element methods (Cristini
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et al., 1998; Toose et al., 1995; Khayat, 2000), finite-element methods (Hu et al., 2001; Ambravaneswaran et al., 2002; Hooper et al., 2001a,b; Kim & Han, 2001) and a finite-difference method (Ramaswamy & Leal, 1999b,a). Keeping track of the moving mesh entails a computational overhead. Furthermore, large displacement of internal domains causes mesh entanglement as happens, for example, when one drop overtakes another. Most importantly, the moving-mesh methods cannot handle topological changes such as breakup and coalescence; the sharp interface formulation breaks down in such cases. As an alternative, fixed-grid methods that regularize the interface have been quite successful in treating deforming interfaces. These include the volume-of-fluid (VOF) method (Li & Renardy, 2000), the front-tracking method (Unverdi & Tryggvason, 1992) and the level-set method (Chang et al., 1996). Instead of formulating the flow of two domains separated by an interface, these methods represent the interface by a scalar “order parameter” that obeys a convection equation. Then a single set of governing equations can be written over the entire domain, and solved on a fixed grid in a purely Eulerian framework.

The diffuse-interface model can be viewed as a physically motivated level-set method. Instead of choosing an artificial smoothing function for the interface, the diffuse-interface model describes the interface by a mixing energy. Thus, the structure of the interface is determined by molecular forces; the tendencies for mixing and separation are balanced through the nonlocal mixing energy. When the interfacial thickness approaches zero, the diffuse-interface model becomes identical to a sharp-interface level-set formulation. It also reduces properly to the classical sharp-interface model (Elder et al., 2001). Besides its handling of the interface, the method has another advantage in its easy incorporation of the complex rheology of microstructured fluids. As long as such microstructures are described by an energy, it can be added into the mixing energy to form the total free energy of the multi-phase system. Then the formal variational procedure applied on the total free energy will lead to the proper constitutive equation for the microstructured fluids. Thus, interfacial dynamics and complex rheology are handled in a unified theoretical framework.

The free energy description

The diffuse-interface method is based on an energy description. Introducing a phase-field variable \( \phi \) which takes on values of \( \pm 1 \) in the two bulk components, the interface is indicated by the level-set of \( \phi = 0 \). The interface stores a mixing energy,

\[
f_{\text{mix}}(\phi, \nabla \phi) = \frac{\lambda}{2} \left[ |\nabla \phi|^2 + \frac{(\phi^2 - 1)^2}{2\epsilon^2} \right],
\]

where \( \lambda \) is the mixing energy density and \( \epsilon \) is a capillary width indicative of the interfacial thickness. The mixing energy ensures that the interface neither spreads wide nor collapses into a singular surface. In the limit of \( \epsilon \to 0 \), \( \lambda/\epsilon \) gives the interfacial tension. By following the evolution of \( \phi \) by a convection-diffusion equation (see Eq. 1.14 below), the interfacial motion and deformation are tracked.

If one or both components are complex fluids, additional terms have to be included in the total free energy. Take for example the blend of a Newtonian fluid and a polymer so-
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olution described by the Oldroyd-B model. There is an elastic energy due to the dumbbell elasticity. If the dumbbells have an elastic constant $H$ and a configuration distribution $\Psi(Q)$ about the connector vector $Q$, the average energy is (Bird et al., 1987b)

$$f_d = \int_{R^3} \left( kT \ln \Psi + \frac{1}{2} H Q \cdot Q \right) \Psi dQ,$$

where $k$ is the Boltzmann constant, $T$ is the temperature, and the integration is over all possible configurations of $Q$. Now the total free energy density of the two-phase system is:

$$f = f_{mix} + \frac{1 + \phi}{2} n f_d,$$

where $n$ is the number density of the dumbbells. Note that $\phi = 1$ in the polymer solution and $\phi = -1$ in the Newtonian fluid. A similar free energy can be written out for a Newtonian-liquid crystal system. For brevity, however, we only write the equations based on Eq. 1.9 in the following. Details on the liquid crystalline mixture can be found in Yue et al. (2004) and chapter 5 and 6.

**Governing equations**

The general procedure for deriving the governing equations have been outlined in our recent work (Yue et al., 2004, 2006b). In the following, therefore, we will simply list the equations for our particular system of a blend of a Newtonian fluid and a polymer solution. The field variables are velocity $v$, pressure $p$, phase function $\phi$ and polymer stress $\tau_d$. We write the continuity and momentum equations in the usual form:

$$\nabla \cdot v = 0,$$

$$\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \nabla \cdot \sigma,$$

where $\sigma$ is the stress tensor consisting the viscous stress, interfacial stress $\sigma^i$ and the viscoelastic stress denoted as $\tau_d$ due to the dumbbell energy $f_d$. The interfacial stress tensor is derived from the mixing energy following a variational procedure(Yue et al., 2004):

$$\sigma^i = -\lambda (\nabla \phi \otimes \nabla \phi).$$

$\tau_d$ obeys the Maxwell equation:

$$\tau_d + \lambda_H \tau_d^{(1)} = \mu_p [\nabla v + (\nabla v)^T],$$

which has been given earlier as Eq. 1.1.

The phase-field variable $\phi$ obeys the Cahn-Hilliard equation:

$$\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \gamma \nabla^2 G,$$
where \( G = \lambda [-\nabla^2 \phi + \phi(\phi^2 - 1)/\epsilon^2] \) is often called the chemical potential, and \( \gamma \) is the interface mobility. The boundary conditions for the velocity and stress components depend on the geometric and physical setup of the problem, as is typical in the literature of non-Newtonian fluid mechanics. For the phase-field \( \phi \), the following conditions are used on the outer boundary of the domain:

\[
\frac{\partial \phi}{\partial n} = 0, \\
\frac{\partial^3 \phi}{\partial n^3} = 0.
\]

(1.15)

(1.16)

Note that in the diffuse-interface framework, the phase boundaries are seen as part of the interior and require no boundary conditions.

### 1.3.3 Finite element method

The finite element method is attractive since our applications involve complex geometries. Furthermore, the unstructured grid allows convenient adaptive meshing to refine the interfacial region. The discretization of the governing equations follows the standard Galerkin formalism (Hu et al., 2001). However, the Cahn-Hilliard equation requires special attention. With \( C^0 \) elements, which are smooth within each element and continuous across their boundaries, one cannot represent spatial derivatives of higher order than 2. Thus the fourth-order Cahn-Hilliard equation has been decomposed into two second-order equations:

\[
\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \frac{\gamma \lambda}{\epsilon^2} \Delta \psi + s \phi, \\
\psi = -\epsilon^2 \Delta \phi + (\phi^2 - 1 - s) \phi,
\]

(1.17)

(1.18)

where \( s \) is a positive number to enhance stability of the numerical method (Shen, 1995). For all the calculations reported hereafter, \( s = 0.5 \) is used. The chemical potential \( G \) in Eq. (1.14) is now simply \( G = \frac{\lambda}{\epsilon^2} \psi + s \phi \).

We seek the following weak solution: \( (\mathbf{v}, p, \tau_d, \phi, \psi) \in \mathcal{U} \times \mathcal{P} \times \mathcal{T} \times \mathcal{S} \times \mathcal{S} \). For 2D or 3D axisymmetric flows, the solution spaces satisfy \( \mathcal{U} \in H^1(\Omega)^2, \mathcal{P} \in L^2(\Omega), \mathcal{T} \in L^2(\Omega)^3 \) (\( L^2(\Omega)^4 \) for axisymmetric flow) and \( \mathcal{S} \in H^1(\Omega) \). Using basis functions \( (\tilde{\mathbf{v}}, \tilde{p}, \tilde{\tau}, \tilde{\phi}, \tilde{\psi}) \), we write the following weak forms of the governing equations:

\[
\int_{\Omega} \left\{ \left[ \rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} - \mathbf{g} \right) - G \nabla \phi \right] \cdot \tilde{\mathbf{v}} + (-p \mathbf{I} + \mathbf{\sigma}) : \nabla \tilde{\mathbf{v}} \right\} d\Omega = 0, \\
\int_{\Omega} (\nabla \cdot \mathbf{v}) \tilde{p} d\Omega = 0, \\
\int_{\Omega} \{ \mathbf{\tau} + \lambda H \mathbf{\tau}_{d(1)} - \mu_p \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right] \} : (\tilde{\mathbf{\tau}} + \alpha \mathbf{v} \cdot \nabla \mathbf{v}) d\Omega = 0,
\]

(1.19)

(1.20)

(1.21)
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\[ \int_{\Omega} \left[ \left( \frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi \right) \tilde{\phi} + \frac{\gamma \lambda}{\epsilon^2} \nabla (\psi + s\phi) \cdot \nabla \tilde{\phi} \right] d\Omega = 0, \quad (1.22) \]

\[ \int_{\Omega} \left\{ \left[ \psi - (\phi^2 - 1 - s)\phi \right] \tilde{\psi} - \epsilon^2 \nabla \phi \cdot \nabla \tilde{\psi} \right\} d\Omega = 0, \quad (1.23) \]

where \( \sigma \) consists of viscous stress and polymer stress. In Eq. (1.19), the interfacial stress tensor is replaced by an equivalent form \( G \nabla \phi \) that can be seen as a body force. We have adopted the streamline upwind Petrov-Galerkin scheme for the constitutive equations to improve stability (Brooks & Hughes, 1982).

In the derivation of the weak formulation, all surface integration has been neglected for simplicity, which implies that natural boundary conditions are satisfied. The boundary conditions can be thus summarized as:

\[ \mathbf{v} = \mathbf{v}_g, \quad \text{on } (\partial \Omega)_u \]

\[ (-pI + \tau) \cdot \mathbf{m} = 0, \quad \text{on } (\partial \Omega)_\tau \]

\[ \tau_d = \tau_{in}, \quad \text{on } (\partial \Omega)_{in} \]

\[ \nabla \phi \cdot \mathbf{m} = \nabla \psi \cdot \mathbf{m} = 0, \quad \text{on } \partial \Omega \]  

(1.27)

where \( \partial \Omega = (\partial \Omega)_u \cup (\partial \Omega)_\tau \) and \( (\partial \Omega)_u \cap (\partial \Omega)_\tau = \emptyset \), \( (\partial \Omega)_{in} \) is the inflow boundary, and \( \mathbf{m} \) is the unit normal to the boundary. The zero-flux conditions in Eq. (1.27) help maintain volume conservation of the phases.

On an unstructured triangular mesh (see next subsection for adaptive meshing), we have used piecewise quadratic (P2) elements for \( \mathbf{v}, \phi \) and \( \psi \), and piecewise linear (P1) elements for \( p \) and \( \tau_d \). Second-order implicit methods are used for time discretization. Details of the discretization scheme can be found in Yue et al. (2006b). The non-linear algebraic system generated by Eqs. (1.19) to (1.23) is solved using an Inexact Newton’s method with backtracking (Eisenstat & Walker, 1996). Within each Newton iteration, the sparse linear system is solved by preconditioned Krylov methods (van der Vorst, 2000; Saad, 1996) such as the Generalized Minimum Residual (GMRES) method and the Biconjugate Gradient Stabilized (BCGSTAB) method, both of which turn out to have similar performance, although GMRES is expected to be more stable (Saad, 1996). ILU(0) and ILU(t) preconditioners (Saad, 1996; Benzi, 2002) are found to be robust for our simulations (Yue et al., 2006b; Zhou et al., 2006). By design, our grid size varies greatly from the interface to the bulk. This gives rise to a highly ill-conditioned sparse matrix and numerical difficulties. This is resolved by a scaling procedure whereby a diagonal scaling matrix is left-multiplied to the mass matrix prior to applying the aforementioned preconditioners. Thus, each row of the matrix is scaled by the inverse of the sum of the absolute values of the entries in that row before the linear system is sent to the preconditioned Krylov solvers.

1.3.4 Adaptive meshing

As mentioned in the above subsection, the phase-field model allows one to use a fixed Eulerian mesh to capture moving internal boundaries. To achieve high accuracy at
modest computational cost, we need a mesh with dense grids covering the interfacial region and coarser grids in the bulk. As the interface moves out of the fine mesh, the mesh in front needs to be refined while that left behind needs to be coarsened. Such adaptive meshing is achieved by using a general-purpose mesh generator GRUMMP, which stands for Generation and Refinement of Unstructured Mixed-Element Meshes in Parallel (Freitag & Ollivier-Gooch, 1997). GRUMMP generates a mesh by using Delaunay refinement, and allows control of the internal grid size by using a scalar field. GRUMMP produces triangular elements in 2D and tetrahedral elements in 3D.

GRUMMP controls the spatial variation of grid size using a length scale $L_S$, which specifies the intended grid size at each location in the domain. One determines the local grid size by:

$$L_S(p) = \min \left[ \frac{l_s(p)}{R}, \min_{\text{Neighbors } q_i} \left( L_S(q_i) + \frac{|q_i - p|}{G} \right) \right]$$

(1.28)

where the inner minimum is taken among all pre-existing neighboring points $q_i$, and $R$ and $G$ are user-supplied constant resolution and grading parameters. In our framework, the grid size distribution is dictated by the need to resolve thin interfaces. Since the phase-field variable $\phi$ is constant ($\pm 1$) in the bulk but varies steeply across the interface, we can impose a prescribed small grid size $h_1$ on the interface by making $L_S$ depend on $|\nabla \phi|$ on every node:

$$L_S(x, y) = \frac{1}{|\nabla \phi| \sqrt{\frac{\sqrt{2}}{C} + \frac{1}{h_\infty}}}$$

(1.29)

where $h_\infty$ is the mesh size in the bulk, and the constant $C$ controls the mesh size in the interfacial region: $h_1 = L_S|_{\phi=0} \approx C \cdot \epsilon$, $\epsilon$ being the capillary width. In previous work, we have used $C$ values between 0.5 and 1; $h_1 \leq \epsilon$ ensures that the thickness of the interface typically contains on the order of 10 grid points (Yue et al., 2004). Figure 1.2 shows an example of the mesh inside a square containing an ellipse.

Note that the interface is enveloped in a ribbon of fine grids. Depending on the normal velocity of the interface, it will approach the boundary of the “fine-mesh ribbon” in a certain number of time steps, at which time GRUMMP is called to refine and coarsen the neighboring regions in the front and rear, respectively. This ribbon is taken to comprise 3 layers of the finest triangles. When the interface goes beyond the second triangle from the middle, remeshing is invoked. The solution of the last time step is then projected onto the new grid in a scheme described by Hu et al. (2001) The speed at which the interface traverses the fine-mesh ribbon also constrains the time step $\Delta t$. We require that the interface not advance more than a whole cell at one time step:

$$\Delta t \leq \Delta t_{\text{int}} = \min_{\text{All interfacial cells}} \frac{h}{|v \cdot n|},$$

(1.30)

where $v$ is the interfacial velocity, $n$ is the unit normal to the interface and $h$ is the cell size along $n$.

In the above, we have outlined the theoretical model and numerical methods common to all the applications that will be described in detail in the rest of the thesis. Each of the
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Figure 1.2: (a) An unstructured triangular mesh generated by GRUMMP with interfacial refinement. The parameters are $G = 3$, outer boundary mesh size $h_2 = 0.5$, interior mesh size $h_3 = h_2/2$, and interfacial mesh size $h_1 = h_2/64$. (b) Magnified view of a portion of the interfacial region. The bold curve indicates the interface $\phi = 0$, which is centered in a belt-like region of refined triangles.

Following chapters is a self-contained manuscript that is either published in or submitted to peer-reviewed journals. Chapter two is a study on the simple and compound drop formation in microfluidic flow-focusing devices. Chapter three models the neutrophil transit and transport in pulmonary capillaries. Chapter four is on compound drop deformation through a contraction. Chapter five to chapter six concern the rise of a bubble or drop in a liquid crystal. For Chapter five, we studied a unique “inverted-heart” shape of a bubble when it rises in the liquid crystal. Chapter six focuses on the transformation of the topological defects near the rising bubble or drop. Chapter seven simulates the self-assembly of many droplets dispersed in a liquid crystal matrix. Finally, chapter eight investigates capillary breakup of nematic fibers, a problem of direct applications in self-reinforcing polymer composites.
Bibliography


Bibliography


Chapter 2

Formation of simple and compound drops in microfluidic devices *

2.1 Introduction

The recent upsurge in microfluidic research has arisen from the confluence of maturing microfabrication techniques and the increasing need to manipulate small amounts of fluids, often for the purpose of fast and inexpensive analysis of biological and chemical samples (Stone & Kim, 2001; Stone et al., 2004; Thilmay, 2005; Squires & Quake, 2005). An important issue in microfluidics is the control of fluid interfaces, in particular the generation and manipulation of droplets (Atencia & Beebe, 2005; Joanicot & Ajdari, 2005). From a fundamental standpoint, the significance of interfacial dynamics in microfluidics is easy to understand. The miniaturization of flow geometries greatly increases the ratio of surface area to volume, therefore accentuating the role of interfacial forces. In practical applications, droplets in microchannels form the centerpiece of many lab-on-a-chip devices. For instance, a variety of mechanisms can be employed to move a droplet as a means of pumping fluids (Stone et al., 2004; Laser & Santiago, 2004). Another oft-cited application is the use of droplets as chemical reactors where the kinetics can be monitored and controlled very precisely (Bringer et al., 2004). Recently, droplets have also been used as templates for producing microparticles with specialized biological, chemical and optical properties (Lu et al., 2004; Dendukuri et al., 2005; Fernandez-Nieves et al., 2005).

The application of the greatest relevance to this paper is the use of microfluidic channels for producing highly monodisperse emulsions. Traditionally, emulsions are made by shearing immiscible fluids in macroscopic mixers (Becher, 2001). The droplets thus produced have a wide range of sizes, and the size distribution is often poorly controlled. Recently, two types of microfluidic devices have been developed for producing droplets with precisely controlled sizes: the T-junction and the flow-focusing device (Stone et al., 2004). Integration of multiple units allows the efficient production of monodisperse emulsions consisting of a great number of droplets (Link et al., 2004; Fernandez-Nieves et al., 2005). Moreover, compound drops may be produced either using a two-step procedure of two T-junction units in tandem, with alternating surface wetting properties (Okushima et al., 2004), or by clever use of multiple injection ports in a one-step procedure (Utada et al., 2005). These allow one to engineer double emulsions with much more precisely controlled dimensions and properties than those produced using conventional methods (Grossiord & Seiller, 1998; Goubault et al., 2001), with potential impacts in drug delivery, controlled release and other applications (Olivieri et al., 2003).

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Chapter 2. Formation of simple and compound drops in microfluidic devices

In comparison with the rapid experimental advances, very little theoretical or numerical work has been done on interfacial dynamics in microfluidic channels. Aside from scaling arguments on the drop size and conditions for drop formation (Utada et al., 2005; Umbanhowar et al., 2000), we know of only one numerical simulation of drop formation in the flow-focusing device (Davidson et al., 2005). Our current knowledge about the working of various devices is mostly empirical. Many fundamental questions on interfacial behavior in small dimensions and close proximity of bounding walls remain to be answered. For example, what physical mechanisms govern the process? Do drops form through the same capillary instability as operates in macroscopic scales? How does the final drop size depend on various geometric, material and flow parameters? To answer such questions, systematic theoretical and numerical studies need to be carried out. Moreover, a coherent understanding of micro-scale interfacial flows is essential for a rational design and manufacturing strategy.

Thus, this computational study was motivated not only by the technological potential of microfluidics, but also by the fundamental fluid dynamics behind the devices. By exploring the process over ranges of the material and operating parameters, we seek to clarify the underlying physics, and to provide guidelines for further technological developments. Furthermore, we introduce non-Newtonian rheology into the picture. This is an important addition because the sample fluids in the targeted applications are often biological complex fluids that contain macromolecules. Despite the typically slow flow rates, the small dimension of micro-channels implies large strain rates capable of distorting the microstructure of the fluids and thus producing viscoelasticity (Stone et al., 2004). Besides, the elasticity of polymer molecules may be exploited to produce fluidic control and memory elements (Groisman et al., 2003). So far, little experimental attention has been given to non-Newtonian fluids in microfluidics. Indeed, Stone et al. (2004) have identified this as one of the major thrust areas in microfluidic research in the near future. Our numerical work will provide the first indications of the effects of non-Newtonian rheology on drop formation and behavior in microfluidic flows.

In the context of computational fluid dynamics, the process of drop formation in the flow-focusing devices is a formidable task. Besides the complex geometry, the moving and deforming internal boundary is a well-known numerical difficulty. Moving-grid methods use grid points to track the interfaces, and tend to break down when the interfaces undergo topological changes such as breakup and coalescence (Cristini & Tan, 2004). Fixed-grid methods avoid this problem by regularizing the interface and converting the Lagrangian description of moving boundaries into an Eulerian description. The price is the need for an additional scalar field and adequate resolution of the interfacial region (Feng et al., 2005). Incorporating non-Newtonian rheology is a further challenge.

Recently, we have developed a finite-element algorithm with adaptive meshing that possesses the strengths of both fixed and moving grids (Yue et al., 2006). Couched in a diffuse-interface framework, the method is particularly suited for simulating interfacial dynamics in complex fluids. In this model, the two components are assumed to mix in a narrow interfacial layer, across which physical properties change steeply but continuously. The interfacial position and thickness are determined by a phase-field variable whose
evolution is governed by a mixing energy. This way, the structure of the interface is rooted in molecular forces and calculated from a convection-diffusion equation; there is no longer a need for tracking the interface. Moreover, the model uses an energy-based formulation that incorporates the rheology of microstructured fluids with ease.

We have set three objectives for this study: (a) to demonstrate that our diffuse-interface method is capable of reproducing the experimentally observed processes of simple- and compound-drop formation; (b) to map out the ranges of operating and material parameters so as to provide guidelines for future design and development; and (c) to explore the effects of viscoelastic rheology on the process.

2.2 Theory and numerical methods

Yue et al. (2004) have described a theoretical model that incorporates non-Newtonian rheology into a diffuse-interface framework, presented a numerical algorithm using spectral discretization, and conducted numerical experiments to validate the code. Recently, Yue et al. (2006) have developed a more versatile and powerful version of the numerical toolkit, dubbed AMPHI, using finite elements with Adaptive Meshing using a phase field ($\phi$). Since the numerical schemes in AMPHI and their validation have been discussed in detail, we will only summarize the main ideas and give the governing equations here. Consider a pair of “immiscible” fluids in contact. To be specific, we take one fluid to be Newtonian and the other a viscoelastic Oldroyd-B fluid. The diffuse interface has a small but non-zero thickness, inside which the two components are mixed and store a mixing energy. We define a phase-field variable $\phi$ such that the concentrations of the non-Newtonian and Newtonian components are $(1 + \phi)/2$ and $(1 - \phi)/2$, respectively. Then $\phi$ takes on a value of 1 or $-1$ in the two bulk phases, and the interface is simply the level set $\phi = 0$. Starting with the system’s free energy, comprising the mixing energy of the interface and the bulk elastic energy in the Oldroyd-B fluid, we can derive the following set of governing equations (Yue et al., 2005b, 2006):

$$\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma \nabla^2 G,$$

$$G = \lambda \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\epsilon^2} \right],$$

$$\tau_p + \lambda H \tau_p(1) = \mu_p [\nabla \mathbf{v} + (\nabla \mathbf{v})^T],$$

$$\tau = \left( \frac{1 - \phi}{2} \mu_n + \frac{1 + \phi}{2} \mu_s \right) [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] + \frac{1 + \phi}{2} \tau_p,$$

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = \nabla \cdot (-p \mathbf{I} + \tau) + G \nabla \phi + \rho \mathbf{g},$$

$$\nabla \cdot \mathbf{v} = 0,$$

where $G$ is the chemical potential and $\gamma$ is the mobility parameter; $\lambda$ is the interfacial energy density and the capillary width $\epsilon$ represents the interfacial thickness. With decreasing $\epsilon$, the diffuse-interface model approaches the classical sharp-interface model and
λ/ϵ gives the interfacial tension (Yue et al., 2004). The polymer stress $\tau_p$ obeys the Maxwell equation, with the subscript $(1)$ denoting the upper convected derivative and $\lambda_H$ being the polymer relaxation time. $\mu_p$ and $\mu_s$ are the polymer and solvent contributions to the shear viscosity of the Oldroyd-B fluid, and $\mu_n$ is the viscosity of the Newtonian phase. $\rho$ is a mixture density:

$\rho = \frac{1 + \phi}{2} \rho_1 + \frac{1 - \phi}{2} \rho_2$, $\rho_1$ and $\rho_2$ being the densities for the Oldroyd-B and Newtonian components, and $g$ is the gravitational acceleration.

These equations are discretized on a finite-element grid using the Galerkin formulation with streamline upwinding for the constitutive equation. We will concern ourselves only with axisymmetric geometry in this study, and the 2D computational domain is covered by an unstructured grid of triangular elements. Prior experience has shown that the key to accurate phase-field simulations is sufficient resolution of the interfacial region (Feng et al., 2005). Thus, we have built an adaptive meshing scheme using the method contained in the public-domain package GRUMMP (Freitag & Ollivier-Gooch, 1997). The scheme allows one to control the spatial gradient of grid size using a scalar field. In our application, the phase-field variable $\phi$ is a natural choice for this function. Thus, we have a belt of refined triangles covering the interfacial region. As the interface approaches the edge of the belt, remeshing is performed with the mesh upstream of the interface being refined by edge bisection and/or node insertion while that left behind being coarsened. Typically the interfacial layer requires roughly 10 grid points to resolve, and remeshing happens over tens of time steps. We use implicit time-stepping, with Newton iteration at every step to handle the nonlinearity in the equations. The time step is automatically adjusted according to a set of criteria based on the normal velocity of the interface and the bulk velocity. Numerical experiments with grid refinement and time-step refinement have been carried out (Yue et al., 2006), and adequate resolution is ensured for the simulations presented in the following.

2.3 Results and discussion

2.3.1 Drop formation at an orifice

We first consider the growth and detachment of drops from a tip of a capillary tube that discharges into an ambient fluid at a small constant flow rate. This relatively simple process has been studied in the past by several groups, theoretically by lubrication analysis (Eggers, 1997), experimentally (Wilkes et al., 1999; Notz et al., 2001; Christanti & Walker, 2001; Shore & Harrison, 2005) and computationally (Wilkes et al., 1999; Notz et al., 2001; Ambravaneswaran et al., 2002). A summary of the main results can be found in a recent review (Basaran, 2002). Important aspects of the process, e.g., the drop size, the critical length of the thread prior to pinch-off and satellite drop formation, have been explored as functions of geometry, flow rate and fluid properties, including viscoelasticity. A comparison of our simulation with results in the literature will serve as a validation of our numerical method and code. Although Yue et al. (2006) presented numerical examples for benchmarking the method, they did not examine interface rupture and pinch-off, phenomena that are key to the drop formation in microchannels. For our
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purpose, we will focus on a computational study by Wilkes et al. (1999), who used a moving-grid finite-element method to simulate the formation of drops of Newtonian liquids issuing from a capillary into air.

Let us denote the viscosity and density of the fluid inside the capillary by \( \mu_i \) and \( \rho_i \), and those of the ambient matrix fluid by \( \mu_o \) and \( \rho_o \). Other parameters of the problem are the radius of the nozzle \( a \), the average velocity in the capillary \( V_i \), interfacial tension \( \sigma \) and gravitational acceleration \( g \). The process is controlled by five dimensionless groups:

\[
\begin{align*}
Bo &= \frac{(\rho_i - \rho_o)ga^2}{\sigma}, \\
Ca &= \frac{\mu_i V_i}{\sigma}, \\
We &= \frac{\rho_i V_i^2 a}{\sigma}, \\
\alpha &= \frac{\rho_i}{\rho_o}, \\
\beta &= \frac{\mu_i}{\mu_o},
\end{align*}
\]

where the Bond number \( Bo \), the capillary number \( Ca \) and the Weber number \( We \) indicate the ratio of gravity, viscous force and inertia to capillarity. The Reynolds and Ohnesorge numbers are also used in the literature: \( Re = We/Ca \), \( Oh = Ca/We^{1/2} \).

We start with an initial condition where the interface is flush with the opening of the capillary tube, and a parabolic velocity profile with average \( V_i \) is imposed upstream. Figure 2.1 shows two snapshots of a typical simulation, one at an early stage of drop formation and the other immediately after the drop pinches off. Note that the finite-element grid is refined near the interface. As the interface deforms, the mesh evolves accordingly. In this example, the mesh is generated by enforcing a grid size \( h_1 = 0.003a \) on the interface, \( h_2 = 0.15a \) inside the inner fluid and \( h_3 = 0.2a \) in the far field of the outer fluid. Numerical experiments with mesh refinement have shown such resolutions to be sufficient. The small \( h_1 \), relative to the capillary width \( \epsilon = 0.006a \), implies that there are about 15 grid points across the interfacial layer, more than adequate for resolving the interfacial profile and producing an accurate interfacial tension (Yue et al., 2004).

The scenario of drop growth and pinch-off is similar to prior simulations by Wilkes et al. (1999) To be more quantitative, we compare the drop radius \( r \) as a function of \( Bo \) in Fig. 2.2. Note that in both computations, \( We \) and \( Ca \) are very small. Thus, inertial and viscous forces are negligible, and the process is dominated by the balance between capillary force and gravity: \( \sigma a \sim (\rho_i - \rho_o)g r^3 \). This leads to the well-known scaling (de Gennes et al., 2004):

\[
\frac{r}{a} \propto Bo^{-1/3}.
\]

Note first that the power law is borne out by both sets of results. In addition, the agreement between the two results is within 5% throughout the \( Bo \) range. This is despite the differences in \( \alpha \) and \( \beta \) as inertia and viscosity have negligible effects in this limiting
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Figure 2.1: Formation and detachment of a drop at the tip of a capillary. The drop and matrix fluids are both Newtonian, with density ratio $\alpha = 2$ and viscosity ratio $\beta = 1$. Other dimensionless parameters are $Bo = 0.465$, $Ca = 3.05 \times 10^{-3}$ and $We = 2.95 \times 10^{-4}$. (a) Early stage of drop growth at dimensionless time $tV_i/a = 2.71$. The left half shows the finite-element grid and the right half plots the interface and streamlines. (b) Shortly after the pinch-off, $tV_i/a = 4.14$.

regime as long as the density difference is matched properly through $Bo$. This validation indicates that our numerical scheme handles interfacial deformation and pinch-off accurately.

In fact, the diffuse-interface treatment affords an advantage over sharp-interface methods in simulating breakup and coalescence. These topological changes are no longer mathematical singularities to be circumvented by ad hoc schemes that cut and reconnect the interface. Rather they are controlled by a short-range molecular force akin to the van der Waals force (Yue et al., 2005a). To further illustrate this point, Fig. 2.3 plots the thinning of the neck in time. Except for the final moment, $R_n(t)$ approximates a $2/3$ power-law which would obtain for an inertio-capillary pinch-off (Eggers, 1997). In our case, $Oh = 0.178$, $Bo = 0.465$, and the small viscous and gravity effects may have caused the deviation from the scaling. However, the most interesting feature is the abrupt dive of $R_n$ once it reaches a threshold value $R_n^* \approx 0.01a$. This is when the short-range force inherent in the Cahn-Hilliard model begins to dominate. Owing to the phenomenological nature of this model, however, the degree to which this short-range force reflects reality
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Figure 2.2: Comparison of the drop size between our simulation and Wilkes et al. (1999). In our calculations, $\alpha = 2$, $\beta = 1$. $Bo$ is varied by using different fluid densities and interfacial tension; $We$ varies between $1.90 \times 10^{-4}$ and $2.68 \times 10^{-4}$, and $Ca$ between $2.87 \times 10^{-5}$ and $3.55 \times 10^{-3}$. Wilkes et al. (1999) treated the drop surface as a free surface such that $\alpha = \infty$, $\beta = \infty$. $We$ and $Ca$ are of the same order of magnitude as ours.

in a particular experiment is not known a priori. Thus, we may consider the threshold $R^*_{n}$ the smallest length scale that is resolved with confidence in our simulations. Note that $R^*_{n}$ is close to $2\epsilon$ and is roughly half of the interfacial thickness.

2.3.2 Formation of simple drops in a flow-focusing device

The simulations to be discussed in this subsection are motivated by the experiments of Anna et al. (2003), who produced water drops in oil in a flow-focusing geometry. However, the setup of the numerical problem differs from its experimental counterpart in several ways. First, the experimental channels have rectangular cross-sections, and the flow field is 3D. We have adopted a 2D axisymmetric geometry illustrated in Fig. 2.4. The length scales are similar to those in the experiment but a precise match is impossible. Our main motivation for using an axisymmetric geometry is to reduce the computational cost. But axisymmetric devices have practical advantages over the more common rectangular microchannels for drop encapsulation (Takeuchi et al., 2005). Second, the solid surfaces in Anna et al.’s microchannel seem to be hydrophobic since the interface apparently never makes contact with the outer walls in the experiment. In our phase-field formulation, a contact angle of $90^\circ$ is the default although it may be modified through the free energy
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Figure 2.3: Variation of the minimum neck radius $R_n$ on the thread with time $t$ for the simulation in Fig. 2.2. $R_n$ is scaled by the nozzle radius $a$ and $t$ by the flow time $a/V_i$. (Jacqmin, 2000). As a result, our interface may touch the wall at very low flow rates, which we have avoided in the simulations to reflect the experimental hydrophobicity. Finally, surfactants (Span 80) are added to the oil phase in the experiment to prevent coalescence of the drops after they are formed. It is unclear whether the surfactants have affected the drop formation process, and we have made no such provisions in the simulations, except assuming a reduced interfacial tension of $\sigma = 10$ mN/m. This is approximately the limiting interfacial tension between water and hexacane with saturating Span 80 surfactants on the interface (Campanelli & Wang, 1999).

At the inlet, parabolic velocity profiles are imposed for both the inner fluid and the outer fluid, with average velocities $V_i$ and $V_o$, respectively. At the outlet, the normal stress and the radial velocity vanish, while at the axis of symmetry, the radial velocity and all radial gradients are put to zero. The physical parameters are taken from the experiments (Anna et al., 2003), with the inner fluid being water and the outer silicone oil. The density and viscosity ratios are $\alpha = \rho_i/\rho_o = 1.11$ and $\beta = \mu_i/\mu_o = 0.167$. Other dimensionless parameters of the problem are the various length ratios, $We$ and $Ca$ for the inner fluid: $We = \rho_i V_i^2 a/\sigma$ and $Ca = \mu_i V_i/\sigma$, and the ratio of flow-rates $\Gamma = Q_i/Q_o$ between the inner and outer streams. Except for results in Figs. 2.8 and 2.12, we have fixed $\Gamma = 1/4$ in this subsection according to a series of experiments in Anna et al. (2003) The $We$ and $Ca$ values cited below correspond to flow rates and material constants from the experiments and a characteristic length $a = 20$ $\mu$m, close to half of the actual orifice width of 43.5 $\mu$m. Mesh sizes are similar to those used in Fig. 2.1: $h_1 = 0.005a$ on the
interfaces, $h_2 = 0.08a$ in the bulk of the inner fluid and $h_3 = 0.1a$ for the bulk of the outer fluid. The capillary width is $\epsilon = 0.01a$.

Two regimes, dripping and jetting, have been identified in previous experiments on drop formation at the tip of a capillary discharging into stationary air (Ambravaneswaran et al., 2004) or a co-flowing stream (Umbanhowar et al., 2000; Cramer et al., 2004), and most recently in flow-focusing devices (Utada et al., 2005). Similar regimes have been observed in our simulations. The dripping regime is characterized by periodic formation of highly uniform spherical drops outside the orifice, and prevails at low flow rates. With increasing flow rates, there is a transition to the jetting regime, where a jet extends downstream from the orifice, with drop formation at the tip of the jet. In the following, we will analyze each regime in turn and discuss the transition.

1. Dripping regime

The flow focusing occurs through the strong contraction upstream of the nozzle, which stretches the inner fluid into a filament inside the nozzle. Upon exiting the orifice, the expansion decelerates the flow, and interfacial tension produces a nearly spherical bulb at the end of the filament (Fig. 2.5a). The bulb is fed by the filament and grows gradually. Meanwhile a neck forms at the base of the bulb (Fig. 2.5b). Shortly after, oscillations are observed on the neck (Fig. 2.5c,d). The oscillation is amplified in time, and after several periods the neck pinches off and the bulb disconnects from the filament and travels downstream (Fig. 2.5e). Then a new cycle commences. This process is highly periodic and produces drops of very uniform size (Fig. 2.5f).

The oscillation of the neck before drop pinch-off is more clearly shown by the time-sequence in Fig. 2.6. During periodic drop formation, the interfacial shape upstream of the nozzle hardly varies in time, and the oscillation is largely localized to the neck region. This oscillation calls to mind the well-known Rayleigh instability. Because the filament ends in the bulb, however, capillarity works through both the Rayleigh instability and the end-pinching mechanism (Stone & Leal, 1989). To investigate the development of capillary waves on the filament, we have carried out a simulation where the length of the nozzle is elongated to 3 times of the original size (Fig. 2.7). The growth of capillary waves within the nozzle, apparent in Fig. 2.7(a), is more precisely represented by the filament.
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Figure 2.5: Snapshots of drop formation in the dripping regime at $Ca = 1.70 \times 10^{-3}$, $We = 5.75 \times 10^{-4}$. The time is made dimensionless by $a/V_i$. In dimensional terms, the frequency of drop formation is roughly 189 Hz.

Figure 2.6: The radius of the neck, measured at its thinnest part, oscillates in time before dropping to zero. $R_n$ is scaled by $a$ and $t$ by $a/V_i$. The period of oscillation, converted using dimensional parameters in Anna et al.’s experiment, is about 0.16 ms.

radius in Fig. 2.7(b). Clearly, the capillary wave travels downstream with increasing amplitude. The wave-speed $v_w = 40.6V_i$ is close to the fluid speed on the interface
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Figure 2.7: Development of the capillary wave inside a long nozzle. All other parameters are the same as Fig. 2.5. (a) Geometry of the domain; (b) radius of the thread as a function of the axial distance from the inlet of the nozzle to the outlet. The radius and the position are scaled by the nozzle radius $a$.

$v_i = 37.1V_i$. ($v_i$ itself agrees with the theoretical prediction of Eq. 2.16 to within 3%). Thus, the capillary wave grows while riding on the interface and traveling downstream. A Fourier analysis identifies a dominant wavelength $\lambda = 9.24r_f$, $r_f$ being the average radius of the filament inside the nozzle. Theoretical prediction by (Mikami & Mason, 1975), who extended Rayleigh’s theory to a viscous cylinder surrounded by another viscous fluid and confined in a tube, gives the fastest-growing wavelength as $9.42r_f$, in close agreement with our numerical value. Since the bulb and the neck hardly move forward, the traveling wave produces the oscillation in Fig. 2.6 as it arrives at the neck. The period at the neck is roughly twice that of the wave inside the nozzle.

Thus we have confirmed the existence and growth of capillary waves. But is capillary instability the direct cause of the breakup of the filament and pinch-off of the drop? For capillary breakup, the drop radius $r_d$ would be proportional to the radius of the filament $r_f$. The latter can be easily estimated from the flow-rate ratio $\Gamma$ and viscosity ratio $\beta$ by assuming parabolic velocity profiles in the nozzle and matching the shear stress at the
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Figure 2.8: Dependence of the drop radius $r_d$ on the flow-rate ratio $\Gamma$. (a) Effect of varying one flow rate while keeping the other fixed. The intersection of the two curves, at $\Gamma = 0.167$, $Ca = 1.70 \times 10^{-3}$ and $We = 5.75 \times 10^{-4}$ for the inner fluid and $Ca_o = 2.49 \times 10^{-2}$ and $We_o = 2.84 \times 10^{-3}$ for the outer fluid, is near the transition point; decreasing either $Q_i$ or $Q_o$ causes dripping while increasing either leads to jetting. (b) Comparison between two fixed $Q_i$ values while $Q_o$ varies: lower $Q_i$ with $Ca = 1.06 \times 10^{-2}$, $We = 5.75 \times 10^{-4}$ and higher $Q_i$ with $Ca = 1.06 \times 10^{-2}$, $We = 2.25 \times 10^{-2}$. The former experiences the transition at $\Gamma = 0.167$ while the latter is entirely in the jetting regime.

For our simulations, $\beta = 0.167$ and $\Gamma < 1$, and the above is well approximated by a power-law: $r_f/a \sim \Gamma^{1/2}$. We have confirmed that the computed $r_f$ follows this scaling closely. Then we would expect the radius of the drops $r_d$ to scale with $\Gamma^{1/2}$ as well. This scaling, as it turns out, fails to represent the numerical results in Fig. 2.8. Moreover, the drop size also depends strongly on the diameter of the downstream collection tube (Fig. 2.9). Therefore, the pinch-off of the drop is not entirely determined by the capillary instability. The complex geometry—expansion from the nozzle to the collection tube—and the outer flow field play important parts as well.

For drop formation in a co-flowing ambient fluid without flow-focusing, Umbanhowar et al. (2000) suggested a scenario of drag-induced pinch-off similar to that of a pendant drop under gravity. This seems to be consistent with the trend in Fig. 2.9, where the slower outer flow for larger expansion ratio $r_e/a$ results in less drag on the bulb and larger drop size. Balancing a Stokes-like viscous drag and the capillary force on the filament: $\mu_o v_o r_d \sim \sigma r_f$, where $v_o \sim Q_o/r_e^2$ is the velocity of the outer fluid in the collection tube,
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Figure 2.9: The drop radius $r_d$ increases with the radius of the downstream collection tube $r_e$. $\Gamma = 0.25$, $\alpha = 1.11$, $\beta = 0.167$, $Ca = 1.70 \times 10^{-3}$ and $We = 5.75 \times 10^{-4}$. A linear fit to the numerical data is $r_d/a = 0.38r_e/a + 0.65$.

\[
\frac{r_d}{a} \sim \frac{\sigma \Gamma^\frac{1}{2} r_e^2}{\mu_o Q_o} \sim \frac{\sigma \Gamma^\frac{3}{2} r_e^2}{\mu_o Q_i}.
\]  

(2.14)

According to this, $r_d$ should scale with $\Gamma^\frac{3}{2}$ for fixed $Q_i$, and with $r_e^2$ for fixed $\Gamma$. However, the former is contradicted by the data in Fig. 2.8 while the latter by Fig. 2.9.

We are led to the conclusion that the pinch-off is the combined effect of both capillary instability and stretching of the neck by viscous drag (Davidson et al., 2005). Imagine setting $Q_i$ and $Q_o$ suddenly to zero. The filament hanging outside the nozzle will break into droplets by end-pinching: the end forms a bulb and the neck pinches in with the fluid being squeezed out by the high capillary pressure in the neck. In the actual simulations, the flow in and around the filament changes this picture. On the one hand, the inner flow supplies fluid to the neck and resists its continuous thinning (Fig. 2.10a). On the other hand, the outer flow exerts a drag on the bulb that tends to stretch and thin the neck. As a result, the neck radius reaches smaller minima in successive cycles of oscillation with the incoming waves (Fig. 2.6). During the shrinking phase of the neck’s oscillation, the forward velocity in the filament is impeded, and the fluid accumulates upstream of the neck (Fig. 2.10b). Periodically, this fluid mass merges into the end drop as the neck size reaches its maximum. Thus, as the minimum neck radius diminishes in the oscillation, the maximum increases as shown in Fig. 2.6. Eventually, a critical point is reached when the neck size gets so thin that the forward flow in the filament is completely arrested.
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Figure 2.10: The velocity field near the drop at (a) \( tV_i/a = 6.59 \) and (b) \( tV_i/a = 6.67 \) shortly before pinch-off. The parameters are the same as in Fig. 2.5. The maximum velocity (dark) is nearly \( 120V_i \) and the minimum (white) is below \( 0.6V_i \).

Figure 2.11: A cycle of drop formation in the jetting regime at \( Ca = 1.06 \times 10^{-2}, \) \( We = 2.25 \times 10^{-2} \). The time is made dimensionless by \( a/V_i \). In dimensional terms, the frequency of drop formation is roughly \( 1027 \) Hz.

(Fig. 2.10b). The vortex ring before the neck is caused by the high capillary pressure at the neck that drives the fluid into reverse motion. Then end-pinching and stretching by viscous drag conspire to effect the pinch-off. The interplay of various factors is such that an argument based on capillary instability or viscous drag alone is inadequate.

2. Jetting regime

As the flow rates increase, dripping gives way to jetting. While dripping produces drops right after the nozzle, jetting features a long jet that extends several orifice di-
ameters downstream into the collection tube. Drops form at the forefront of the jet periodically. A cycle of drop pinch-off is shown in Fig. 2.11.

The mechanism for drop formation seems to be qualitatively the same as in the dripping regime, i.e., via a combination of viscous drag and capillary instability, the latter comprising Rayleigh waves and end-pinching. Inside the nozzle, viscous shear stretches the interface and produces a thin filament as before (cf. Eq. 2.13). Upon entering the collection tube, the expansion reduces the outer flow velocity and the viscous shear on the filament. Capillary retraction then causes the jet to become thicker. Nevertheless, capillary waves are evident on the jet. As in the dripping regime, it does not seem that the drop pinch-off is due entirely to the growth of the capillary wave. If it is, the period of drop formation should be given by the time required for capillary breakup, which in our low-viscosity case scales as $t_c \sim (\rho_1 r_j^3/\sigma)^{1/2}$, $r_j$ being the jet radius in the collection tube. Then the drop size $r_d$ can be calculated from $(Q_i t_c)^{1/3}$. If we assume $r_j$ to follow the same scaling as $r_f$ in Eq. (2.13), then the drop size $r_d$ scales with $\Gamma^{1/4}$ with $Q_i$ fixed, and $\Gamma^{7/12}$ with $Q_o$ fixed. Neither agrees with the trend of the data in Fig. 2.8. Instead, the $r_d(\Gamma)$ relationship seems to be qualitatively the same in the dripping and jetting regimes. Thus, we surmise that the same mechanism underlies the pinch-off in both regimes.

However, there are notable differences from dripping. The most obvious is the appearance of the long jet in the collection tube. This is related to the faster speed of the filament at higher $Q_i$ and $Q_o$, and will be discussed in detail below as related to the dripping-jetting transition. Second, because the jet gets rather thick, the bulb at the tip of the jet moves downstream with a velocity comparable to the jet velocity. Thus, there is no oscillation at the neck, in contrast to the dripping regime where the waves travel into an essentially stationary drop and get absorbed. The thicker jet also leads to larger drops than in the dripping regime for the same geometry and $\Gamma$ (cf. Fig. 2.8b). Finally, the jetting regime exhibits somewhat greater irregularity than the dripping regime. The polydispersity, defined by the standard deviation in drop radius divided by the mean, is about 1%. In the dripping regime, no variation of drop size is detectable in the numerical data; the process is perfectly periodic up to the accuracy of our numerical resolution.

The transition from dripping to jetting is often seen as a competition between two time scales: a capillary time $t_c$ for the growth of interfacial disturbance and a flow time $t_f$ for the convection of the fluid (Ambravaneswaran et al., 2004). If $t_c < t_f$, pinch-off occurs shortly after the orifice, giving rise to dripping. Conversely the disturbance is carried downstream before it gets amplified, and jetting obtains. Depending on the Ohnesorge number of the flow, the capillary disturbance can be dominated by viscosity or by inertia (Lister & Stone, 1998). In our case, $Oh \sim O(10^{-2})$ and the pertinent capillary time is the inertial time: $t_c = C(\rho_1 r_j^3/\sigma)^{1/2}$. Numerical tests show $C \approx 26$ for the geometry and fluid properties used here. We take $t_f$ to be the time needed for one waveform to travel downstream: $t_f = \lambda_w/v_w$, where $\lambda_w$ and $v_w$ are the capillary wavelength and wave speed in the collection tube. As noted before, inside the nozzle the wave speed is roughly equal to the interfacial speed. In the collection tube, we assume a similar equality: $v_w = v_j$, $v_j$ being the interfacial velocity on the jet. Now the critical condition for dripping-jetting
transition can be formulated in terms of a modified We number:

\[ \tilde{We} = \frac{t^2_{c}}{t^2_{f}} = \frac{C^2 \rho_i v_j^3 v_j^2}{\sigma \lambda_w^2} = 1. \] (2.15)

Thus, we set the dripping-jetting transition at the point where the jet consists of one waveform beyond the orifice. Such a criterion is necessarily arbitrary insomuch as the transition is gradual in the simulations as well as the experiments (Ambravaneswaran et al., 2004). The jet radius \( r_j \) and jet surface velocity \( v_j \) can be estimated using the same arguments as led to Eq. (2.13). In particular,

\[ v_j = \frac{2Q_o}{\pi r_e^2} \left[ 1 + \frac{\Gamma}{1 + \sqrt{1 + \Gamma^2}} \right], \] (2.16)

where \( r_e \) is the radius of the expansion tube.

For the dripping simulation depicted in Fig. 2.5, \( \tilde{We} = 0.539 \). For the jetting run in Fig. 2.11, \( \tilde{We} = 21.52 \). These are consistent with the criterion in Eq. (2.15). We carried out a series of simulations to determine the transition point, from the visual criterion of whether the jet carries one or more waveforms between the orifice and the neck behind the bulb. Results put \( \tilde{We} \) between 0.877 and 1.022, as expected. From the dependence of \( r_j \) and \( v_j \) on \( \Gamma \), one may show that for small \( \Gamma \), \( \tilde{We} \sim \Gamma^{-1/2} \) for fixed \( Q_i \) and \( \tilde{We} \sim \Gamma^{3/2} \) for fixed \( Q_o \). This explains the observations in Fig. 2.8 that dripping gives way to jetting with increasing \( \Gamma \) at a fixed \( Q_o \), and with decreasing \( \Gamma \) at a fixed \( Q_i \). In other words, this transition takes place when either \( Q_i \) or \( Q_o \) increases.

3. Comparison with prior work

As mentioned before, our axisymmetric simulations approximate the conditions of the 3D flow in the microfluidic device of Anna et al. (2003). Over a range of flow rates, they reported interfacial morphologies resembling our dripping and jetting regimes. The drop size decreases with the outer flow rate and increases with the inner flow rate. This trend has been confirmed by our simulations; see Fig. 2.8. More quantitative comparison is possible if we take the width of the experimental nozzle to be our nozzle diameter \( 2a \), and the thickness of the expansion channel to be our \( 2r_e \). For instance, we predict a drop radius \( r_d = 36.4 \mu m \) at \( Ca = 1.70 \times 10^{-3}, \tilde{We} = 5.75 \times 10^{-4} \), whereas the drops in the experiment have \( r_d = 36 - 39 \mu m \) at roughly matching flow rates; the agreement is within about 10%.

Davidson et al. (2005) did similar simulations using a VOF method, with which our results agree well. In both dripping and jetting regimes, the drop diameter agrees within 2%, and the critical jet length at pinch-off is within less than 5% for jetting and 10% for dripping. This discrepancy may be due to the different strategies for handling interface rupture. The VOF method requires external intervention to effect breakup and reconnection, while our phase-field theory allows such events to evolve naturally (Yue et al., 2005a). Moreover, the oscillation of the neck is a prominent feature of our simulations that reveals the mechanism for pinch-off (cf. Fig. 2.6). In their figures and online movies, on the other hand, no such oscillation can be discerned. An online video
clip for Utada et al.’s experiment (Utada et al., 2005) shows neck oscillation very similar to our simulation.

Utada et al. (2005) noted that the jetting regime exhibits greater irregularity than the dripping regime, with a polydispersity of 3% in the former and 1% in the latter. These are greater than predicted here but the trend is the same. The frequency of drop formation ranges from 100 to 5000 Hz in the experiments. Our numerical predictions fall in that range. Another interesting feature of Utada et al.’s experiment is that their dripping-jetting transition is accompanied by a discontinuous jump in the drop size. This has to do with the geometry of their setup, where the outer fluid does not go through a long conduit before exiting into the collection tube. Thus it has a roughly flat velocity profile at the orifice, and develops a parabolic profile only far downstream. The drop formation at the orifice in dripping, consequently, differs qualitatively from the pinch-off far downstream in jetting. This contrasts our geometry where both streams develop parabolic profiles inside the relatively long nozzle. Our dripping-jetting transition is gradual and there is no sudden change in the drop size (Fig. 2.8). Finally, Utada et al. considered drop pinch-off in their jetting regime as due entirely to capillary instability, and this is supported by a scaling relationship for the drop size. As indicated earlier, a similar scaling does not hold in our case.

In addition to dripping and jetting, we have also observed a regime for large outer flow rates $Q_o$ coupled with small inner flow rates $Q_i$ where a very thin jet is drawn into the nozzle and breaks up into small droplets inside the nozzle, with diameter on the order of $1/10$ of the nozzle radius $a$ (Fig. 2.12). For its resemblance to the so-called “tipstreaming” phenomenon (Taylor, 1934), we may call this the tipstreaming regime. In the literature, tipstreaming is usually regarded as due to accumulation of surfactants at the downstream stagnation point of a drop (de Bruijn, 1993; Eggleton et al., 2001; Renardy et al., 2002). In appearance, it is also similar to electrospaying where a micro-thread is drawn from the tip of a Taylor cone by electrostatic forces (Cloupeau & Prunetfoch, 1994). But our tipstreaming involves neither surfactants nor electric fields, and is purely hydrodynamic. Previous theoretical models have shown the possibility of surfactant-free tipstreaming when a thin filament is drawn from a drop by an extensional flow (Tomotika, 1936; Sherwood, 1984). In our simulation of the flow-focusing devices, the contraction flow into the nozzle creates a similar scenario in the limit of small $\Gamma = Q_i/Q_o$. When the
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Figure 2.13: Geometric setup for simulating the formation of compound drops. Shown is the meridian plane of an axisymmetric device, and the computational domain is the top half.

thin thread enters the nozzle, it breaks up into small drops due to Rayleigh instability. Finally, Garstecki et al. (2005) reported a peculiar capillarity-independent “displacement regime” for forming bubbles and drops in a flow-focusing device at exceedingly low flow rates. We did not attempt to reproduce it computationally.

2.3.3 Formation of compound drops in a flow-focusing device

A compound drop consists of an inner fluid enclosed by a fluid shell that is suspended in an outer fluid. For the past few decades, double emulsions composed of water-in-oil-in-water compound drops have been studied as a means for delivering drugs dissolved in the inner aqueous phase enterally (Engel et al., 1968; Oba et al., 1992). But the conventional method of shearing in mixers produces double emulsions whose size distribution is hard to control. New techniques for making compound drops have appeared, including the breakup of compound jets under electrohydrodynamic forcing (Loscertales et al., 2002) and microencapsulation by a solvent exchange method (Yeo et al., 2004). More recently, several groups demonstrated the possibilities of using microfluidic devices for mass-producing highly monodisperse compound drops (Atencia & Beebe, 2005; Joanicot & Ajdari, 2005) and for fabricating micron-sized polymer capsules and vesicles (Utada et al., 2005; Takeuchi et al., 2005). A great advantage is the precise control, through the flow rates, of the inner and outer drop sizes as well as the number of droplets encapsulated in each larger drop.

In this subsection, we describe numerical simulations aimed at elucidating the formation of compound drops in a flow-focusing device. The axisymmetric computational domain in Fig. 2.13 is loosely based on the experimental device of Utada et al. (2005), which employs three streams to produce compound drops in a single step. In our setup, the three streams flow in the same direction, while in the experiment, the outermost stream issues from openings located on the shoulder of the contraction. Thus, it comes in the opposite direction and forms a contact line with the intermediate fluid on the outer
In either case, a compound jet forms and is forced through the contraction. Mesh sizes are $h_1 = 0.01a$ on the interfaces, $h_2 = 0.1a$ in the bulk of the middle fluid and $h_3 = 0.2a$ for the bulk of the inner and outer fluid. The capillary width $\epsilon = 0.02a$, and the interface is resolved adequately.

One may choose the following set of dimensionless parameters for the process: a capillary number $Ca$ and a Weber number $We$ for the inner fluid (defined using the average velocity in the inner tube, the inner fluid density and viscosity, and the inner-middle interfacial tension), the density, viscosity and flow-rate ratios among the three fluids, the ratio of interfacial tensions among the fluid pairs, and various length ratios. In this work, we did not aim to map out the entire parameter space; indeed that task would be extremely laborious if at all possible. Instead, we have probed a few parameters, including $Ca$, $We$ and the viscosity ratios, with the goal of achieving a preliminary understanding of the process. Utada et al. used two grades of silicone oil for the inner and outer fluid and a water-glycerol mixture for the middle fluid, with inner-middle-outer viscosity ratios of 1 : 1 : 9.6. In our phase-field model, however, it is cumbersome to represent three species, and we have thus made the inner and outer fluids identical. Furthermore, we fix the inner-middle-outer flow-rate ratios at 3 : 6 : 40, and the middle-outer density ratio at $\alpha = 1$. The middle-outer viscosity ratio $\beta = 1$ except for the results in Fig. 2.16. As an initial condition, we have the middle fluid forming a hemispherical shell enclosing the inner fluid, and the outer fluid filling the rest of the domain. Parabolic velocity profiles are specified at the inlets for the three streams with zero stress conditions at the exit and symmetry conditions along the centerline. Most results are presented in dimensionless form, but a few quantities of more direct practical relevance, such as the frequency of drop formation, are given in dimensional form. These are computed using characteristic values based on experiments: $a = 20 \mu m$, $\rho = 1 \text{ g/cm}^3$ and $\sigma = 20 \mu \text{N/m}$.

Figure 2.14 illustrates the temporal evolution of the process that consists of the formation of a co-axial compound jet and its subsequent breakup into compound drops. The inner jet undergoes what appears to be Rayleigh instability, with capillary waves growing on the interface. Meanwhile, capillary waves develop on the outer interface as well, with a longer wavelength. The shrinking neck on the outer interface pinches in on the inner interface, and helps the inner jet to pinch off at a point some distance upstream of its naturally occurring neck (Fig. 2.14a). Thus, the waveform behind the front bulb of the inner jet is divided, with the front part shrinking forward and merging into the inner drop (Fig. 2.14b). Then the outer interface pinches off and encapsulates the inner drop (Fig. 2.14c,d). The process then starts again. One notable difference from the formation of simple drops is that the process here is much more irregular. The position on the inner jet where the outer jet pinches in varies somewhat from one cycle to the next, resulting in 3.4% and 4.5% variations in the inner and outer drop sizes. The duration of each cycle varies by 14.6%. Averaged over 10 drops in the run depicted in Fig. 2.14, the inner drop radius is $0.97a$ and the outer drop radius is $1.40a$, and the frequency of drop formation is 1672 Hz. These are comparable to experimental values. The loss of near-perfect periodicity is apparently due to the two modes on the two interfaces not being in harmony.
Compound jets are known to be liable to multiple modes of capillary instability (Radev & Tchavdarov, 1988; Chauhan et al., 2000). In this case, the hydrodynamic mechanisms for breakup of the compound jet are similar to those previously discussed for simple jets. For the parameters used here, the inner and middle fluids have roughly the same velocity in the compound jet. Thus, there is little viscous shear on the inner interface and the breakup is dictated by capillary forces. In contrast, there is considerable shear on the outer interface. Its breakup must have been the combined effect of capillary waves and stretching by a viscous drag. Note, however, that the pinch-off on the inner and outer interfaces are coupled through capillary pressure in the middle fluid.

Indeed, this coupling is essential for achieving successful encapsulation and controlling the morphology of the compound drop. While the process involves a large number of geometric, material and flow parameters, we have only systematically explored the effects of the flow rates and viscosity ratio. The great sensitivity of the encapsulation process to the flow rates is illustrated in Fig. 2.15. Panel (b), a later snapshot from the simulation depicted in Fig. 2.14, shows a proper compound drop with a single inner drop, at $Ca = 4.50 \times 10^{-3}$ and $We = 3.24 \times 10^{-4}$. Panel (a) has the three flow rates reduced by 25%, at $Ca = 3.38 \times 10^{-3}$ and $We = 1.82 \times 10^{-4}$, while (c) has the flow rates increased by 25%, at $Ca = 5.63 \times 10^{-3}$ and $We = 5.06 \times 10^{-4}$. In (a), the smaller flow rates imply a thicker jet and breakup nearer to the expansion, similar to observations of simple drop formation. The wavelength on the outer jet is much longer than that on the inner jet so that two inner drops are encapsulated in one outer drop. In (c), on the other hand, the jet is thinner and longer at higher flow rates. The outer jet necks at a position that is roughly half a waveform upstream from the base of the inner bulb. After pinch-off, the inner drop has a thin thread attached to its base which breaks off into a satellite drop. Thus, we
have qualitatively confirmed observations by Utada et al. (2005) that encapsulation of one or more drops can be controlled by varying the flow rates. In principle, the number of inner drops depends on the ratio of the wavelengths on the two interfaces. In the narrow range of parameters tested, we have successfully encapsulated no more than two inner drops.

With the flow-rate ratios fixed at 3 : 6 : 40 for the inner, middle and outer streams, we have constructed a “phase diagram” in Fig. 2.16 for ranges of the viscosity ratio $\beta$ and inner-flow capillary number $Ca$. Successful encapsulation of one or two inner drops occurs only within a narrow band on the $Ca - \beta$ plane. In particular, if $\beta$ and/or $Ca$ is too low, the middle fluid goes through the contraction much more readily than the more viscous inner fluid. The shell thus ruptures too early and fails to encapsulate the inner fluid (see left panel). On the other hand, if $\beta$ and/or $Ca$ is too high, the breakup of the outer interface is delayed, partly because of viscous damping within the middle fluid and partly because of the small viscous drag exerted on the outer bulb by the low-viscosity outer fluid. In the meantime, the inner jet advances without breaking up for lack of pinching from the outer interface. Thus, the inner bulb eventually presses and ruptures the outer interface, again causing loss of the inner fluid and failure of encapsulation (right panel).

Utada et al. (2005) have observed a dripping regime at low flow rates and a jetting
Figure 2.16: Phase diagram for compound drop formation. The circle indicate formation of compound drops with one or two inner drops, and the crosses failure of encapsulation. The inner and the outer fluids are identical, and the viscosity ratio $\beta$ is between the middle and the outer fluid. $Ca$ is defined for the flow in the inner tube. The inner-middle-outer flow-rate ratios are fixed at $3:6:40$.

regime at high flow rates. Our simulation in Fig. 2.14 corresponds to the latter. In Fig. 2.15, we see that the position of drop pinch-off moves upstream as the flow rates decrease. But encapsulation fails when the flow rates become too small, and we have not reproduced the dripping regime for compound drop formation. Comparing our simulations with video footage from Utada et al.’s experiment, we recognize several possible reasons for this discrepancy. First, we have rectangular corners in the channel that produce a sudden contraction and expansion, while the experiment had smooth and gradual transitions. The latter geometry seems to be more favorable to the innermost fluid getting into the nozzle. A common mode of failure in our simulations, when the flow rates are small, is the failure to draw the inner fluid into the nozzle. It is excluded from the contraction for long, and eventually presses and ruptures the middle fluid upstream of the nozzle (Fig. 2.16, left panel). Second, our fixed flow-rate ratios $3:6:40$ may inhibit dripping. The relatively large middle flow rate implies a thick middle shell, which tends to jet forward before the inner fluid makes its way into the nozzle. In contrast, Utada et al.’s inner-to-middle flow-rate ratio is $4:1$; the inner and middle streams co-flow into the nozzle as a compound jet and pinch-off together. Finally, Utada et al.’s outer fluid is 10 times as viscous as the other two fluids. This may have played a role in dripping as well.

To sum up, many parameters affect the formation of compound drops, of which we have examined only two: $Ca$ and $\beta$. We may speculate that for different flow-rate ratios, the boundaries in Fig. 2.16 will shift. If a compound drop does form, the inner-to-outer drop radius ratio should be determined by the inner-to-middle flow-rate ratio because of mass conservation. Experiments show that the outer drop size decreases with increasing
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outer flow rate (Utada et al., 2005), which is consistent with our simulations for simple drop formation (Fig. 2.8). A more comprehensive parametric study is required to generate a more detailed “operation map” that indicates how drop size and morphology can be controlled via geometry, flow rates and fluid properties.

2.3.4 Effects of viscoelasticity

Many microfluidic applications involve non-Newtonian fluids. Macromolecules occur naturally in biological fluids, and synthetic polymers may be introduced into the fluid components for fabricating micro-scale polymer capsules (Utada et al., 2005; Takeuchi et al., 2005). When the fluids deform, so do the macromolecules. Then viscoelastic stresses arise that may modify the flow and interfacial behavior in return. Such flow-microstructural coupling is well studied in non-Newtonian fluid mechanics. The simulations reported next represent an exploration of similar coupling in drop formation in flow-focusing devices.

The viscoelastic component is modeled by the Oldroyd-B equation (cf. Eqs. 2.3, 2.4), based on a dilute suspension of elastic dumbbells in a Newtonian solvent. The relaxation time of the dumbbells, $\lambda_H$, scaled by the characteristic flow time $t_f = a/V_i$, gives rise to the Deborah number

$$De = \frac{\lambda_H V_i}{a}. \quad (2.17)$$

Rheological predictions of the Oldroyd-B model can be found in Bird et al. (1987) The following parameters are used in the simulations. In simple drop formation, we fix the density ratio $\alpha = 1.11$, viscosity ratio $\beta = 0.167$ and flow rate ratio $\Gamma = 0.25$. We define $\beta$ using the total viscosity $\mu_t = \mu_p + \mu_s$ of the Oldroyd-B model, with equal contribution from the polymer and the solvent $\mu_p = \mu_s$. This $\beta$ is matched with the Newtonian $\beta$ when comparing with simulations in preceding subsections. The geometry is the same as in Fig. 2.4 except that the length of the nozzle is shortened to $2a$. In compound drop formation, we use the same geometry as in Fig. 2.13 and again take the innermost fluid to be identical to the outermost. Furthermore, the viscosity ratio and density ratio between the inner and middle fluids are set to 1, while the inner-middle-outer flow-rate ratios are fixed at $3 : 6 : 40$.

We have simulated the formation of simple drops when the inner fluid (drop phase) is viscoelastic and the outer fluid is Newtonian. The viscoelastic effect turns out to be quite different for the dripping and jetting regimes. Figure 2.17 compares a viscoelastic simulation with its Newtonian counterpart in the dripping regime, all parameters being the same except for the Deborah number. With the non-Newtonian inner fluid, the drop size is larger and the pinch-off occurs further downstream. The polymer tensile stress $\tau_{pyy}$, in the flow direction, attains its maximum at the entrance into the contraction because of the strong acceleration and elongation of the inner fluid. Scaled by the nominal viscous shear stress $\mu_t V_i / a$, this maximum value is $\tau_{pyy} = 3.33 \times 10^3$. Once inside the nozzle, the flow becomes mostly shear and $\tau_{pyy}$ relaxes gradually and vanishes upon exiting the nozzle. Therefore, this stress has no direct bearing on the drop formation. A second local maximum of $\tau_{pyy}$ occurs at the neck where the drop pinches off. Its most significant effect is to delay the pinch-off of the drop. This is evident from the oscillation of the neck.
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Figure 2.17: Simple drop formation in the dripping regime when the inner fluid is (a) viscoelastic, and (b) Newtonian. The snapshots are taken shortly before the drop detaches. $Ca = 2.26 \times 10^{-3}$, $We = 1.02 \times 10^{-3}$. In (a), $De = 0.113$, and the grey-scale contours depict the polymer tensile stress $\tau_{pyy}$ along the flow direction. The drop size is 7.5% larger than in (b), while the critical jet length, from the orifice to the point of pinch-off, is 10.1% longer.

Before the last cycle, the oscillation is similar to its Newtonian counterpart in Fig. 2.6. The period of oscillation $T = 0.20$ ms is slightly longer than the Newtonian period, as the wave speed and the interfacial fluid velocity are both smaller in the viscoelastic case. The last cycle of oscillation, however, takes nearly 0.40 ms. The situation is similar to the capillary breakup of a polymeric thread, where the elevated tensile stress (or elongational viscosity) is known to prolong the thinning of the thread and delay the pinch-off (Li & Fontelos, 2003). As a result, the frequency of drop formation is reduced from 272 Hz in the Newtonian case to 218 Hz. This gives the drop more time to grow from imbibing the fluid through the neck. By the same token, the location of pinch-off is also further downstream.

In the jetting regime, the viscoelastic effect seems to be opposite to that in dripping: the drop size is smaller and the jet length is shorter (Fig. 2.18). The latter can be attributed to the normal stress $\tau_{pyy}$ in the jet, which, unlike in the dripping regime, extends some way downstream beyond the nozzle. This tensile stress, along with capillarity, resists the stretching of the jet by the faster outer fluid. Thus, the jet is shorter. Besides, the most unstable wavelength is shorter on a viscoelastic jet than on a comparable Newtonian one. This has been shown by analysis (Funada & Joseph, 2003) as well as experimental data (e.g., Fig. 8 of Christanti & Walker (2001)). The shorter wavelength implies smaller drops for viscoelastic fluids, as is indeed the case in our simulations. For the same inner flow rate $Q_i$, the pinch-off frequency is higher for the Oldroyd-B drops, 681 Hz compared with 602 Hz for Newtonian drops. Similar to the dripping regime, a second maximum of polymer stress occurs at the neck before the bulb. Although this
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Figure 2.18: Simple drop formation in the jetting regime when the inner fluid is (a) viscoelastic and (b) Newtonian. $Ca = 7.15 \times 10^{-3}$, $We = 1.02 \times 10^{-2}$. In (a), $De = 0.357$, and the grey-scale contours depict the polymer tensile stress $\tau_{pyy}$ along the flow direction, with a maximum $\tau_{pyy} = 1.49 \times 10^3$, scaled by $\mu L V_i / a$. Compared with the Newtonian case, the jet length is 9.0% shorter for the viscoelastic case and the drops are 4.0% smaller in diameter.

tends to prolong the pinch-off process, its effect is apparently overwhelmed by the effects discussed above.

In compound drop formation, viscoelasticity in each of the three streams may have different effects on the process. Motivated by experiments that employ compound drops for making polymeric hollow spheres (Utada et al., 2005; Takeuchi et al., 2005), we have only simulated the situation where the middle fluid is an Oldroyd-B fluid while the inner and outer streams are identical Newtonian fluids (Fig. 2.19). Results show that the viscoelastic effect on the compound drop is similar to that on the simple drop in the jetting regime (Fig. 2.18). The length of the outer jet (from the orifice to the point of pinch-off) is shorter by 5.3%, and the outer drop size is smaller by 2% than their Newtonian counterparts. The inner-outer drop size ratio is unaffected by viscoelasticity as long as a single inner drop is enclosed in the outer drop, since it is determined by the flow-rate ratio. With the Deborah number $De$ as a new parameter, the phase diagram should be modified as well, but we have not done extensive parameter sweeps to determine such modifications.

Another interesting and potentially useful effect of viscoelasticity in the middle fluid is in suppressing satellite drops when the inner jet breaks up. In an all-Newtonian system, a satellite drop is sometimes enclosed in the outer drop along with the primary drop; see Fig. 2.19(a) and Fig. 2.15(c). Depending on the applications, this may be undesirable. Figure 2.19(b) and (c) show that in otherwise identical conditions, viscoelastic stress in the middle fluid eliminates the satellite drop. This is similar to the suppression of satellite drops by polymers in a jet (Christanti & Walker, 2001). As the inner jet pinches at the neck, the tensile stress $\tau_{pyy}$ develops in a thin sheath around the neck. Apparently
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Figure 2.19: Viscoelastic effects on compound drop formation. All 3 fluids are Newtonian in (a). The middle fluid is viscoelastic in (b) and (c), two snapshots following pinch-off of the inner jet. $Ca = 4.50 \times 10^{-3}$, $We = 3.24 \times 10^{-4}$, and $De = 0.090$ for (b) and (c). The times are made dimensionless by the flow-time $t_f = a/V_i$. The grey-scale contours indicate the level of polymer tensile stress $\tau_{pyy}$ in the middle fluid, with a maximum on the order of $\tau_{pyy} = 4.20 \times 10^3$, scaled by $\mu t_i V_i/a$.

the stretching inside the jet induces similar deformation in its immediate surroundings. Upon pinch-off, the newly formed ends retract much more slowly than in a Newtonian surrounding fluid. Evidently, the large tensile stress in the middle fluid resists the capillary retraction and suppresses end-pinching (Fig. 2.19b,c). Eventually the thread shrinks into the primary drop without secondary breakup. Recent experiments (Chen et al., 2006) have shown that polymer dissolved in the surrounding fluid has similar effects on capillary breakup to that inside the thread. That is, it tends to produce a thin and long-lasting filament and delay the breakup, and sometimes lead to the beads-on-a-string morphology. In our case, we do not see beads-on-a-string. This is probably because the time scale of the process is too short.

2.4 Summary

The numerical simulations presented in this paper have reproduced scenarios of jet breakup and drop formation previously observed in experimental flow-focusing devices. The diffuse-interface model is suitable for such flows involving interface rupture. For
simple drops, parametric studies have shown dripping and jetting regimes for increasing flow rates, and elucidated the effects of flow and rheological parameters on the drop formation process and the final drop size. In particular, the pinch-off is shown to depend on both capillary instability and stretching of the interface by viscous drag. To produce compound drops, the capillary waves on the inner and outer interfaces need to be coordinated and we have identified a narrow window of flow-rate and viscosity ratios in which this can be achieved. Viscoelastic effects are manifested by large elongational stresses in portions of the jet that experience strong stretching. These stresses suppress satellite drops and may increase or decrease the final drop size depending on the flow regime. To varying degrees, these results advance our understanding of the fundamental physics and provide a guideline for design of microfluidic devices.
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Chapter 3

Simulation of neutrophil deformation and transport in capillaries using Newtonian and viscoelastic drop models

3.1 Introduction

Neutrophils often encounter narrow capillary segments during their transit through the pulmonary and systemic microcirculations. Because the neutrophil diameter (6–8 μm) often exceeds the diameter of a pulmonary capillary (2–15 μm) (Doerschuk et al., 1993; Yap & Kamm, 2005b), cell deformation is necessary for passage. It is well known that neutrophils take much longer to traverse the pulmonary capillary bed than erythrocytes (Hogg et al., 1994). As a result, white cells accumulate in the lungs and form a reservoir from which they may be readily recruited when needed (Lien et al., 1987; Doerschuk et al., 1993). As the pulmonary bed consists of 50–100 capillary segments (Huang et al., 2001; Bathe et al., 2002), the longer transit time for neutrophils likely reflects their relatively poor deformability (Wiggs et al., 1994; Doerschuk, 1999), which in turn depends on the structure and mechanical properties of the cell: membrane rigidity, cytoplasmic viscosity and viscoelasticity, and the properties of the nucleus.

Measuring leukocyte deformation and transit in vivo is a difficult task (Hogg et al., 1994), and so far our understanding of the mechanical behavior of leukocytes has come mostly from micropipette aspirations in vitro. By measuring the time-dependent cell deformation at a controlled pressure, cell viscosity, cortical tension and elastic modulus can be estimated by treating the cell as a homogeneous continuum (Evans & Yeung, 1989; Hochmuth, 2000). As a sort of rheometry, aspiration experiments yield fundamentally important data. But they do not produce direct information on cell transit in capillaries. by particle-tracking while the cell undergoes structural changes and activation. This cannot be reflected in our simulations as an advantage. The Cell Transit Analyzer (Fisher et al., 1992) combines the aspiration process with subsequent passage through cylindrical pores, and allows rapid measurements of transit time. However, the cell entry and departure from the micropore is monitored from the attendant pulses in electric conductivity across the filter. The actual deformation of the cell is unknown and the interpretation of the signal is subject to much uncertainty (Fisher et al., 1992; Drochon, 2005).

Recently, Yap & Kamm (2005b) carried out an experiment using microfluidic channels

that seems to have overcome previous difficulties. The device allows direct observation of neutrophil deformation and activation upon entering a microfluidic channel, as well as measurement of the cell entrance time as a function of the pressure drop imposed across the microfluidic channel. The present work is motivated by Yap and Kamm’s experiment, and aims to extract a fundamental understanding of the cell entry process using dynamic simulations. Yap & Kamm (2005b) also reported interesting results on neutrophil activation probed by microrheology and pseudopod formation. These will not be accounted for in our simulations.

Analyzing the physical and mechanical processes on the single-cell level remains a challenge, especially when taking the living and dynamic nature of the cell into consideration (Bao & Suresh, 2003). Lim et al. (2006) reviewed the quantitative mechanical models developed so far for the cell. Generally, these adopt either a microstructural approach or a continuum approach. The former is based on the cytoskeleton as the main structural component, and has been used widely to investigate cytoskeletal mechanics in adherent cells (Stamenovic & Ingber, 2002). On the other hand, the continuum approach takes the cell as comprising homogeneous materials with certain effective properties. Although providing less insight into the details of intra-cellular processes, the latter is simpler and has found applications in simulating large-scale transient behavior of suspended cells such as the corpuscles in the blood (Kamm, 2002; Pozrikidis, 2003a, 2005).

Continuum cell models come in several flavors. The Newtonian liquid drop model (Yeung & Evans, 1989; Evans & Yeung, 1989) sees the cell as a homogeneous Newtonian drop enclosed by a cortex that has a constant and isotropic tension and negligible viscous dissipation. Non-Newtonian drop models, such as the shear-thinning model (Tsai et al., 1993) and the viscoelastic Maxwell model (Dong et al., 1988), have since been developed to reflect the non-Newtonian rheology of the cytoplasm in leukocytes. Furthermore, compound drop models (Dong et al., 1991; Hochmuth et al., 1993; Kan et al., 1998, 1999) explicitly account for the cell nucleus as a drop suspended in the cytoplasm. The cell and nuclear membranes are taken to be interfacial layers with differing interfacial tensions. So far, micropipette aspiration has been the benchmark problem for testing these models, and the prediction has been remarkably good considering the simplicity of the models (Dong et al., 1988; Yeung & Evans, 1989; Dong & Skalak, 1992; Drury & Dembo, 2001). Moreover, the models have been used to simulate other modes of controlled deformation in relatively simple geometries, e.g., recovery in a quiescent medium (Tran-Son-Tay et al., 1991, 1998; Kan et al., 1999) and deformation in elongational flows (Kan et al., 1998) and shear flows (Pozrikidis, 2003b, 2005). Most recently, the compound drop models have been applied in simulating the adhesion of leukocytes on the endothelium (Li & Wang, 2004; Khismatullin & Truskey, 2005; Jadhav et al., 2005). However, only a few simulations have been carried out on the transit of suspended neutrophils, either through a single capillary (Tran-Son-Tay et al., 1994; Bathe et al., 2002) or an idealized capillary network (Huang et al., 2001).

The present study consists of dynamic simulations, based on the Newtonian and viscoelastic drop models, of the deformation and transit of neutrophils through capillaries that roughly correspond to the experiments of Yap & Kamm (2005b). Specifically, we
study the entry of a neutrophil from a larger vessel into a narrow capillary using geometry and parameter values based on the Yap-Kamm experiments. The entrance time, the cell deformation and the subsequent motion within the capillary will be compared with observations. The focus of the study will be on how cytoplasmic rheology affects the entry of a neutrophil into a thin capillary. The nucleus is not explicitly accounted for, and the cytoplasmic rheology should be understood as an averaged property of the complex mixture of the nucleus, cytosol and suspended organelles. Furthermore, we have neglected two physiologically important factors. First, the cell membrane is treated as thin interfaces having a constant cortical tension, with no elastic resistance against bending and in-plane shearing and no viscous dissipation. We recognize that membrane elasticity has an important role in cell deformation that has received a great deal of research (Eggleton & Popel, 1998; Pozrikidis, 2003a). Although membrane elasticity may be incorporated into the phase-field theory (Du et al., 2004; Du & Zhu, 2006), we defer the implementation to a future effort. Second, we have not accounted for the glycocalyx on the inner walls of the capillary, which is known to greatly increase resistance on red blood cells (Feng & Weinbaum, 2000; Secomb et al., 2001). This is partly because very little is known of the glycocalyx on the pulmonary endothelium, and partly because incorporating the porous layer model would greatly increase the complexity of the flow simulation. So far, the only multi-dimensional computation that accounts for the glycocalyx used a drastically simplified model of a frictionless contact surface (Bathe et al., 2002).

In the context of computational fluid dynamics, our problem is a complex one because of the moving and deforming interfaces and the non-Newtonian rheology of the fluid components, each being a major computational challenge (Sethian & Smereka, 2003; Owens & Phillips, 2002). Recently, we have developed a diffuse-interface method that incorporates the moving interface and non-Newtonian rheology in a unified variational framework (Yue et al., 2004; Feng et al., 2005). Implemented using spectral methods and finite elements, the method has been applied successfully to several problems in drop dynamics of complex fluids (Yue et al., 2005a,b,d,c, 2006b; Zhou et al., 2006; Yue et al., 2006a), and will be adapted here to the task of neutrophil deformation and transport.

3.2 Theory and numerical methods

Our diffuse-interface model was developed mainly for simulating interfacial dynamics in complex fluids. For any binary blend, the two nominally immiscible components are assumed to mix in a narrow interfacial layer and store a mixing energy. Across the interfacial layer, physical properties such as viscosity and density change steeply but continuously. The interfacial position and thickness are determined by a phase-field variable $\phi$ whose evolution is governed by a Cahn-Hilliard equation. The interfacial tension is given by the mixing energy. This way, the structure of the interface is rooted in molecular forces and calculated from a convection-diffusion equation; there is no longer a need for tracking the interface. Moreover, the model uses an energy-based formulation that incorporates the non-Newtonian rheology of microstructured fluids with ease. This is the main reason for our selecting this methodology. A more in-depth discussion of
the advantages and disadvantages of the diffuse-interface model, vis-à-vis the classical sharp-interface model and other interface regularization methods, can be found in the literature (Lowengrub & Truskinovsky, 1998; Yue et al., 2004; Feng et al., 2005).

The above methodology has been implemented in a finite-element package AMPHI (Adaptive Meshing with phase field φ). Yue et al. (2006b) have described the code in detail and presented numerical experiments to establish its validity and accuracy. In this paper, we will only summarize the main ideas and give the governing equations. To be specific, consider a Newtonian fluid in contact with a viscoelastic Oldroyd-B fluid, the interface between the two being diffuse with a small but non-zero thickness. We define a phase-field variable \( \phi \) such that the concentrations of the non-Newtonian and Newtonian components are \( (1 + \phi)/2 \) and \( (1 - \phi)/2 \), respectively. Then \( \phi \) takes on a value of 1 or \(-1\) in the two bulk phases, and the interface is simply the level set \( \phi = 0 \). Starting with the system’s free energy, comprising the mixing energy of the interface and the bulk elastic energy in the Oldroyd-B fluid, we can derive the following set of governing equations (Yue et al., 2005a, 2006b):

\[
\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma \nabla^2 G, \tag{3.1}
\]

\[
G = \lambda \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\epsilon^2} \right], \tag{3.2}
\]

\[
\mathbf{\tau}_p + \lambda_H \mathbf{\tau}_{p(1)} = \mu_p [\nabla \mathbf{v} + (\nabla \mathbf{v})^T], \tag{3.3}
\]

\[
\mathbf{\tau} = \left( \frac{1 - \phi}{2} \mu_n + \frac{1 + \phi}{2} \mu_s \right)[\nabla \mathbf{v} + (\nabla \mathbf{v})^T] + \frac{1 + \phi}{2} \mathbf{\tau}_p, \tag{3.4}
\]

\[
\begin{align*}
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) &= \nabla \cdot (-p \mathbf{I} + \mathbf{\tau}) + G \nabla \phi + \rho g, \\
\nabla \cdot \mathbf{v} &= 0,
\end{align*} \tag{3.5}
\]

where \( G \) is the chemical potential and \( \gamma \) is the mobility parameter; \( \lambda \) and \( \epsilon \) are the interfacial energy density and capillary width, respectively. The polymer stress \( \mathbf{\tau}_p \) obeys the Maxwell equation, with the subscript \((1)\) denoting the upper convected derivative and \( \lambda_H \) being the polymer relaxation time (Bird et al., 1987). \( \mu_p \) and \( \mu_s \) are the polymer and solvent contributions to the shear viscosity of the Oldroyd-B fluid, and \( \mu_n \) is the viscosity of the Newtonian phase. \( \rho \) is a mixture density: \( \rho = \frac{1 + \phi}{2} \rho_1 + \frac{1 - \phi}{2} \rho_2 \), \( \rho_1 \) and \( \rho_2 \) being the densities of the Oldroyd-B and Newtonian components, and \( g \) is the gravitational acceleration. As demonstrated elsewhere (Yue et al., 2005a, 2006b), the diffuse interface has two important features: (a) The interface has a thickness on the order of \( 5\epsilon \). The Cahn-Hilliard dynamics ensures that it neither collapses into a sharp surface nor diffuses into a wide region. (b) In the limit of \( \epsilon \to 0 \), the above system reduces to the familiar sharp interface formulation, and \( 2\sqrt{2}\lambda/3\epsilon \) gives the interfacial tension (Yue et al., 2004). The velocity and shear stress are continuous across the interface and the normal stress has a jump consistent with the interfacial tension. To accurately reproduce the cortical tension on a thin “membrane”, therefore, we must use an \( \epsilon \) that is much smaller than the overall dimension and must resolve the \( \phi \) profile adequately within the thin interface. This is why adaptive meshing is essential to AMPHI (Yue et al., 2006b).
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Figure 3.1: The geometric setup for simulating a neutrophil’s entrance into a capillary. Two cylindrical tubes are connected by an arc of 90°. Shown is the meridian plane and the upper half is the computational domain.

These equations are discretized on a finite-element grid using the Petrov-Galerkin formulation with streamline upwinding for the constitutive equation. We will concern ourselves only with axisymmetric geometry in this study, and the 2D computational domain is covered by an unstructured grid of triangular elements. To resolve the thin interfacial region, we have used an adaptive meshing scheme based on the public-domain package GRUMMP (Freitag & Ollivier-Gooch, 1997). The scheme allows one to control the spatial gradient of grid size using a scalar field. In our application, the phase-field variable $\phi$ is a natural choice for this function. Thus, we have a belt of refined triangles covering the interfacial region. As the interface approaches the edge of the belt, remeshing is performed with the mesh upstream of the interface being refined by edge bisection and/or node insertion while that left behind being coarsened. Typically the interfacial layer requires roughly 10 grid points to resolve, and remeshing happens over tens of time steps. We use implicit time-stepping, with Newton iteration at every step to handle the nonlinearity in the equations. The time step is automatically adjusted according to a set of criteria based on the normal velocity of the interface and the bulk velocity. Numerical experiments with grid refinement and time-step refinement have been carried out (Yue et al., 2006b), and adequate resolution is ensured for the simulations presented in the following.

3.3 Simulations using the simple Newtonian drop model

As the simplest model for a neutrophil, we have a liquid drop containing a homogeneous viscous Newtonian fluid that represents the cytoplasm and nucleus in an average sense. The interfacial tension $\sigma$ represents a constant and isotropic tension in the cell membrane. The drop fluid, or “cytoplasm”, has a density $\rho_c$ and a viscosity $\mu_c$, and the cell is suspended in a matrix of density $\rho_m$ and viscosity $\mu_m$. Before deformation, the spherical cell has a radius $r_c$. To simulate the entry of the neutrophil into a capillary, we use the axisymmetric computational domain illustrated in Fig. 3.1. The narrow capillary downstream of the contraction has a radius $a$ and length $L = 10a$. A constant pressure drop $\Delta P$ is applied over the entire length of the domain $19a$. To construct the
Figure 3.2: (a) The microchannel of Yap & Kamm (2005b). The scale bar is 100 μm, and the two arrows indicate the microchannel and the reservoir. (b) Schematic showing the dimensions of the microchannel. Its cross-section is rectangular with a width of 5 μm and a depth of 2.5 μm. After Yap & Kamm (2005b); ©2005 the American Physiological Society.

dimensionless groups controlling the process, we use \( a \) as the characteristic length and \( V_f = \Delta P a^2/(8 \mu_m L) \) as the characteristic velocity. Note that \( V_f \) is the average velocity in a Poiseuille flow through a uniform pipe of radius \( a \) with pressure gradient \( \Delta P/L \). Then five dimensionless groups can be constructed:

\[
Ca = \frac{\mu_m V_f}{\sigma},
\]

\[
Re = \frac{\rho_m V_f a}{\mu_m},
\]

\[
\alpha = \frac{\rho_c}{\rho_m},
\]

\[
\beta = \frac{\mu_c}{\mu_m},
\]

\[
\zeta = \frac{r_c}{a},
\]

where the capillary number \( Ca \) indicates the ratio between viscous and capillary forces, and the Reynolds number \( Re \) represents the ratio between inertial and viscous forces. The characteristic flow time is \( t_f = a/V_f \), and the flow rate will be scaled by \( Q_f = \pi a^2 V_f \).

For brevity, we use the same symbols for dimensional and dimensionless variables, but will explicitly indicate which is meant where confusion may arise.

The cell radius, effective viscosity and cortical tension of the neutrophil are taken from the literature (Evans & Yeung, 1989; Yap & Kamm, 2005b; Lim et al., 2006): \( r_c = 3.5 \mu m, \mu_c = 2.2 \) poise and \( \sigma = 0.035 \) dyn/cm. The plasma density and viscosity are essentially those of water. The neutrophil is nearly neutrally buoyant and we have taken the density ratio \( \alpha \) to be unity in all the simulations. The dimensions in Fig. 3.1, with \( a = 2 \) to 2.5 μm, approximate these in the experiment of Yap & Kamm (2005b) (Fig. 3.2). But their microchannel has a rectangular cross-section and an exact match is impossible. For the typical flow rates in the experiments (Yap & Kamm, 2005b), the capillary number \( Ca \) ranges up to 0.1 and the Reynolds number \( Re = O(10^{-3}) \). Thus inertia has little
part in the dynamics to be discussed. The viscosity ratio $\beta$ is on the order of 200 for an activated neutrophil and may be as large as $10^4$ before activation (Yap & Kamm, 2005b; Evans & Yeung, 1989; Lim et al., 2006). Highly viscous cells deform less and tend to press tightly against the channel walls at the entrance. For lack of a proper treatment of the membrane-wall interaction, such cells often stick to the wall. This drawback limits us to $\beta$ values on the order of 50. For convenience, therefore, we have used relatively small $\beta$ values. Varying $\beta$ between 1 and 16 shows a clear trend in the results and we did not explore higher $\beta$ values systematically.

As mentioned before, we use an adaptive meshing scheme to resolve the thin interfacial region so as to produce an accurate cortical tension. In all the simulations, we have used a capillary width $\epsilon = 0.008a$. The finest grids occur at the interface with grid size $h_1 = 0.005a$, while the bulk mesh size inside and outside the cell are $h_2 = 0.12a$ and $h_3 = 0.2a$, respectively. These, along with the time step $\Delta t$, have been tested in numerical experiments (Yue et al., 2006b) to ensure adequate resolution. At the beginning of the simulation, the cell is placed on the centerline at $x = 5a$ and the velocity is zero everywhere. Then the pressure drop $\Delta P$, imposed over the whole length of the domain, drives a flow from the left to the right in Fig. 3.1. At the inlet and the outlet, we set the boundary conditions to be $v = 0$ and $\partial u/\partial x = 0$. On the centerline we use symmetry conditions: $v = 0$ and $\partial u/\partial y = 0$.

### 3.3.1 The process of cell deformation and entrance

For one set of parameters, the process of cell entrance is illustrated by the snapshots in Fig. 3.3. The variations of the flow rate $Q$ and cell length $l$ are plotted in Fig. 3.4 as functions of time. One may discern four stages in the process. ($i$) First, the neutrophil deforms and moves into the contraction while the flow rate drops sharply ($t < 5$). This is because the front of the cell is sucked into the capillary and plugs most of the flow area. The cell length increases steadily, and this stage continues until roughly half of the cell is within the capillary. ($ii$) Once the plugging of the capillary has reached its maximum level, the flow rate more or less keeps constant until the whole cell enters the capillary ($5 < t < 9$). The elongation of the cell continues in this second stage; its rear is “held” by the contraction while its front is stretched by the flow (Fig. 3.3c). ($iii$) The third stage is a transient as the rear of the cell clears the contraction ($9 < t < 12$). As the contraction loses its “grip” on the cell (Fig. 3.3d), the high capillary pressure inside its rear produces a sudden forward flow and a retraction of the cell’s back surface. This temporary shortening of the cell (see Fig. 3.4) in turn increases the blockage in the capillary and causes the flow rate to drop. Both $l$ and $Q$ recover in time as the cell attains an equilibrium shape. ($iv$) Finally, the cell moves downstream with a constant shape and velocity ($t > 12$).

The scenario described above is observed for most of the simulations but is not universal; some aspects vary depending on the parameter values. In section 3.3.3, we will see different behaviors of the flow rate in stage ($ii$) for higher and lower cell viscosities (cf. Fig. 3.7). In the more extreme case of very high pressure drops, both the flow rate
Figure 3.3: Snapshots of the neutrophil during its entrance into the capillary. $Ca = 0.0893$, $\beta = 3$ and $\zeta = 1.4$. Time is made dimensionless by $t_f = a/V_f$.

Figure 3.4: Variations of the flow rate $Q$ and cell length $l$ during the entrance process. $Q$ is made dimensionless by $Q_f$. The cell length $l$ is the distance between the foremost and rearmost points of the cell and is scaled by $a$. $Ca = 0.0893$, $\beta = 3$ and $\zeta = 1.4$.

and the cell length vary monotonically, and no obvious stages can be discerned. This is because the cell is highly elongated by the contraction flow upstream of the capillary and the entry becomes relatively uneventful. We have observed in the simulations that the flow rate $Q$ and cell length $l$ generally vary in opposite directions (cf. Fig. 3.4). This will be explained in the next subsection in terms of the increased flow resistance due to the cell.
Figure 3.5: Log-log plot of the dimensionless entrance time $\tau_{\text{ent}}$ as a function of the capillary number $Ca$. The data points are numerical results while the solid curve represents Eq. (3.18) derived from scaling arguments. $\beta = 3$ and $\zeta = 1.4$. Time is made dimensionless by $a/V_f$, and $Ca$ is defined using the applied pressure $\Delta P$ in Eq. (3.7).

### 3.3.2 The entrance time

As in Yap and Kamm’s experiment (Yap & Kamm, 2005b), we define the entrance time $\tau_{\text{ent}}$ as the time interval between the leading edge of the cell crossing the entry to the capillary (namely, the axial position where the straight portion of the capillary starts) and its trailing edge clearing the entry. Figure 3.5 shows the numerically computed $\tau_{\text{ent}}$ for a range of applied pressure drop (or capillary number). The dimensionless entrance time increases with the imposed pressure; the slope suggests a weak power-law with an index of around 0.1. Intuitively, the dimensional $\tau_{\text{ent}}$ should decrease with $\Delta P$ or the velocity $V_f$ since a higher pressure will induce a faster flow and a more rapid entry of the cell. If the cell followed the surrounding fluid perfectly, its velocity would be proportional to $V_f$ and the dimensionless entrance time, scaled by $a/V_f$, would be independent of the imposed pressure or the flow rate. In reality, however, the cell’s motion is hindered by the channel walls. The weak increase of $\tau_{\text{ent}}$ with $Ca$ in Fig. 3.5 suggests that the cell lags the matrix fluid more at faster flow rates. In the following, we will provide a more quantitative explanation for the effect using scaling arguments.

With negligible inertia, the constant pressure drop $\Delta P$ is entirely expended on overcoming the viscous friction on the channel walls. The presence of the cell increases the wall friction in its vicinity. To quantitate this effect, we adopt a simplified geometry of the cell. Figure 3.3 suggests that during much of the entry process, the rear of the cell is constricted by the pinch and hardly moves forward. The front of the cell extends into the capillary in a slug shape. We make three assumptions about the gap $\delta$ between the cell and the capillary wall: (a) $\delta$ is much smaller than the capillary radius $a$; (b) $\delta$ is constant
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along the length of the cell $l_c$ that is inside the capillary; (c) $\delta$ does not change in time during the entry process. Volume conservation of the cell then allows us to calculate $\delta$ from the cell length $l_c$ at the end of the entry process:

$$\delta = a - \sqrt{\frac{4r_c^3}{3l_c}},$$

(3.12)

$r_c$ being the radius of the initial spherical cell. Note that we have assumed a cylindrical shape for the part of the cell inside the capillary. Now the pressure drop $\Delta P$ can be divided into two parts: $\Delta P_{\text{cell}}$ to overcome the elevated wall friction over the cell length $l_c$ inside the capillary, and $\Delta P_{\text{wall}}$ for the rest of the channel wall. The former will be calculated from the shear rate inside the gap $\delta$, while the latter is to be estimated from the pressure drop needed to drive the same flow rate in the absence of the cell. This dichotomy is not exact, and further simplifications will be made in the following. The errors will be lumped in the end into a single adjustable coefficient.

At the instantaneous flow rate $Q$, the velocity within the gap scales with $Q/(2\pi a \delta)$ and the viscous shear stress scales with $\mu_m Q/(2\pi a \delta^2)$. Because of the tangential velocity on the cell surface, the actual flow rate through the gap $\delta$ is smaller than $Q$. But this discrepancy will be accounted for by the adjustable coefficient. Balancing $\Delta P_{\text{cell}}$ against the shear stress in the gap leads to the scaling

$$\Delta P_{\text{cell}} \propto \frac{\mu_m}{\pi a^2 \delta^2} Q l_c,$$

(3.13)

For $\Delta P_{\text{wall}}$, we modify the Poiseuille formula on account of the wider section and the contraction upstream of the capillary:

$$\Delta P_{\text{wall}} = \frac{9.9\mu_m}{\pi a^4} Q (L - l_c),$$

(3.14)

where the coefficient 9.9 is determined for our geometry from pressure drop in the absence of the cell. Now we may write the total pressure drop as

$$\Delta P = \Delta P_{\text{wall}} + \Delta P_{\text{cell}} = \frac{9.9\mu_m}{\pi a^4} Q (L - l_c) + c \frac{\mu_m}{\pi a^2 \delta^2} Q l_c.$$

(3.15)

The adjustable parameter $c$ accounts for the geometric simplifications made above and the slip velocity on the cell surface. Therefore, it should depend on the geometry and the cell-matrix viscosity ratio $\beta$. It is to be determined by fitting the entrance time. As the presence of the cell increases the local wall friction, Eq. (3.15) implies that if $l_c$ increases, the flow rate $Q$ will decrease and vice versa. This explains the trend in Fig. 3.4.

As $l_c(t)$ is the cell length within the capillary, it increases in time from 0 at the start of cell try to $l_e$ at the end. Thus, the entry time $\tau_{\text{ent}}$ is largely determined by how fast the cell is elongated by the flow. Since the rear of the cell moves little in this process (cf. Fig. 3.3), cell elongation depends on the motion of its leading edge. We assume that this

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Figure 3.6: The cell length $l_e$ at the end of the entry process as a function of the capillary number $Ca$ for $\zeta = 1.4$ and $\beta = 3$.

Figure 3.6: The cell length $l_e$ at the end of the entry process as a function of the capillary number $Ca$ for $\zeta = 1.4$ and $\beta = 3$.

motion is at the instantaneous average velocity within the capillary: $dl_c/dt = Q/(\pi a^2)$. Then Eq. (3.15) leads to an ordinary differential equation for the cell length $l_c(t)$:

$$\Delta P = \mu_m \left[ \frac{9.9(L - l_e)}{a^2} + \frac{cl_e}{\delta^2} \right] \cdot \frac{dl_c}{dt}.$$  \hfill (3.16)

Now the entrance time $\tau_{ent}$ can be obtained by integrating the above equation:

$$\tau_{ent} = \frac{\mu_m}{\Delta P} \left[ \frac{4.95(2Ll_e - l_e^2)}{a^2} + \frac{cl_e^2}{2\delta^2} \right].$$  \hfill (3.17)

Noting that $L = 10a$ and scaling $\tau_{ent}$ by $t_f$ and the lengths by $a$, we arrive at the dimensionless entrance time

$$\tau_{ent} = \frac{1}{80} \left( 99l_e - 4.95l_e^2 + \frac{cl_e^2}{2\delta^2} \right).$$  \hfill (3.18)

The cell length $l_e$ depends on $\Delta P$ or $Ca$. Figure 3.6 indicates that the cell is longer (and thinner) inside the capillary at higher capillary number. This dependence cannot be easily modeled, however. Generally speaking, $l_e(Ca)$ is determined by the balance between capillary and viscous forces. But it is also influenced by the wall confinement and the inner circulation. Thus, we have decided to use the numerical results Fig. 3.6 in Eq. (3.18). Finally the coefficient $c$ can be determined by a least-square fitting of the equation to numerical data in Fig. 3.5. The best fitting is achieved for $c = 0.13$ in this case. The fact that $c < 1$ is mainly because the flow rate through the gap $\delta$ is typically only a fraction of $Q$ on account of the cell’s motion.

Equation (3.18) describes the numerical results well at low $Ca$, but underestimates $\tau_{ent}$ at high $Ca$. As the pressure drop $\Delta P$ and $Ca$ increase, the cell becomes thinner and
more elongated. Not only does this violate the assumption $\delta \ll a$, but the cell develops a conic nose and the uniform gap assumption becomes less accurate. Hence the failure of the scaling at higher $Ca$. Finally, the scaling argument indicates that the weak increase of $\tau_{ent}$ with $Ca$ in Fig. 3.5 is due to the weak rise of the cell length $l_e$ with $Ca$ in Fig. 3.6. Since the latter is plotted in dimensionless parameters, it can be interpreted alternatively as the cell length $l_e$ decreasing with the interfacial tension $\sigma$, which is intuitively obvious. Thus, the entrance time $\tau_{ent}$ is expected to decrease with the cortical tension $\sigma$ at a constant pressure drop.

### 3.3.3 Effect of cytoplasmic viscosity

In the above simulations, the viscosity ratio between the fluid inside the cell and the suspending medium is set to be $\beta = 3$. This is much below the cytoplasm-plasma viscosity ratio in vivo (Yap & Kamm, 2005b; Evans & Yeung, 1989), as well as the experimental value in Yap & Kamm (2005b) who used water as the suspending fluid. As indicated earlier, the use of a modest $\beta$ value is a numerical expedient. In this subsection, we will vary the viscosity ratio to see how the cytoplasmic viscosity affects the process of neutrophil entry and passage in a capillary.

We carried out a series of numerical simulations at capillary numbers $Ca = 0.0893$. The viscosity ratio $\beta$ is varied between $1/16$ to 16 with all other dimensionless groups unchanged. At higher $Ca$, we were able to reach larger $\beta$ values without having the cell stuck on the walls, but the results have the same trend as discussed below. For three $\beta$ values, Fig. 3.7 illustrates the temporal evolutions of the flow rate $Q$ and total cell length $l$. In all three cases, the flow rate manifests the stages described in Section 3.3.1. However, the character of the second stage changes with $\beta$. For a small $\beta$, $Q$ keeps
constant or even increases in this stage, whereas for a large $\beta$, $Q$ continues to decrease, albeit at a milder slope than in the previous stage. Recall that at the second stage, the cell has reached maximum blockage of the capillary, with roughly half of the cell inside the capillary (cf. Fig. 3.4). The differing trends in $Q$ are because the cell approaches the capillary entrance with differing shapes and thus causes differing degrees of blockage. For a lower cell viscosity and smaller $\beta$, the cell deforms more quickly in the contraction flow upstream of the capillary, and has already developed the protruding nose by the time the cell starts to enter the capillary. As the front of the cell extends further into the capillary, the rear deflates simultaneously, thereby enlarging the gap between the cell surface and the wall at the “shoulder” of the contraction where the blockage is the greatest. Thus, $Q$ increases in time in stage two. A more viscous cell, on the other hand, has a stouter shape when it approaches the capillary and thus plugs the entry more severely. The inset in Fig. 3.7(b) shows a narrower gap at the shoulder for $\beta = 16$ than $\beta = 1$, and this explains the generally lower $Q$ for higher $\beta$. Moreover, as the cell continues to deform and its front protrudes into the capillary, the gap between the cell and the wall is squeezed further at the shoulder, causing the continued decline in $Q$ until the cell is completely inside the capillary.

Then it comes as no surprise that the entrance time $\tau_{ent}$ increases with $\beta$ (Fig. 3.8). The effect is rather weak, and follows a power law with an index of $1/7$. Evidently, this is because a more viscous cell deforms more slowly as in Fig. 3.7(b). In fact, the cell has an inherent visco-capillary time scale $\hat{\mu}r_c/\sigma$, where $\hat{\mu}$ is a certain combination of the cell and matrix viscosities (Yue et al., 2006a). The fact that $\tau_{ent}$ scales with $\beta^{1/7}$ instead of $\beta$ is because the external fluid, whose viscosity is kept constant, also affects the deformation process.
3.3.4 Effects of capillary diameter and geometry

While the human neutrophil has a diameter close to 7 μm, the diameter of the pulmonary capillary ranges from 2 μm to 15 μm (Yap & Kamm, 2005b). Naturally, a neutrophil will enter and traverse a larger capillary much more readily than a narrower one. In exploring how the entrance time $\tau_{ent}$ depends on the capillary diameter $a$, it is more convenient to use the cell radius $r_c$ as the characteristic length. Then varying $a$ amounts to varying the size ratio $\zeta = r_c/a$ without affecting any of the other dimensionless groups. However, to match the data in prior subsections where $r_c = 1.4a$, we have used $r_c/1.4$ instead of $r_c$ as the characteristic length. Similarly, the characteristic velocity $V_f = \Delta P(r_c/1.4)^2/(8\mu_m L)$ is used in scaling $\tau_{ent}$ and $Q$ and in defining the capillary and Reynolds numbers. The radius of the upstream vessel is kept constant at $1.43r_c$.

Not surprisingly, the entrance time increases steeply as the capillary narrows (Fig. 3.9a). The $\tau_{ent}(\zeta)$ curve does not follow a power-law, its slope on the log-log plot increasing from 3.2 for the smallest $\zeta$ to 5 at the upper bound. Bathe et al. (2002) computed the transit time of a cell in a capillary with a constriction, and correlated the results with the minimum radius at the nip of the constriction. If we equate this minimum radius with our capillary radius $a$, their correlation is $\tau_{ent} = \tau_0(\zeta^5 - 1)$ in our notation. Despite the different geometry, the 5th power law is comparable to our data in Fig. 3.9(a) for large $\zeta$. As $\zeta$ decreases toward unity, Bathe et al.’s empirical equation deviates from a 5th power law, as do our data. Since the pre-factor $\tau_0$ cannot be defined unambiguously for our geometry, a more detailed comparison cannot be made.

As an indication of the transit time of the cell once it is entirely inside the capillary, Fig. 3.9(b) plots the instantaneous flow rate $Q_e$ at the end of the entrance process (when the cell’s trailing edge clears the entry) as a function of the capillary radius. Note that $Q_e$ has been scaled by a characteristic value $\pi(r_c/1.4)^4\Delta P/(8\mu_m L)$ that is independent
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Figure 3.10: A snapshot of a neutrophil entering the capillary with an elliptic obstacle after the entrance. $Ca = 0.0893$, $\beta = 3$ and $\zeta = 1.4$.

of $a$. For the Poiseuille flow in a pipe, the flow rate is expected to scale as $a^4$ or $\zeta^{-4}$. Over the range of $\zeta$ in Fig. 3.9(b), the data fall on a gentle curve whose slope is close to $-4$. The deviation from the power law is such that toward the upper bound of $\zeta$ (i.e., for the smallest capillaries), $Q_e$ decreases more than $\zeta^{-4}$ as the capillary radius decreases. This is because of the impenetrable cell surface hindering the flow in its vicinity. The effect becomes stronger for smaller capillaries which are more severely plugged by the cell.

A related issue is how a neutrophil traverses a partially blocked capillary. It has long been known that in falciparum malaria, parasitized erythrocytes tend to adhere and block the lumen of brain capillaries (Yoeli & Hargreaves, 1974), with potentially fatal consequences. More recently, direct visualization in a microfluidic channel demonstrated that P. falciparum-infected erythrocytes lose their elasticity and deformability and become lodged in the channel (Shelby et al., 2003). Bathe et al.’s simulation (Bathe et al., 2002) used a geometry of a cylindrical capillary with a constriction formed by a smooth protrusion on the inner walls. Although this is intended to mimic the entrance to a segment in the pulmonary capillary network, their result suggests that the passage of a neutrophil will be greatly delayed by blockage of a capillary.

Our computational geometry in Fig. 3.10 is based on images of brain capillaries partially obstructed by sequestered erythrocytes (Yoeli & Hargreaves, 1974). The blockage is modeled by an annular pinch in the shape of half an ellipse in the meridian plane. The major axis of the ellipse is fixed and equal to the capillary radius $a$, and its minor axis is varied to change the degree of constriction. We denote the height of the protrusion (or the minor semi-axis of the ellipse) by $h$. The constriction is right after the entry; the ellipse starts where the circular arc of the contraction would have connected to the wall of the capillary. In the results to be presented, we have reverted to using $a$ as the characteristic length.

Figure 3.11 shows that the entrance time $\tau_{ent}$ increases with $h$, and the increase becomes steeper when the blockage gets more severe. When the obstacle height is 30% of the capillary radius, $\tau_{ent}$ is almost doubled. Conceivably, for a critical $h$ value, the cell will fail to pass completely, and this critical $h$ should increase with the imposed pressure drop or $Ca$. Figure 3.11 also plots the aforementioned correlation of Bathe et al. (2002) recast in terms of $h$. Since our obstacle is elliptic and theirs is part of a circular arc, the pre-factor $\tau_0$ is determined by taking the average between the major and minor axes of our ellipse as the diameter of the circular arc. The correlation shows a much stronger effect than our results. This is mostly because in their geometry, the obstacle has a radius.
greater than the cell radius \( r_c \). Therefore, during much of the passage the cell is entirely within the constricted segment. In our geometry, the extent of the constriction is much smaller (cf. Fig. 3.10), and therefore the correlation does not apply.

### 3.3.5 Comparison with experiment

As mentioned before, this numerical work was motivated by the experiment of Yap & Kamm (2005b), and naturally the numerical results should be compared with their measurements. The experimental device includes a microchannel connecting two water-filled reservoirs that maintain a constant pressure drop during the transit of a single neutrophil (Fig. 3.2). By adjusting the water level, the pressure drop can be varied systematically in a series of experiments. The microchannel is rectangular in its cross section with an effective radius of 2 \( \mu \)m. The human neutrophils have a diameter close to 7 \( \mu \)m and a very large viscosity, around 2.2 poise in the adherent spread cells and even higher in passive round cells.

Yap and Kamm observed that if the pressure drop is below a threshold of 3.92 Pa (0.4 mm \( \text{H}_2\text{O} \)), the cell fails to enter the orifice. We observed a similar stoppage at a pressure of 3.0 Pa, and found the threshold pressure to be sensitive to the geometric parameters. For instance, the threshold is lower for the rounded corner shown in Fig. 3.1, and increases markedly as the entry corner gets sharper. It also increases when the reservoir-to-capillary contraction ratio increases. However, the resemblance between simulation and experiment may belie an important difference. In micropipette aspiration at a pressure lower than that required to suck the whole cell into the pipette, the cell seems to completely block the flow and make solid contact with the walls (Hochmuth, 2000). It is not clear whether the same happened in Yap and Kamm’s experiment. In
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Figure 3.12: Comparison of the dimensional entrance time with experimental data. A pressure drop $\Delta P = 100$ Pa corresponds to $Ca = 0.0893$. In both simulations and experiments, the cell-to-capillary size ratio is $\zeta = 1.75$. The experimental viscosity ratio $\beta = 220$ for the activated cell while the simulation has $\beta = 16$. The triangles are data extrapolated from $\beta = 16$ to 220 using the 1/7 power law of Fig. 3.8.

our simulations, the cell is always separated from the walls by a thin fluid layer, and the stoppage is owing to the cell’s cortical tension resisting deformation. Yap and Kamm reported entrance time data at several driving pressure drops, and these are reproduced in Fig. 3.12. As expected, the dimensional entrance time decreases with increasing pressure drop. We have carried out a series of simulations for comparison with the experiments. The capillary radius $a = 2$ μm matches that in the experiment. However, it is difficult to reproduce the experimental flow conditions owing to a numerical limitation. When the cell viscosity is high and/or the pressure drop is small (but still above the threshold), the cell deformation is mild and its surface is pressed against the channel walls. In the experiment, Yap and Kamm treated the PDMS walls with a copolymer surfactant solution to passivate the surface and deter cell adhesion. In the simulations, on the other hand, there is no cell membrane. The Cahn-Hilliard energy implies neutral wettability of the cell fluid. So the cell tends to adhere to the walls with its surface at a $90^\circ$ contact angle (Yue et al., 2006b; Zhou et al., 2006). This problem does not arise if the cell deforms readily, say at high pressure or low cell viscosity. Thus, we have a numerical dilemma between probing low pressure and high cell viscosity. Although the difficulty can be alleviated by modifying the expression for the surface energy to increases the hydrophobicity of the wall (Jacqmin, 2000), we have not yet implemented this capability in our code. In Fig. 3.12, we present data for $\beta = 16$ and $\Delta P$ above the experimental range.

Despite the non-overlapping pressure ranges, the numerical data exhibit a trend that is consistent with the experimental data. Quantitatively, the numerical $\tau_{ent}$ appears
lower than the experimental value, owing probably to the low $\beta$ value. Since the effect of cytoplasmic viscosity has been established in subsection 3.3.3, we have extrapolated the $\tau_{\text{ent}}$ data for $\beta = 16$ to $\beta = 220$ by using the $1/7$ power law of Fig. 3.8. These are in better agreement with the measured values in Fig. 3.12; the difference is roughly 18% if extrapolated to lower $\Delta P$.

3.4 Viscoelastic effects

The idea of the leukocyte cytoplasm being viscoelastic comes not only from its content—numerous organelles behaving as deformable capsules and various biopolymers—but also from phenomenological observations of transient effects in micropipette aspiration (Dong et al., 1988; Lim et al., 2006). The Maxwell model has been used to simulate cell deformation during aspiration (Dong et al., 1988) and passage through a capillary with a constriction (Bathe et al., 2002). In the latter study, Bathe et al. examined the transit time as dependent on the viscoelastic parameters of the model and the geometry.

We have simulated the entrance of a neutrophil when the cytoplasm is modeled as a viscoelastic Oldroyd-B fluid and the outer matrix is Newtonian. The Oldroyd-B model (cf. Eqs. 3.3, 3.4), based on a dilute suspension of elastic dumbbells in a Newtonian solvent (Bird et al., 1987), is essentially the same as the Maxwell model except for an additional viscous stress due to the solvent. This viscous stress has two benefits: it avoids the unphysical situation of a Maxwell cell having zero viscosity at startup of deformation, and it enhances numerical stability (Owens & Phillips, 2002). The viscoelasticity is represented by a new dimensionless group, the Deborah number

$$De = \frac{\lambda_H V_f}{a},$$

which is the relaxation time of the dumbbells $\lambda_H$ scaled by the characteristic flow time $t_f = a/V_f$.

The geometry is the same as in Fig. 3.1, and the following parameters are used in the simulations. We fix the density ratio $\alpha = 1$ and viscosity ratio $\beta = 3$. We define $\beta$ using the total viscosity $\mu_t = \mu_p + \mu_s$ of the Oldroyd-B model, with equal contribution from the polymer and the solvent: $\mu_p = \mu_s$. This $\beta$ is matched with the Newtonian $\beta$ when comparing with simulations in the preceding section. The radius of the undeformed cell is still $r_c = 1.4a$, and the capillary number will be given later for individual runs. Inertia is negligible. For the viscoelastic relaxation time, Bathe et al. (2002) obtained $\lambda_H = 0.167$ s from cell indentation. Dong et al. (1991) found a somewhat larger value of 0.25 s by fitting micropipette aspiration data. Under our flow conditions, these correspond to $De = 416$ and 624, respectively.

Figure 3.13 illustrates the effect of the Deborah number $De$ on the entrance time $\tau_{\text{ent}}$ with all other parameters being fixed. This corresponds, in dimensional terms, to varying the relaxation time of the cytoplasm. The entrance time decreases monotonically when the Deborah number increases. To understand this trend, we show in Fig. 3.14 the flow and stress fields inside a viscoelastic cell that is roughly 2/3 through the entry. Roughly
Chapter 3. Simulation of neutrophil deformation and transport in capillaries

Figure 3.13: The entrance time $\tau_{\text{ent}}$ decreases with the Deborah number $De$ when the relaxation time $\lambda_H$ increases. $Ca = 0.0893$, $\beta = 3$ and $\zeta = 1.4$. The arrow indicates the entrance time for the comparable Newtonian cell.

Speaking, the flow field consists of three zones. The middle of the cell contains mostly rotational flow with closed streamlines. The rear is practically a “dead water” zone with low deformation and stress. Finally, there is a small area in the front where the flow is extensional. Except for the front, the elastic dumbbells within the cytoplasm experience a very low level of strain rate. Note that our $De$ is defined using the nominal shear rate $V_f/a$ in the capillary. The actual strain rate within the cell is much smaller, and the actual $De$ is as low as 0.15. As a result, the dumbbells largely remain in the coiled state and the stress level is low. This is reflected by the low shear stress $\tau_{\text{pxy}}$ in Fig. 3.14. Note that $\tau_{\text{pxy}}$ is scaled by $\tau_{\text{cell}} = \mu u_m/a$, $u_m$ being the maximum horizontal velocity in the cell. The fact that $\tau_{\text{pxy}} < 1$ in most of the cell implies that the cytoplasm assumes a lower shear stress than expected for steady shear at the strain rate $u_m/a$. This is because the viscoelastic stress takes a finite time ($\lambda_H$) to develop, and attains only a fraction of $\tau_{\text{cell}}$ under the transient strain on the recirculating streamlines. For longer relaxation times or higher values of $De$, even lower levels of stress can be achieved. Therefore, the cytoplasm manifests a lower effective viscosity at a larger $De$. Thus, the entry time becomes shorter as the relaxation time increases for the same reason as shown in Fig. 3.8. This argument is also borne out by Fig. 3.15, which shows that with increasing $De$, not only the flow rate increases, but the $Q(t)$ curve develops a more prominent upswing in stage two, resembling the case of a lower cytoplasmic viscosity $\beta = 1$ in Fig. 3.7(a).

It is interesting to compare the above with Bathe et al.’s results (Bathe et al., 2002). They observed that the transit time increases with the modulus $G$ of the Maxwell model for smaller $G$ and levels off for large $G$. They interpreted the saturation as the limit of purely Newtonian rheology because the elastic spring becomes too stiff to stretch. Since the relaxation time $\lambda_H = \mu_p/G$, their increase of $\tau_{\text{ent}}$ with $G$ corresponds to our decrease with $De$. Moreover, their insight on the elastic and viscous responses is entirely
Figure 3.14: The streamline pattern (upper half) and contours of the shear stress \( \tau_{pxy} \) (lower half) inside the cell during its entrance. The nominal Deborah number is \( De = 25 \) and the dimensionless time \( t = 7.66 \). The streamlines are in a reference frame fixed on the front of the cell. The shear stress is scaled by \( \tau_{cell} = \mu_t u_m/a \), where \( u_m \) is the maximum horizontal velocity in the cell.

Figure 3.15: Effects of the Deborah number on the temporal evolution of the flow rate. \( Ca = 0.0893, \beta = 3 \) and \( \zeta = 1.4 \). Note that with increasing \( De \), the \( Q(t) \) curve assumes a resemblance to that of a Newtonian cell with a lower cell viscosity (cf. Fig. 3.7a).

consistent with our analysis above. Note that Bathe et al. used the linear Maxwell model which would differ from our nonlinear model for large strains. This and the difference in geometry preclude a quantitative comparison. But the viscoelastic response is qualitatively the same.

The dumbbell stretching can be boosted by increasing the flow rate or \( \Delta P \) while keeping the relaxation time \( \lambda_H \) fixed. This amounts to increasing the Deborah number \( De \) and the capillary number \( Ca \) simultaneously. Figure 3.16 shows that the entrance time for the viscoelastic cell increases toward that of the comparable Newtonian cell as \( Ca \) increases, and catches up with the latter approximately at \( Ca = 1.01 \), estimated
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Figure 3.16: The ratio of entrance times between the viscoelastic cell and the Newtonian one increases with the flow rate, indicated by $Ca$. $\beta = 3$ and $\zeta = 1.4$. The Deborah number $De$ increases with $Ca$ in proportion: $De = 25$ at $Ca = 0.0893$ and $De = 250$ at $Ca = 0.893$.

from interpolation. For still higher $\Delta P$, $\tau_{ent}$ exceeds that of the Newtonian cell. This is because at high flow rates, the cytoplasm experiences increasingly severe deformation and the viscoelastic stress can grow beyond that of the Newtonian fluid (Bird et al., 1987; Yue et al., 2005a).

3.5 Summary

In this paper, we have examined the entrance time of a neutrophil as affected by the size and geometry of the capillary and the viscosity and viscoelasticity of the cytoplasm. The results are explained by investigating the fluid mechanics of the process. Qualitatively, the results are consistent with prior numerical and experimental data. Within the ranges of parameters covered, the results can be summarized as follows.

(a) The entrance time $\tau_{ent}$ decreases when the pressure drop over the capillary is increased, and the numerical results are in semi-quantitative agreement with the measurements of Yap & Kamm (2005b).

(b) The entrance time increases sharply with decrease of the capillary diameter, and also when an obstacle inside the entry constricts the capillary.

(c) The entrance time increases with the cell viscosity according to a power-law with an index of $1/7$.

(d) Viscoelasticity inside the cell tends to facilitate cell deformation and shorten $\tau_{ent}$ at moderate flow rates. With increasing flow rate, this effect is reversed when the cytoplasm develops large viscoelastic stresses.

Harking back to the sequestration of leukocytes in the lung, the longer transit time
for leukocytes, as compared with erythrocytes, seems to involve two of the above mechanisms: the white cells are larger in size \(b\), and they have a more viscous interior than the red cell \(c\). Besides, the white cell also has a highly viscous nucleus, but that is neglected in the simulations. The simulations predict the correct trend, but a more detailed comparison is hampered by simplifications in the models and the geometric setup of the simulations. In particular, we should emphasize the limitations in the physical models employed in the simulations. First, the cell membrane is represented by a fluid interface with a constant and isotropic tension. No elastic resistance to in-plane shearing and bending is incorporated. Second, the neutrophil membrane is wrinkled with roughly 100\% excess area over that of a smooth sphere enclosing the same volume, whereas in our simulations, the interface in principle has unlimited extensibility. Third, the cell undergoes internal structural adaptation when it deforms and activates under mechanical load (Yap & Kamm, 2005a). Such dynamics are ignored in our model, and indeed little work has been done on the multi-scale coupling between the cytoskeleton conformation and the mechanics of the cell as a whole. In light of the above, this work represents an initial step in an effort to simulate cell mechanics using continuum models.
Bibliography


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Chapter 4

Deformation of a compound drop through a contraction in a pressure-driven pipe flow *

4.1 Introduction

A compound drop consists of an inner drop enclosed in a shell of an immiscible liquid. When a large number of compound drops are suspended in another liquid medium, the resulting mixture is known as a double or multiple emulsion. Water-in-oil-in-water (W/O/W) emulsions have received much attention since they were proposed as a drug delivery vehicle for insulin (Engel et al., 1968). Previous studies on W/O/W emulsions have been mostly concerned with formulation and stabilization (Jiao & Burgess, 2003; Omuki et al., 2004; Bozkir & Hayta, 2004), and relatively little has been done on the deformation and morphological evolution of compound drops in flow fields. The latter process is practically important since shear-induced burst of the oil shell is an important mechanism for drug release (Muguet et al., 2001). The hydrodynamics of the multiple interfaces is also central to the preparation of multiple emulsions, either through intense shearing in a mixer (Goubault et al., 2001) or through compound jet breakup in microfluidic devices (Utada et al., 2005; Zhou et al., 2006). Finally, compound drop dynamics is relevant to the deformation and migration of eukaryotic cells, with the inner drop representing the cell nucleus suspended in the cytoplasm (Kan et al., 1998; Khismatullin & Truskey, 2005; Jadhav et al., 2005).

For the most part, fluid mechanical studies of compound drops have dealt with three types of flow geometries: translation in a quiescent fluid (Johnson & Sadhal, 1985), dynamics in extensional flows (Stone & Leal, 1990; Kan et al., 1998), and dynamics in shear flows (Stroeve & Varanasi, 1984; Smith et al., 2004). In particular, Kan et al. (1998) investigated the deformation, relaxation and breakup in uniaxial elongation, and interpreted the coupling between the inner drop and the outer shell in terms of two time scales. If the relaxation time of the inner drop matches that of the shell, the compound drop will behave like a homogeneous one. Toose et al. (1999) incorporated non-Newtonian rheology into the shell fluid and computed the deformation of the compound drop in elongational flow. More recently, Smith et al. (2004) constructed a phase diagram depicting the morphology of daughter drops after shear-induced breakup at various values of the capillary number and interfacial tension ratio between the inner and outer surfaces. Notably, all prior work has been done in homogeneous far-field flows. Little is known about

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compound drop deformation caused by *inhomogeneous* flows in confined geometries, as may be relevant to transport of cells and vesicles in microcirculation and drug delivery using multiple emulsions.

Simulating the deformation of a compound drop is a computational challenge because of the two moving and deforming interfaces. Recently, we have developed a diffuse-interface method that accounts for the moving interfaces in a variational framework (Yue et al., 2004; Feng et al., 2005). Implemented using finite elements with adaptive meshing, the method has been applied successfully to several problems in drop dynamics (Yue et al., 2006a, b). In particular, we simulated the deformation of a simple drop through a contraction in a pressure-driven pipe flow (Zhou et al., 2007). This note represents an application of the same methodology to compound drops deformation. The geometry is a prototype for entry of eukaryotic cells into capillaries or micropipettes (Wiggs et al., 1994; Hochmuth, 2000) and the transport of double emulsions (Garti, 1997). It generates a mixed-type flow having shear and extensional characters in different regions, and is thus an extension of prior studies in simple shear and uniform elongational flows.

### 4.2 Theory and numerical methods

We treat the interface between two nominally immiscible fluids as a thin but finite mixing layer characterized by a capillary width $\epsilon$ and a Ginzburg-Landau mixing energy in terms of a phase field $\phi$ (Lowengrub & Truskinovsky, 1998). In such a diffuse-interface framework, the scalar field $\phi$ determines the position of the interface, and the governing equations can be written uniformly throughout the two-phase system. The interfacial tension arises from the mixing energy density, and appears in the momentum equation as a forcing term. A more detailed discussion of the advantages and disadvantages of the diffuse-interface model, vis-à-vis the classical sharp-interface model and other interface regularization methods, can be found in the literature (Lowengrub & Truskinovsky, 1998; Yue et al., 2004; Feng et al., 2005).

Since a compound drop consists of three fluid components separated by two interfaces, a general diffuse-interface representation requires the introduction of an additional phase field and additional interaction energies. The resulting theoretical model is rather complex and cumbersome for numerical computations (Kim et al., 2004). In this initial study, therefore, we have limited ourselves to the W/O/W type of compound drops made of two rather than three fluid components. Then the conventional phase-field description is adequate as the innermost and outermost fluids are identical. This simplified model allows exploration of the fundamental hydrodynamic mechanisms, but precludes a comprehensive parametric study of general three-component compound drops.

The system of equations governing the motion of a two-component Newtonian mixture...
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Figure 4.1: Geometric setup for simulating the deformation of a compound drop through a 2:1 contraction. Two cylindrical tubes are connected by an arc of radius $a$ and central angle 90$^\circ$. Shown is the meridian plane and the upper half is the computational domain.

is as follows (Yue et al., 2004):

\[
\nabla \cdot \mathbf{v} = 0, \quad (4.1)
\]

\[
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \nabla \cdot \left\{ \mu \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right] \right\} + G \nabla \phi, \quad (4.2)
\]

\[
\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma \nabla^2 G, \quad (4.3)
\]

\[
G = \lambda \left[ -\nabla^2 \phi + \frac{\phi (\phi^2 - 1)}{\epsilon^2} \right], \quad (4.4)
\]

where $G$ is the chemical potential and $\gamma$ is the mobility parameter; $\lambda$ and $\epsilon$ are the interfacial energy density and capillary width, respectively. The phase field $\phi$ takes on values of $\pm 1$ in the two bulk phases, and the average density and viscosity are simply $\rho = \frac{1+\phi}{2} \rho_1 + \frac{1-\phi}{2} \rho_2$ and $\mu = \frac{1+\phi}{2} \mu_1 + \frac{1-\phi}{2} \mu_2$. Note that the $G \nabla \phi$ term in the momentum equation is a diffuse-interface representation of the interfacial tension. The interface typically has a thickness $\sim 5\epsilon$; the Cahn-Hilliard equation (Eq. 4.3) ensures that it neither collapses into a sharp surface nor diffuses into a wide region. In the limit of $\epsilon \to 0$, the above system reduces to the familiar sharp-interface formulation, and $2\sqrt{2} \lambda/(3\epsilon)$ gives the interfacial tension $\sigma$ (Yue et al., 2004).

To accurately capture the interfacial tension, we must use an $\epsilon$ that is much smaller than the overall dimension and then resolve the $\phi$ profile adequately within the thin interface. For this purpose, we have developed a finite-element package AMPHI (Adaptive Meshing with phase field $\phi$) that has adaptive meshing as an essential ingredient. Yue et al. (2006b) have described the algorithm in detail and validated the numerical toolkit by benchmark problems. In the following, we use unstructured triangular elements in an axisymmetric computational domain, with time steps and grid sizes that are fine enough to ensure accuracy of the numerical results.

4.3 Numerical results

The axisymmetric flow geometry is illustrated in Fig. 4.1, consisting of two cylindrical tubes connected by a circular arc. The downstream tube has radius $a$ and length $L = 10a$, 76
while the upstream tube is twice as thick with a length of $8a$. The compound drop has a core fluid of density $\rho_c$ and viscosity $\mu_c$, and a shell fluid of $\rho_s$ and $\mu_s$. As mentioned above, the suspending fluid (matrix) is identical to the core fluid. The core-shell and shell-matrix interfaces have the same constant interfacial tension $\sigma$. Initially, the two interfaces are concentric and spherical with radii $r_c$ and $r_s$, centered at $z = 6a$, and there is no flow throughout the domain. At $t = 0$, a constant pressure drop $\Delta P$ is applied over the entire length ($19a$) of the domain. On the upstream and downstream boundaries ($z = 0$ and $19a$), we set the boundary conditions to $v_r = 0$ and $\frac{\partial v_z}{\partial z} = 0$. On the centerline we use symmetry conditions: $v_c = 0$ and $\frac{\partial v_c}{\partial r} = 0$. Thus, the flow rate $Q$ varies as the drop traverses the conduit. To construct the dimensionless groups controlling the process, we use $a$ as the characteristic length and $V = \Delta P a^2/(8\mu_c L)$ as the characteristic velocity. Note that $V$ is the average velocity in a Poiseuille flow through a uniform pipe of radius $a$ with pressure gradient $\Delta P/L$. Then six dimensionless groups can be constructed:

\begin{align}
Ca &= \frac{\mu_c V}{\sigma}, \\
Re &= \frac{\rho_c Va}{\mu_c}, \\
\alpha &= \frac{\rho_s}{\rho_c}, \\
\beta &= \frac{\mu_s}{\mu_c}, \\
\zeta_c &= \frac{r_c}{a}, \\
\zeta_s &= \frac{r_s}{a},
\end{align}

where the capillary number $Ca$ indicates the ratio between viscous and capillary forces, and the Reynolds number $Re$ represents the ratio between inertial and viscous forces. The characteristic flow time is $t_f = a/V$, and the flow rate will be scaled by $Q_f = \pi a^2 V$. For brevity, we use the same symbols for dimensional and dimensionless variables, but will explicitly indicate which is meant where confusion may arise. In the simulations presented here, we have fixed $\alpha = 1$, $\beta = 1$ and $\zeta_s = 1.4$. We will explore a range of $\zeta_c$ to examine the core size effect on the transit process.

The entry of the compound drop into the contraction consists of three distinct stages, which are illustrated by the snapshots of Fig. 4.2 and the temporal variations of the instantaneous flow rate and drop length in Fig. 4.3. In the first stage ($0 < t < 4$), the compound drop approaches the contraction. The strong elongational flow causes the shell to form a protrusion, while the core also experiences moderate deformation. The shoulder of the drop progressively blocks the flow area at the contraction, thus causing the continual decrease in flow rate $Q$ (Fig. 4.3a). The length of the drop $l$ increases in the mean time (Fig. 4.3b). At the beginning of the second stage ($4 < t < 8$), maximum blockage at the contraction corresponds to a minimum $Q$. Afterwards, the core moves forward along with the shell fluid, thereby deflating the rear of the drop (Fig. 4.2c). This enlarges the gap between the outer surface and the wall at the contraction and causes
a recovery of $Q$ in stage two. Note the small dip in the $Q(t)$ curve at $t = 5$; it is the result of the core passing the constriction. At the end of the second stage, both the flow rate $Q$ and the drop length achieve a local maximum. In stage three ($t > 8$), the rear of the drop, consisting of only the shell fluid, passes the contraction into the thinner tube. As the contraction loses its “grip” on the drop (Fig. 4.2d), the capillary pressure due to the high curvature in its rear produces a sudden forward flow and a temporary retraction of the drop’s overall length (Fig. 4.3b). This temporary shortening of the drop in turn increases the blockage in the capillary (Fig. 4.2e) and causes the flow rate to drop sharply (Fig. 4.3a). Then both $Q$ and $l$ recover as the compound drop translates in the downstream tube. Simulations using longer tubes indicate that $Q$ and $l$ approach roughly constant values. But the core continues to move slowly forward relative to the shell fluid. This will be seen (cf. Fig. 4.5) as due to the recirculation in the shell fluid. Eventually the two interfaces are pressed into each other and the shell breaks. Diffuse interfaces are known to coalesce prematurely (Yue et al., 2006a), and the rupture of the shell may not reflect reality.

Qualitatively, the transit process is similar to that of a simple drop, which is also shown in Fig. 4.3 for comparison. But the core tends to resist deformation of the compound drop and this modifies the process quantitatively. Throughout the drop entry, both $Q$ and $l$ are below those for the simple drop. The fluctuation in $Q$ also has larger magnitudes. After the core is inside the capillary, its surface hampers the recirculation in the shell fluid and causes a slight bulge on the outer surface (Fig. 4.2c onward). A more viscous core ($\beta < 1$) should amplify these differences although we have not explored this systematically. Note that in terms of suppressing the flow rate and drop deformation, the presence of the core is tantamount to an elevated viscosity in a simple drop (Zhou et al.,

Figure 4.2: Snapshots of the transit of a compound drop into the capillary. $Ca = 0.179$, $Re = 1.56 \times 10^{-2}$ and $\zeta_c = 0.72$. Time is scaled by $a/V$. 

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Figure 4.3: Temporal variations of the instantaneous flow rate $Q$ and the length of the compound drop $l$ for the process of Fig. 4.2. For comparison, we have also plotted results for a simple drop of the same size (radius $1.4a$) and fluid properties as well as for a compound drop with a more viscous shell ($\beta = 3$).

2007). From an energetic viewpoint, the impenetrable inner surface causes more dissipation inside the compound drop, and deformation of the inner drop entails an additional energy penalty in the increased interface area.

We have also explored the effect of a more viscous shell fluid as is relevant to typical W/O/W emulsions. The most prominent difference from the equal-viscosity case occurs in the second stage (Fig. 4.3). Instead of a strong recovery, $Q$ remains more or less constant, or even decrease somewhat for larger $\beta$. This is because a more viscous shell reacts more slowly to the ambient flow. As the core enters the downstream tube, the rear of the drop does not deflate rapidly enough to boost the total flow rate $Q$. By the same token, the cell length $l$ is generally smaller for larger $\beta$, and the transit time $\tau_{\text{trans}}$ is longer. The effect of shell viscosity is similar to that of the drop viscosity for a simple drop (Zhou et al., 2007).

It is no surprise that the compound drop takes longer time to traverse the passage than a simple drop of the same size. Figure 4.4(a) plots the “transit time” $\tau_{\text{ent}}$, defined as the interval between the moments when the leading and trailing edges of the drop enter the thinner tube, as a function of the capillary number. As $\tau_{\text{ent}}$ has been scaled by the flow time $t_f = a/V$, its increase with $Ca$ does not withstand the decrease of the dimensional transit time with the pressure drop or flow rate. Surprisingly, $\tau_{\text{ent}}$ shows a non-monotonic dependence on the core size $\zeta_c$ (Fig. 4.4b). Intuitively one expects $\tau_{\text{ent}}$ to increase with $\zeta_c$ since the larger the inner drop, the larger the energy penalty in deforming it so that the drop can enter the capillary. This seems to hold for $\zeta_c$ up to 0.6. To understand the anomalous decrease of $\tau_{\text{ent}}$ for larger $\zeta_c$, we compare the flow patterns for $\zeta_c = 0.64$ and 0.80 in Fig. 4.5.

When the drop first approaches the entry, the above intuition is indeed borne out and
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Figure 4.4: (a) Effect of the inner drop on the transit time with changing pressure drop with $\zeta_c = 0.72$. The Reynolds number varies in the range $7.81 \times 10^{-3} \leq Re \leq 7.81 \times 10^{-2}$. (b) Transit time as a function of the core radius, represented by $\zeta_c$, at $Ca = 0.179$ and $Re = 1.56 \times 10^{-2}$. In both plots the size of the outer drop is fixed with $\zeta_s = 1.4$.

Figure 4.5: Flow fields inside the compound drop toward the end of the entry process for two core radii: (a) $\zeta_c = 0.64$, (b) $\zeta_c = 0.80$. In both cases, $Ca = 0.179$, $Re = 1.56 \times 10^{-2}$. The streamlines are drawn in a reference frame fixed to the leading edge of the compound drop, which has an instant velocity of $0.81V$ in (a) and $1.21V$ in (b). The gray-scale contours are for the horizontal velocity $u$.

the drop with the larger core attains a lower speed. After the core completely enters the capillary, however, the larger core, though more elongated, requires no additional energy to maintain its shape. Now the smaller inner drop continues to move forward relative to the outer drop surface (Fig. 4.5a); its instantaneous velocity is $0.11V$ relative to the front tip of the compound drop. But the larger core has practically stopped moving forward as a whole (Fig. 4.5b), with a relative velocity of $0.012V$. Meanwhile, internal eddies develop within the inner drop in Fig. 4.5(b) to accommodate the recirculation in the shell fluid.
As a consequence, the smaller core in Fig. 4.5(a) creates stronger velocity gradients on its flanks than the larger core. This translates to a larger drag on the compound drop in Fig. 4.5(a) and a lower speed. This explains the shorter transit time for the drop with the larger core.

The difference in drop speed is reflected by the flow rate. The instantaneous $Q$ at the moment when the drop completely enters the smaller tube is also a non-monotonic function of $\zeta_c$. Besides, one notes the greater drop length $l$ in Fig. 4.5(b) with the larger core. This contrasts the trend in Fig. 4.3(b) and confirms that the drop length also varies non-monotonically with the core size. With even larger $\xi_c$, however, the trend is bound to reverse once more since in the limit of $\xi_c \to \xi_s$, the compound drop approaches a simple one with twice the interfacial tension.

It is interesting to compare our results with compound drop deformation in unbounded elongational flows. With $\beta = 1$, equal interfacial tension on the inner and outer surfaces and $r_c = 0.5r_s$, Stone & Leal (1990) and Kan et al. (1998) found that for capillary numbers much below the critical value $Ca_{cr}$ for breakup, the deformation of the compound drop in an elongational flow is nearly the same as a simple drop of the same fluid and size. This is because the recirculation within the shell fluid is weak and the core deforms little. Thus, the inner surface hardly hinders the overall deformation of the drop. As $Ca$ approaches $Ca_{cr}$, however, the shell is so stretched that the outer interface presses against the core. Then the core does affect the deformation and breakup of the compound drop (Stone & Leal, 1990; Kan et al., 1998). In our confined flow geometry, on the other hand, the compound drop is subject to a geometric constraint that dictates the deformation of the inner drop as well as the shell, regardless of the capillary number. Hence the compound drop sustains milder deformation than the simple drop in Fig. 4.3, and the difference increases with flow speed or $Ca$. Obviously, as $\zeta_c$ becomes sufficiently small, the difference between simple and compound drop deformation should vanish.

### 4.4 Summary

This note presents simulations of the morphological evolution of a compound drop as it moves along the centerline of a circular tube with a 2:1 gradual contraction. The flow is driven by a fixed pressure difference imposed on the matrix fluid. The deformation of the two interfaces is captured by a phase-field representation, with an interfacial tension determined by the mixing energy in the thin but diffuse interfaces. Results show that the inner core generally hinders deformation of the compound drop and prolongs the transit time. However, the effect is non-monotonic in the core size; it is greatest for an intermediate core radius. The underlying mechanism is the core hampering the inner circulation and subjecting the compound drop to stronger shear inside the shell.

The expedient of using a binary phase-field model places a limitation on our study: the inner core fluid must be identical to the suspending fluid. This is appropriate for W/O/W compound drops encountered in drug delivery. A more general compound drop involves three different fluid components. Such systems call for tertiary phase-field models as have recently appeared in the literature (Kim et al., 2004; Burman et al., 2004). For
example, a white blood cell has a nucleus that is much more viscous than the cytoplasm, which is in turn different from the suspending plasma. Biological cells, of course, contain additional complexities such as membrane elasticity that are not easily represented in a compound drop model.
Bibliography


Bibliography


Chapter 5

Heart-shaped bubbles rising in anisotropic liquids *

5.1 Introduction

To investigate the impact of solids on viscoelastic liquids, Akers & Belmonte (2006) dropped spheres of diameter \(d \sim 1\) cm into an aqueous solution of the wormlike micellar system cetylpyridinium chloride (CPCl)/sodium salicylate (NaSal). Occasionally air bubbles were entrained into the fluid, and would rise in the wake of the ball (Fig. 5.1). Such a bubble assumes a peculiar shape while in the near wake, resembling an inverted heart or a spade \((a)\). The upper surface has sloped shoulders that join in a point. The bottom is relatively flat with a small conical protrusion in the middle. As it rises, both points on top and bottom quickly retract and the bubble appears roughly spherical \((b)\). Further up, the bubble assumes the familiar shape with a round top and a long pointed tail at the bottom \((c)\). The last image resembles that seen of bubbles in viscoelastic polymer solutions (Liu et al., 1995; Herrera-Velarde et al., 2003), the tail being produced by the tensile stress in the wake of the bubble. The inverted-heart shape in the first image, on the other hand, has never been reported before. A possible explanation is that the micellar solution has been temporarily transformed into an anisotropic nematic liquid in the near wake of the falling ball. The ordered micelles have a preferred orientation (the “easy direction”) with respect to the bubble surface, deviation from which is penalized by an anchoring energy (Rapini & Papoular, 1969; de Gennes & Prost, 1993; Rey, 2000). Such surface anchoring may compete with the interfacial tension and the bulk molecular order and force the bubble into the peculiar shape. Farther away from the ball, the micelles relax and lose the nematic order, and the bubble shape reverts to that commonly seen in viscoelastic liquids.

Although Akers and Belmonte did not present direct evidence for the orientational order in the near wake, a flow-induced nematic state can be inferred from two facts. First, a falling ball produces strong elongation in its wake that tends to modify the microstructural conformation of the fluid. Both flexible polymers and wormlike micelles have been observed to align into “birefringent strands” in the near wake (Harlen, 1990; Handzy & Belmonte, 2004). Second, semi-dilute and concentrated micellar solutions are known to undergo an isotropic-to-nematic transition under shear, for surfactant concentrations down to 1.09 wt.%(Berret et al., 1994; Kadoma & van Egmond, 1998; Fischer et al., 2002). At higher concentrations, micelles commonly exhibit a nematic phase even in equilibrium (Poulin et al., 1999; Mondain-Monval et al., 1999). The CPCl concentration used by Akers and Belmonte is estimated at 2.87 wt.%, well into the semi-dilute regime.

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It is therefore reasonable to assume an anisotropic nematic state in the near wake, with the micelles predominantly oriented vertically. In such an environment, the bubble shape is affected not only by the hydrodynamic forces and interfacial tension, but also by the surface anchoring and bulk molecular orientation.

### 5.2 Theory and numerical methods

To test this hypothesis, we have carried out dynamic simulations of bubbles rising in a nematic fluid having a vertical far-field orientation. The rheology and orientation of the fluid are modeled by the Leslie-Ericksen theory for liquid crystals (de Gennes & Prost, 1993), and the moving and deforming bubble surface is captured in a diffuse-interface framework (Yue et al., 2004). Details about the theoretical model and numerical method can be found elsewhere (Yue et al., 2005, 2006), and only a brief summary is given here. The free energy of a Newtonian-nematic mixture has three contributions: a mixing energy, a bulk elastic energy and a surface anchoring energy:

\[
f_{\text{mix}} = \frac{\lambda}{2} |\nabla \phi|^2 + \frac{\lambda}{4\epsilon^2} (\phi^2 - 1)^2, \tag{5.1}\]

\[
f_{\text{bulk}} = K \left[ \frac{1}{2} \nabla n : (\nabla n)^T + \frac{(|n|^2 - 1)^2}{4\delta^2} \right], \tag{5.2}\]

\[
f_{\text{anch}} = \frac{A}{2} (n \cdot \nabla \phi)^2. \tag{5.3}\]
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In \( f_{\text{mix}} \), \( \phi \) is the phase-field variable with \( \phi = 1 \) and \(-1\) in the nematic and Newtonian bulk phases and \( \phi = 0 \) at the interface, \( \lambda \) is the mixing energy density and \( \epsilon \) is the capillary width. \( f_{\text{bulk}} \) is the Frank energy with a single elastic constant \( K \), \( n \) being the director, regularized to permit defects where \( |n| \) deviates from unity over a small region of size \( \delta \) (de Gennes & Prost, 1993; Liu & Walkington, 2000). For \( f_{\text{anch}} \), we adopt the Rapini-Popoular form (Rapini & Papoular, 1969) for planar anchoring to our diffuse-interface formalism, with \( A \) being the anchoring energy density and the easy direction being perpendicular to the interface normal \( \nabla \phi \). We have tested homeotropic anchoring as well, but it turns out to be irrelevant to Fig. 5.1 and will not be discussed here. In the sharp-interface limit, \( \frac{2\sqrt{2}}{3}\lambda^3 \) gives the interfacial tension \( \sigma \) and \( \frac{2\sqrt{2}}{3}\lambda^3 \) becomes the anchoring strength \( W \) (Rapini & Papoular, 1969; Yamamoto, 2001; Yue et al., 2004).

A variational procedure on the free energy, supplemented by the appropriate dissipative terms, leads to the governing equations (Yue et al., 2004):

\[
\nabla \cdot v = 0, \quad (5.4)
\]

\[
\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \nabla \cdot \sigma, \quad (5.5)
\]

\[
\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \gamma \lambda \nabla^2 \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\epsilon^2} \right], \quad (5.6)
\]

\[
h = \gamma_1 N + \gamma_2 D \cdot n, \quad (5.7)
\]

where the deviatoric stress tensor

\[
\sigma = -\lambda(\nabla \phi \nabla \phi) - K \frac{1 + \phi}{2}(\nabla n) \cdot (\nabla n)^T - A(n \cdot \nabla \phi)n \nabla \phi + \frac{1 + \phi}{2} \sigma' + (1 - \phi)\mu D, \quad (5.8)
\]

with the Leslie viscous stress (de Gennes & Prost, 1993) \( \sigma' = \alpha_1 D : nnnn + \alpha_2 n N + \alpha_3 N n + \alpha_4 D + \alpha_5 n n D + \alpha_6 D n n, \) and the molecular field \( h = K \left[ \nabla \cdot \left( \frac{1 + \phi}{2} \nabla n \right) - \frac{1 + \phi}{2} \left( |n|^2 - 1 \right) \right]. \)

The governing equations are discretized on a finite-element grid using the Petrov-Galerkin formulation with streamline upwinding for the constitutive equation (Yue et al., 2006). With axisymmetry, the 2D computational domain is covered by an unstructured grid of triangular elements. A key element of the numerical algorithm is an adaptive meshing scheme that deploys the finest grids around the interface and adaptively coarsens and refines the grid as the interface moves. Numerical experiments with grid refinement and time-step refinement have been carried out to ensure adequate resolution, and the accuracy and robustness of the code has been established by benchmarking against rising bubbles in Newtonian fluids and other known solutions (Yue et al., 2006).

### 5.3 Results and discussion

To analyze the effects of flow and molecular order separately, we first computed the equilibrium shape of a stationary bubble in a nematic (Fig. 5.2). The static shape
depends on the competition among the interfacial tension $\sigma$, the anchoring strength $W$ and the bulk elastic energy $K$. Minimizing the total free energy, the bubble typically takes on a lemon shape (Fig. 5.2b), and the degree of elongation is determined by two dimensionless groups: $W/\sigma$ and $Wa/K$, $a$ being the equivalent radius of the bubble. For weak anchoring ($Wa/K < 1$), $n$ readily deviates from the easy direction and bulk elasticity can exert little influence on the bubble shape (Fig. 5.2a). For strong anchoring, however, the bubble becomes more elongated to reduce the bulk distortion at the expense of increased interface area (Fig. 5.2c). Note the “boojum” defects at the poles of the bubble, where bulk distortion creates large surface curvatures. Both the lemon shape and the boojum defects have been reported in prior experiments (Nastishin et al., 2005).

The shape of a rising bubble is also influenced by flow effects, expressed by two dimensionless groups (Grace, 1983): the Morton number $Mo = \frac{g\eta}{\rho\sigma^3}$ and the Eötvös number $Eo = \frac{g\rho a^2}{\sigma}$, $\rho$ and $\eta$ being the liquid density and viscosity and $g$ the gravitational acceleration. In Akers and Belmonte’s experiment (Akers & Belmonte, 2006), the micellar solution is strongly shear-thinning, and its surface tension $\sigma$ also varies depending on the relaxation and redistribution of the surfactants. Based on the data given, the experimental conditions correspond to $8.70 < Eo < 20.3$ and $10^{-2} < Mo < 10^3$. The simulations will use $Eo$ and $Mo$ in these ranges, with the characteristic viscosity $\eta = (\alpha_4 - \alpha_2 + \alpha_6)/2$ being the average between two Miesowicz viscosities (de Gennes & Prost, 1993) and the Leslie coefficients scaling as $\alpha_1 : \alpha_2 : \alpha_3 : \alpha_4 : \alpha_5 : \alpha_6 = 0 : -0.32 : -0.08 : 1.0 : 0.28 : -0.12$. The anchoring strength $W$ and bulk energy $K$ are more difficult to estimate. We have tested a range of $W/\sigma$ and $Wa/K$ values, and their relevance to real materials will be discussed later. For computational conveniences, we have assigned equal density and
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Figure 5.3: Snapshots of the rising bubble in a nematic with planar anchoring. The far-field molecular orientation is vertical. $Eo = 11.2$, $Mo = 1.01$, $W/\sigma = 5$ and $Wa/K = 15$. Time is scaled by $\sqrt{2a/g}$. Steady state is reached in frame (d).

viscosity to the “bubble” and matrix fluid; the buoyancy force is replaced by an upward body force acting on the bubble. The density and viscosity of the bubble phase affect the internal recirculation but not so much the bubble shape.

Figure 5.3 shows snapshots of a bubble during its rise. The initial shape is spherical, with a uniform director field (Fig. 5.3a). Within a time scale of $\eta a/W (=1.41$ in this case), the director relaxes toward the easy direction on the bubble surface, deforming it into a lemon shape resembling Fig. 5.2(b). At this point the bubble velocity is about 46% of its terminal value. As the rise velocity increases, so does the hydrodynamic drag due to viscous and inertial forces. As a result, the shoulders are pushed down and flattened, and the bubble loses fore-aft symmetry (Fig. 5.3c). Eventually a steady state is reached in Fig. 5.3(d), with a bubble shape closely resembling the experimental picture in Fig. 5.1(a). The terminal velocity $U$ corresponds to a Reynolds number $Re = \frac{\rho U a}{\eta} = 3.39$, while the experimental value in Akers & Belmonte (2006) is estimated as $1.72 < Re < 3.90$. The steady-state Ericksen number $Er = \frac{\eta U a}{K} = 2.05$. The flat bottom is reminiscent of the bubble shape in Newtonian liquids (Grace, 1983) at a comparable $Re$, except for the protrusion in the middle due to the boojum defect. This simulation
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offers strong support for our hypothesis that it is the nematic order in the wake of the ball that affords the bubble its unusual shape.

5.4 Summary

Basic features of the inverted-heart shape—sloped shoulders and a flat bottom with a conical protrusion—are obtained if both $W$ and $K$ are sufficiently large; a rough guideline is $W \gtrsim \sigma$ and $K \gtrsim 0.1\sigma a$. These numerical parameters need to be related to the experiment (Akers & Belmonte, 2006). Since no in-situ characterization was done on the micellar solution, we are limited to circumstantial evidence. For nematic wormlike micelles, anchoring arises from entropic effects such as excluded volume, and a scaling argument on $W$ predicts strong planar anchoring ($Wa/K \gg 1$) (Poulin et al., 1999). This has been confirmed experimentally through quadrupolar interactions among colloidal particles (Poulin et al., 1999; Mondain-Monval et al., 1999). Thus, it is reasonable to assume planar anchoring in our computations, and the condition $Wa/K \gg 1$ is consistent with the numerical parameters in Fig. 5.3. However, the estimated $W$ is smaller than the surface tension of common thermotropic liquid crystals (Sonin, 1995). In the experiment (Akers & Belmonte, 2006), the abundance of surfactants may have reduced $\sigma$ below $W$. For lyotropic nematics made of self-assembled molecular aggregates similar to wormlike micelles, $W/\sigma > 1$ has been observed for domains in a bi-phasic system (Kaznacheev et al., 2003; Nastishin et al., 2005).

The mechanism revealed by the heart-shaped bubble has potential applications in other complex fluids that feature nematic-isotropic interfaces, such as nematic emulsions (Tixier et al., 2006) and polymer-dispersed liquid crystals (PDLC) (Mucha, 2003). In self-assembly of colloids for making photonic crystals (Manoharan et al., 2001), a nematic matrix will afford better control of the spatial periodicity as well as the possibility of non-spherical voids with better performance and tunability (Nazarenko et al., 2001; Velikov et al., 2002). In manufacturing PDLC films, planar anchoring inside nematic drops tends to produce a bipolar shape similar to those in Fig. 5.2. The drop shape and orientation can be exploited to maximize the contrast between the on- and off-states (Drzaic & Muller, 1989; Chan et al., 2001). Finally, the phase morphology of bicontinuous polymer-liquid crystal networks (Jeong et al., 1999) and “reversed mode PDLC” (Macchione et al., 2000) depends on the coupling between surface anchoring, bulk elasticity and deformation, and the mechanism discussed in this Letter is expected to play a key role.
Bibliography


Chapter 6

The rise of bubbles and drops in a nematic liquid crystal

6.1 Introduction

Nematic liquid crystals exhibit special electro-optical properties and find applications in numerous modern technologies. As complex fluids, they are distinguished microscopically by molecular alignment and long-range orientation order, and macroscopically by a liquid-solid duality in that they flow as anisotropic viscous fluids but resist orientational distortion as elastic solids (de Gennes & Prost, 1993). In a fluid mechanical context, the motion of a particle or drop in a nematic is of fundamental interest, being the counterpart of the Stokes or Hadamard-Rybczynski problem in viscous Newtonian fluids. Besides, suspensions and emulsions in nematic matrices show intriguing mesoscopic structures and mechanical properties that suggest new applications (Poulin et al., 1997b; Poulin & Weitz, 1998; Loudet et al., 2000; Tixier et al., 2006).

Particle motion in nematic liquid crystals is much more complex than the Stokes problem. Even in a static nematic, insertion of a particle or drop normally causes the nucleation of orientational defects (Poulin et al., 1997b; Lavrentovich, 1998; Feng & Zhou, 2004). The liquid crystal molecules prefer a certain orientation on interfaces, the most common being homeotropic (normal) and planar (tangential) anchoring. If the orientation field surrounding the drop or particle comes into conflict with the far-field orientation, defects form. These may be seen as singularities in the director field \( n(r) \), which represents the average molecular orientation at each spatial point. For a particle with homeotropic anchoring, experiments have recorded two types of defects: a “satellite” point defect (Poulin et al., 1997b; Poulin & Weitz, 1998; Lubensky et al., 1998) and a “Saturn-ring” line defect that encircles the particle on its equator (Mondain-Monval et al., 1999; Gu & Abbott, 2000). With planar anchoring, two surface defects known as “boojums” form at the poles (Poulin & Weitz, 1998). Orientational defects have long been an important subject of liquid crystal physics and indeed condensed matter physics in general (Trebin, 1982; Kléman, 1983).

For moving particles, the earliest studies were falling-ball experiments to measure the effective viscosity of liquid crystals (White et al., 1977; Kuss, 1978). More recently, Poulin et al. (1997a) used the “Stokes drag” to verify the dipolar attraction force between two droplets in a nematic fluid. In such dynamic situations, the flow modifies the director field and defect configuration near the particle. The latter in turn affect the rheology of the liquid crystal and thus the flow field. Therefore, the two-way coupling between flow and microstructure is the key physics governing particle motion in nemat-
ics. In general, such coupling has been formulated by constitutive theories for nematic liquid crystals (de Gennes & Prost, 1993; Rey & Tsuji, 1998; Feng et al., 2000). Owing to the rheological complexity, only a handful of theoretical studies have appeared on the moving particle problem, most of which sought to decouple the flow field and the director field (Stark, 2001). For instance, the director field may be fixed at the static solution, and the resulting flow field and drag are calculated (Ruhwandl & Terentjev, 1996; Stark & Ventzki, 2001). This corresponds to the low Ericksen number (Er) limit, where the viscous forces are too weak to modify the orientational field maintained by elasticity. Conversely, the Newtonian flow field may be prescribed, and the director field \( \mathbf{n}(\mathbf{r}) \) is calculated as a result (Diogo, 1983; Yoneya et al., 2005). This may be linked to the high-Er limit. Stark & Ventzki (2002) seem to be the first to tackle the flow-director two-way coupling at finite \( E_r \). In flow around a sphere with a satellite point defect, they predicted a counter-intuitive flow effect that moves the defect upstream. This was contradicted by Yoneya et al. (2005) who showed that the defect shifts downstream at a similar Ericksen number. But the latter study prescribed the Stokes flow field, and it is unclear whether the decoupling accounts for the discrepancy. To our knowledge, the only other coupled study is Fukuda et al. (2004), who showed that the flow tends to convect the \( \mathbf{n} \) field downstream, while \( \mathbf{n} \) modifies the velocity field and makes it fore-aft asymmetric. Unfortunately, Fukuda et al. assumed an isotropic viscosity and thus omitted an important component of the liquid crystal rheology. Therefore, a “complete solution” that fully couples flow and director fields and incorporates viscous-elastic duality and anisotropy is not yet available.

Most prior calculations assumed rigid anchoring on the particle surface. In reality, the anchoring strength is finite, representable by an anchoring energy, and has a major role in defining the defect configuration (Lubensky et al., 1998; Mondain-Monval et al., 1999). Furthermore, only solid particles have been considered in theoretical studies so far, even though most of the experimental observations have come from emulsions with isotropic droplets suspended in nematics (Poulin & Weitz, 1998). If the interfacial tension is not so strong as to overwhelm the surface anchoring, the interplay between the two is known to lead to unique drop and bubble shapes (Nastishin et al., 2005; Akers & Belmonte, 2006; Zhou et al., 2007). These lacunae in our current understanding have motivated the present simulations based on the Leslie-Ericksen theory.

Simulating the rise of Newtonian drops in a nematic liquid crystal is a computational challenge because of the well-known numerical difficulties in handling moving and deforming interfaces as well as the complex rheology of the nematic liquid crystal. Not only are the rheological properties and stresses discontinuous across the interface, they are anisotropic and evolving with the microstructure in the nematic component. In principle, the balance between the stresses and the surface tension determines the motion of the interface, which must be tracked dynamically on a moving grid while solving for the flow in each component. As an alternative, we have developed an energy-based diffuse-interface method that handles both the interface and the rheology in a unified framework (Yue et al., 2004; Feng et al., 2005). The interface is now a thin diffuse layer defined by a phase-field variable. A mixing energy governs the interaction of the two components.
Chapter 6. The rise of bubbles and drops in a nematic liquid crystal

As long as the microstructure of the complex fluid is describable by a free energy, as is the case for liquid crystals, that energy can be combined with the mixing energy to form the total free energy of the system. A formal variational procedure then leads to the proper governing equations of the two-fluid system. To solve these, Yue et al. (2006b) have developed 2D and axisymmetric finite-element algorithms based on adaptive mesh generation, which is key to resolving the thin interface. The method has proved accurate and efficient in simulating dynamics of viscoelastic drops and jets (Yue et al., 2005d, 2006a; Zhou et al., 2006), and will be adapted to the problem at hand.

This study has three objectives: (1) to demonstrate that the motion of Newtonian drops in a nematic fluid can be successfully simulated by our diffuse-interface method, incorporating complex rheology, deformable interfaces and a variable anchoring strength; (2) to investigate how flow modifies the orientational field and especially the defect configuration near the drop; and (3) to investigate how the director field modifies the flow in return, especially how the rheological anisotropy affects the rising velocity of the drops and the drag force on them.

6.2 Theory and numerical method

Yue et al. (2004, 2006b) have described the theoretical model and the numerical method in detail, and validated the methodology by benchmark problems. Planar 2D and axisymmetric applications to drop dynamics have been reported recently (Yue et al., 2005a,b,c,d, 2006a; Zhou et al., 2006). Therefore, we will only summarize the main ideas and give the governing equations for a two-component mixture of a Newtonian fluid and a nematic liquid crystal. The diffuse interface has a small but non-zero thickness, inside which the two components are mixed and store a mixing energy. We define a phase-field variable $\phi$ such that the concentrations of the nematic and Newtonian components are $(1 + \phi)/2$ and $(1 - \phi)/2$, respectively. Then $\phi = 1$ in the bulk nematic phase, and $\phi = -1$ in the bulk Newtonian phase. The interface is taken to be the level set $\phi = 0$. There are three types of free energies in this system: mixing energy of the interface, bulk distortion energy of the nematic, and the anchoring energy of the liquid crystal molecules on the interface:

$$f_{\text{mix}} = \frac{\lambda}{2} \left[ |\nabla \phi|^2 + \frac{(\phi^2 - 1)^2}{2\epsilon^2} \right], \quad (6.1)$$

$$f_{\text{bulk}} = \frac{K}{2} \left[ \nabla n : (\nabla n)^T + \frac{(n^2 - 1)^2}{2\delta^2} \right], \quad (6.2)$$

$$f_{\text{anch}} = \begin{cases} \frac{A}{2} |\vec{n} \cdot \nabla \phi|^2 & \text{(planar anchoring)} \\
\frac{A}{2} \vec{n}^2 |\nabla \phi|^2 - (\vec{n} \cdot \nabla \phi)^2 & \text{(homeotropic anchoring)} \end{cases} \quad (6.3)$$

In $f_{\text{mix}}$, $\lambda$ is the mixing energy density, $\epsilon$ is the capillary width and the ratio $2\sqrt{2}\lambda/3\epsilon$ produces the interfacial tension $\sigma$ (Jacqmin, 1999; Liu & Shen, 2003; Yue et al., 2004). $f_{\text{bulk}}$ is the Frank energy with a single elastic constant $K$. Different elastic constants may be assigned to different modes of distortion (de Gennes & Prost, 1993), but we use the
one-constant approximation for simplicity. Note that \( f_{\text{bulk}} \) is regularized to permit defects where \( |\mathbf{n}| \) deviates from unity over the defect core of size \( \delta \). The second term, devised by Liu & Walkington (2000) after the Ginzburg-Landau energy of Eq. (6.1), represents the distortion energy of the defect by an energy penalty against the shortening of \( |\mathbf{n}| \), effectively using \( |\mathbf{n}| \) as an order parameter. For \( f_{\text{anch}} \), we adapt the Rapini-Popoular form (Rapini & Papoular, 1969) to our diffuse-interface framework, with \( A \) being the anchoring energy density and \( W = 2\sqrt{2}A/3\epsilon \) giving the surface anchoring strength (Yamamoto, 2001). Now we have the total free energy density for the two-phase material:

\[
f(\phi, \mathbf{n}, \nabla \phi, \nabla \mathbf{n}) = f_{\text{mix}} + \frac{1+\phi}{2}f_{\text{bulk}} + f_{\text{anch}}. \tag{6.4}
\]

A variation on the free energy, supplemented by the various dissipative terms, leads to the following governing equations for the configuration variables \( \mathbf{v}, \rho, \phi \) and \( \mathbf{n} \) (Yue et al., 2004):

\[
\nabla \cdot \mathbf{v} = 0, \tag{6.5}
\]

\[
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \nabla \cdot \mathbf{\sigma} - \rho g e_z, \tag{6.6}
\]

\[
\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma \lambda \nabla^2 \left[ -\nabla^2 \phi + \frac{\phi(\phi^2-1)}{\epsilon^2} \right], \tag{6.7}
\]

\[
h = \gamma_1 \mathbf{N} + \gamma_2 \mathbf{D} \cdot \mathbf{n}. \tag{6.8}
\]

The density \( \rho \) is the average between the nematic density \( \rho_1 \) and the Newtonian density \( \rho_2 \): \( \rho = \frac{1+\phi}{2}\rho_1 + \frac{1-\phi}{2}\rho_2 \). \( g \) is the gravitational acceleration and \( e_z \) is the upward unit vector. The phase-field variable \( \phi \) obeys the Cahn-Hilliard equation, \( \gamma \) being the mobility parameter of the diffuse interface (Yue et al., 2004, 2007). The deviatoric stress tensor

\[
\mathbf{\sigma} = -\lambda (\nabla \phi \otimes \nabla \phi) - K \frac{1+\phi}{2} (\nabla \mathbf{n}) \cdot (\nabla \mathbf{n})^T - G + \frac{1+\phi}{2} \mathbf{\sigma}' + \frac{1-\phi}{2} \mu [\nabla \mathbf{v} + (\nabla \mathbf{v})^T], \tag{6.9}
\]

with \( G = A(\mathbf{n} \cdot \nabla \phi) \mathbf{n} \otimes \nabla \phi \) for planar anchoring and \( G = A[(\mathbf{n} \cdot \nabla \phi) (\mathbf{n} \cdot \nabla \phi) \mathbf{n}] \otimes \nabla \phi \) for homeotropic anchoring, and \( \mu \) being the viscosity of the Newtonian component. \( \mathbf{\sigma}' \) is the Leslie viscous stress in the nematic phase (Leslie, 1968)

\[
\mathbf{\sigma}' = \alpha_1 \mathbf{D} : \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} + \alpha_2 \mathbf{n} \mathbf{N} \mathbf{n} + \alpha_3 \mathbf{N} \mathbf{n} + \alpha_4 \mathbf{D} + \alpha_5 \mathbf{n} \cdot \mathbf{D} + \alpha_6 \mathbf{D} \cdot \mathbf{n} \mathbf{n}, \tag{6.10}
\]

where \( \alpha_1 \) to \( \alpha_6 \) are the Leslie viscous coefficients observing the Onsager relationship (de Gennes & Prost, 1993): \( \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \). \( \mathbf{D} = \frac{1}{2} [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \) is the strain rate tensor, and \( \mathbf{N} = \frac{\mathbf{m}}{\partial t} - \frac{1}{2} (\nabla \mathbf{v})^T - \nabla \mathbf{v} \cdot \mathbf{n} \) is the rotation of the director \( \mathbf{n} \) with respect to the background flow field. The \( \mathbf{n} \) field evolves in the flow according to a balance between elastic and viscous torques as given in Eq. (6.8). The elastic torque is represented by the molecular field (de Gennes & Prost, 1993):

\[
h = K \left[ \nabla \cdot \left( \frac{1+\phi}{2} \nabla \mathbf{n} \right) - \frac{1+\phi}{2} \frac{(\mathbf{n}^2 - 1)\mathbf{n}}{\delta^2} \right] - g, \tag{6.11}
\]
with $g = A(\mathbf{n} \cdot \nabla \phi) \nabla \phi$ for planar anchoring, and $g = A[(\nabla \phi \cdot \nabla \phi) \mathbf{n} - (\mathbf{n} \cdot \nabla \phi) \nabla \phi]$ for homeotropic anchoring. Both $g$ and $G$ derive from the anchoring energy $f_{\text{anch}}$ through a variational procedure (Yue et al., 2004). The coefficients $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_3 + \alpha_2$.

Obviously, the apparent viscosity of the nematic depends on the orientation of $\mathbf{n}$ relative to the flow. This viscous anisotropy is commonly represented by the Miesowicz viscosities in a simple shear flow (de Gennes & Prost, 1993):

$$\eta_1 = \frac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5),$$

$$\eta_2 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6),$$

(6.12), (6.13)

which are measured with $\mathbf{n}$ held perpendicular and parallel to the flow direction, respectively; $\eta_1 > \eta_2$. If $\mathbf{n}$ makes an angle $\theta$ with the flow, the general formula for the shear viscosity is (Carlsson, 1984):

$$\eta(\theta) = \eta_2 - (\alpha_2 + \alpha_3) \sin^2 \theta.$$  

(6.14)

A third Miesowicz viscosity may be defined with $\mathbf{n}$ along the vorticity axis. This is irrelevant to the present study which constrains $\mathbf{n}$ to the meridional plane in axisymmetric geometries. Without external fields or wall anchoring, $\mathbf{n}$ achieves a steady alignment in simple shear if $\alpha_2/\alpha_3 > 0$, but tumbles endlessly if the ratio is negative. Most liquid crystals are of the aligning type (de Gennes & Prost, 1993), and the distinction is insignificant in complex flow fields as simulated here. Thus, we have used $\alpha$ values based on the aligning PAA and MBBA in the rest of this paper.

To arrive at the Cahn-Hilliard equation (6.7), we have omitted from the right-hand-side coupling terms between $f_{\text{mix}}$ and the nematic energies. These are insignificant as long as the interface stays narrow. In fact, the Cahn-Hilliard diffusive dynamics has a visible effect only during singular events such as film rupture (Yue et al., 2005a). In the current context, the diffuse interface may be seen as merely a numerical device for treating a moving internal boundary.

The governing equations are solved, in axisymmetric geometries, by a numerical scheme AMPHI that employs Galerkin finite elements with adaptive meshing (Yue et al., 2006b). The latter has proved to be key to accurate phase-field simulations, and the interface of thickness $O(4\epsilon)$ requires roughly 10 grid points to resolve (Feng et al., 2005). In addition, the defect regions are covered with fine grids as well (see Fig. 6.3b). Since the size of the defect core is comparable to the interfacial thickness (Stark, 1999), $\delta$ is chosen to be $4\epsilon$. We use implicit time-stepping, with the time step automatically adjusted according to the motion of the interface. Numerical experiments with grid refinement and time-step refinement have been carried out (Yue et al., 2006b), and adequate resolution is ensured for the simulations presented in the following.
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6.3 Results and discussion

6.3.1 Simple shear flow as validation

Consider the simple shear flow of a nematic between parallel walls in Fig. 6.1, with rigid homeotropic anchoring on the walls. A 1D analytical solution is available if $\alpha_1$ vanishes, and we will compute the same flow in a 2D domain and use the exact solution to validate our numerical treatment of the Leslie-Ericksen theory. In the 1D solution due to Carlsson (1984), the velocity profile $v(y)$ and orientation profile $\theta(y)$ are given by coupled equations:

$$v(y) = \int_0^y \frac{\tau}{\eta_2 - (\alpha_2 + \alpha_3)\cos^2 \theta(y)} dy - V,$$

$$y(\theta) = \frac{1}{\sqrt{2\tau}} \int_0^\theta \frac{\sqrt{K}}{\sqrt{F(\theta) - F(\theta_m)}} d\theta,$$

$$\tau = \frac{2}{L^2} \left[ \int_0^{\theta_m} \frac{\sqrt{K}}{\sqrt{F(\theta) - F(\theta_m)}} \right]^2,$$

$$F(\theta) = \left( \frac{\alpha_2}{\sqrt{\eta_1\eta_2}} + \sqrt{\frac{\eta_1}{\eta_2}} \tan^{-1} \left( \sqrt{\frac{\eta_2}{\eta_1}} \tan \theta \right) \right) - \theta,$$

where $\tau$ is the constant shear stress on the plates determined from $\theta_m = \theta \left( \frac{L}{2} \right)$, and $\theta_m$, the largest rotation angle at the center between the walls, is in turn determined by the condition $V = v(L)$. This solution assumes $\alpha_1 = 0$, and is written in a slightly simplified form here because of the one-constant approximation.

Our 2D computation uses a domain of length $5L$ divided into 8235 triangular elements. Figure 6.2 compares our solution with Carlsson’s analytical solution, and the two are in excellent agreement. Note that the maximum director angle $\theta_m = 77.5^\circ$ is short of the
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Figure 6.2: Comparison between our results and the 1D exact solution of Carlsson (1984). (a) The director orientation profile; (b) the velocity profile. The Leslie coefficients are \( \alpha_1 = 0, \alpha_2/\alpha_4 = -1.78, \alpha_3/\alpha_4 = -0.056, \alpha_5/\alpha_4 = 1, \alpha_6/\alpha_4 = -0.83, \) and the Leslie angle \( \theta_0 = \tan^{-1} \sqrt{\alpha_2/\alpha_3} = 80^\circ. \) The flow velocity corresponds to an Ericksen number \( Er = 35. \)

Leslie angle \( \theta_0 = 80^\circ \) because at \( Er = \bar{\eta}VL/K = 35, \) the viscous effect is not strong enough to completely dominate the elastic effect. In \( Er, \) the characteristic viscosity of the nematic is taken to be \( \bar{\eta} = (\eta_1 + \eta_2)/2 = (\alpha_3 + \alpha_4 + \alpha_5)/2. \) The rotation of \( n \) into the flow direction reduces the local viscosity, and the velocity profile \( v(y) \) reacts by diminishing the shear rate at the walls and increasing it in the center to maintain a constant shear stress. In this case, the minimum viscosity at the center \( \eta_m \) is such that \( \eta_1/\eta_m = 13.4 \) and \( \eta_m/\eta_2 = 2.55. \)

### 6.3.2 Static orientational defects

When a drop has planar anchoring on its surface, boojums are the only possible defects, even when the drop is moving in the liquid crystal. With homeotropic anchoring, on the other hand, multiple defect patterns may appear and interesting transformations take place. Thus we will only consider homeotropic anchoring in this subsection, examining defects surrounding stationary particles as a preface to the flow-induced transformation discussed in the next subsection. A more or less coherent picture has emerged about defects near a stationary particle (Ruhwandl & Terentjev, 1997; Stark, 2001; Feng & Zhou, 2004). The Saturn ring and the satellite point defect are the two possible configurations (Fig. 6.3a and c), and their stability depends on the relative importance of surface anchoring and bulk elasticity, represented by the dimensionless group

\[
A_K = \frac{Wa}{K}, \tag{6.19}
\]
a being the effective radius of the drop. A Saturn ring incurs more distortion to the surface anchoring while a satellite costs more bulk energy. Thus, rings are favored at smaller $A_K$. Indeed, the point defect becomes unstable below a critical $A_K$, and spontaneously opens into a Saturn ring. For sufficiently weak anchoring, the Saturn ring shrinks onto the particle surface or even into the particle as an “imaginary ring” (Kuksenok et al., 1996). For larger $A_K$, both point and ring defects are stable, and either can be realized from proper initial conditions. The point defect becomes energetically more favorable with increasing $A_K$, but it is unclear whether the ring ever becomes unstable (Ruhwandl & Terentjev, 1997; Feng & Zhou, 2004).

In regularizing the Leslie-Ericksen theory to allow defects (Eq. 6.2), we treat $n(r)$ as a vector field. In reality, the molecular orientation is a pseudo-vector that does not distinguish $n$ and $-n$. As a consequence, our vector-based theory cannot allow defect lines of half strength; the surrounding $n$ field inevitably contains an apparent discontinuity between $n$ and $-n$ and thus incurs an infinite elastic energy. Instead of the Saturn-ring defect with a strength of $-1/2$, therefore, we predict a surface ring as shown in Fig. 6.3(d). With this caveat, we reproduce all the features noted above, including the effect of $A_K$ on defect stability. In particular, for strong enough anchoring, the satellite defect is produced if the initial $n$ is radial near the drop surface, while the surface ring arises from an initially uniform $n$ field. An additional parameter,

$$A_\sigma = \frac{W}{\sigma}, \quad (6.20)$$

governs the shape of the drop, and a small value is used in most of the simulations to ensure a nearly spherical drop. Figure 6.4 plots the position of the satellite point defect as a function of $A_K$. The increase of anchoring energy moves the point defect farther from the drop, as is noted by Ruhwandl & Terentjev (1997). At the limit of $A_K \to \infty$, $r_d/a \to 1.35$, which agrees well with prior calculations ($r_d/a = 1.26$ by Lubensky et al. 1998 and $\sqrt{2}$ by Pettey et al. 1998) and measurement ($r_d/a = 1.4 \pm 0.1$ by Cluzeau et al. 2001). With decreasing $A_K$, the defect approaches the drop and causes a protrusion on the interface. As $A_K$ falls below a threshold value, around 10 in this case, the point defect opens up into a surface ring. This threshold $A_K$ is close to the previous Monte Carlo prediction of approximately 7 (Ruhwandl & Terentjev, 1997). The distance $r_d$ has some practical implications. Potentially it can be used as a measurement of the anchoring strength $W$, which is otherwise difficult to determine. Furthermore, $r_d$ also determines the particle spacing in self-assembled arrays of droplets in nematic emulsions (Poulin & Weitz, 1998).

### 6.3.3 Flow-induced transformation of defect configuration

Static defects may be driven from one configuration to the other by an external electric or magnetic field (Terentjev, 1995; Loudet & Poulin, 2001). It will be interesting to see whether similar transitions can be effected by the flow surrounding a rising drop. Figure 6.5 shows schematically the computational domain for simulating rising drops in a nematic medium. A spherical drop of radius $a$ is initially centered at $(0, 4a)$, with either
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Figure 6.3: Defect configurations near a drop with homeotropic anchoring. (a) The satellite point defect, indicated by the black dot, within the $n$ field. $A_\sigma = 0.05$, $A_K = 100$. (b) The finite-element mesh for (a) is refined around the interface and the satellite defect. (c) Drawing of the director field for a Saturn-ring defect. (d) The surface-ring defect for $A_\sigma = 0.05$, $A_K = 100$, indicated by black dots on the equator of the drop.
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Figure 6.4: Position of the satellite point defect near a stationary drop with homeotropic anchoring. $r_d$ is the distance between the defect core and the centroid of the drop. For $A_K < 10$, the point defect loses stability and gives way to a surface ring on the equator. $A_\sigma = 0.05$.

Figure 6.5: Computational domain for a Newtonian drop rising in a nematic whose far-field orientation is vertical. The geometry is axisymmetric and only half of the meridian plane is used in the computation. The drawing is not to scale; $H = 20a$ and $L = 10a$. 
homeotropic or planar anchoring, although the latter will not be discussed until the next subsection. The far-field director orientation is vertical and parallel to the drop motion. A horizontal far-field $\mathbf{n}$ would upset axisymmetry and require a fully 3D simulation. We also disallow azimuthal components of $\mathbf{n}$ and $\mathbf{v}$. Thus, $\mathbf{n} = (0, 1)$ on the bottom, side and top walls. The velocity vanishes on the bottom and side walls, but the top is assigned a stress-free condition. On the axis of symmetry, we require $\partial/\partial r = 0$ for all variables except the radial components of $\mathbf{n}$ and $\mathbf{v}$: $n_r = 0$ and $v_r = 0$. For numerical parameters, the capillary width $\epsilon = 0.01a$, and a small grid size $h_1 = 0.006a$ is used on the interface and near the defect (cf. Fig. 6.3b). Inside the drop and in the matrix, the grid sizes are $h_2 = 0.08a$ and $h_3 = 0.1a$, respectively. These prescribed values are guidelines for mesh generation, and the actual mesh is spatially unstructured and varies adaptively during the simulation.

The rise of drops or bubbles in a nematic fluid is governed by 10 dimensionless numbers:

\begin{align*}
\alpha & = \frac{\rho_2}{\rho_1} \quad \text{(drop-to-matrix density ratio)}, \\
\beta & = \frac{\mu}{\eta} \quad \text{(drop-to-matrix viscosity ratio)}, \\
Eo & = \frac{\Delta \rho g a^2}{\sigma} \quad \text{(Eötvos number)}, \\
Mo & = \frac{\Delta \rho \bar{\eta}^4}{\rho_1^2 \sigma^3} \quad \text{(Morton number)},
\end{align*}

plus the 4 ratios of the 5 independent Leslie viscosities and the static parameters $A_\sigma$ and $A_K$. In $Eo$ and $Mo$, $\Delta \rho = \rho_1 - \rho_2$. Drop and bubble shapes deviate from the spherical at large $Eo$ (Grace et al., 1976), and our code has been shown to accurately capture this effect for Newtonian fluids (Yue et al., 2006b). For all results presented hereafter, $\alpha = 0.5$ and $\beta = 0.514$. A set of Leslie coefficients based on those of PAA (Chandrasekhar, 1992) and MBBA (de Gennes & Prost, 1993) are chosen as the baseline. Values of $\alpha_1$, $\alpha_3$, $\alpha_4$ and $\alpha_5$ are fixed at the ratio of $\alpha_1 : \alpha_3 : \alpha_4 : \alpha_5 = 5 : -1 : 18 : 18$. This also fixes the characteristic viscosity $\bar{\eta} = (\alpha_3 + \alpha_4 + \alpha_5)/2$. Then the viscosity ratio $\eta_1/\eta_2$ is varied through $\alpha_2$ (and $\alpha_6$ according to the Onsager relationship) to probe the effect of viscous anisotropy. Based on the terminal velocity $U$ of the rising drop, we determine the steady-state Reynolds number $Re = \rho_1 U a / \bar{\eta}$ and Ericksen number $Er = \bar{\eta} U a / K$.

Our results show that the flow shifts the orientation field downstream, and modifies the relative stability of the ring and point defects. The “phase diagram” in Fig. 6.6 depicts the stability of each configuration near a steadily rising drop, parametrized by $Er$ and $A_K$ that denote respectively the strengths of flow and surface anchoring as compared with the bulk elasticity. Six zones may be identified with different defect configurations. In zone I, the drop has an imaginary ring inside but no defects outside. In zone II, the surface ring is the sole stable configuration, while in zone IV, only point defects occur. In zone III, V and VI, both the surface ring and the satellite point defect are locally stable and either may appear depending on initial conditions.
For vanishing $Er$, the transitions from zone I to II and III with increasing anchoring strength are well known from static studies (Kuksenok et al., 1996; Ruhwald & Tertenjiev, 1997). This simple picture holds up to $Er \sim 1$. In this weak-flow regime, the only flow effect is to shift the surface ring or satellite defect downstream. The shift is more pronounced for higher $A_K$, since stronger surface anchoring favors a smaller ring. For higher $Er$, a transition from zone II to V or from zone III to IV takes place depending on $A_K$. In zone V, the point defect becomes locally stable; an initial point defect can now be stabilized in the wake of the drop by a sufficiently strong flow whereas in zone II, it would have opened up into a ring defect. If the initial condition has a ring defect, it remains stable in zone V but shifts downstream and shrinks in radius with increasing $Er$.

Going from zone III to IV with increasing $Er$, the ring defect loses stability. On a drop that initially bears a surface ring, the flow sweeps the ring downstream on the drop as it rises. If its terminal velocity puts it in zone IV, the surface ring will be shed into a satellite point defect in the wake. Starting with an initial point defect, we have only simulated the configuration with the defect in the wake of the drop. Having a point defect upstream of the drop appears unlikely in reality and may indeed be unstable to 3D disturbances. Throughout zone III and zone IV, the point defect remains stable and shifts downstream with increasing $Er$. The steady-state position of the ring and point defects is shown in Fig. 6.7 as a function of $Er$ that crosses from zone III to IV.

Increasing $Er$ further from zone IV, there is another transition to zone VI where the surface ring regains stability. At such high $Er$, the drop assumes an oblate shape, and an initial equatorial ring turns into a small surface ring near the bottom that cannot be shed into the wake as a point defect. Figure 6.8 shows an example of the steady-state director field in zone VI. Thanks to the oblate shape, the flow near the rear stagnation

Figure 6.6: A “phase diagram” of steady-state defect configurations. $A_K$ and $Er$ are varied by tuning $K$ and $g$, respectively. $A_\sigma = 0.01$, $\eta_1/\eta_2 = 3$. 

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Figure 6.7: Steady-state position of the defect near a rising drop as a function of the Ericksen number. $r_d$ is the distance between the centroid of the drop and the point defect ($r_d/a > 1$) or the center of the surface ring ($r_d/a < 1$). The arrow indicates the transition from zone III to IV at $Er = 1.10$ when the surface ring defect gives way to a point defect. $A_\sigma = 0.01$, $A_K = 30$, $\eta_1/\eta_2 = 3$.

Figure 6.8: Director orientation around a steadily rising oblate drop in zone VI, with a small surface ring indicated by two black dots in the rear of the drop. $\eta_1/\eta_2 = 3$, $A_\sigma = 0.01$, $A_K = 20$, $Er = 53.6$, $Eo = 1.20$, $Mo = 1.22 \times 10^{-6}$ and $Re = 21.9$. 
point of the drop is much reduced as compared with zone IV. The viscous forces are thus much weaker and can no longer drive the surface ring off. Similar configurations occur at high $Er$ in zone V. In fact, zone V and VI are connected at the top, and their division is mostly a result of our describing the phase diagram in terms of increasing $Er$ from equilibrium. The multiplicity of defect configurations in zone III, V and VI implies hysteresis. For example, raising $Er$ transforms a ring in zone III into a point defect in IV. Upon lowering $Er$ back into zone III, however, the point defect remains (cf. Fig. 6.7).

The trend in Fig. 6.7, showing defects being “convected” downstream by flow, agrees with the results of Yoneya et al. (2005) and Fukuda et al. (2004), but contradicts the prediction of Stark & Ventzki (2002) that defects shifts upstream under flow. As defects are orientation patterns rather than material properties, the convective effect is not intuitively obvious. Thus, we designed an experiment using silicone oil drops rising in the nematic 5CB (Khullar et al., 2007). Both the Saturn ring and the point defect shift downstream as the rising velocity increases. At high enough speed, the Saturn ring is shed into the wake as a point defect. This settles the question on the direction of convection, and confirms the flow-induced ring-to-point transformation predicted here.

The experimental conditions correspond to $A_K \approx 25$ and $Er \approx 0.25$, comparable to the values in Fig. 6.7. Note that Yoneya et al. (2005) have predicted a similar transformation at $Er \sim 10$, but with the flow field prescribed as the Stokes solution and with rigid anchoring ($A_K \to \infty$).

We should mention that the ranges of dimensionless parameters in the preceding discussion correspond to common small-molecule nematics under reasonable flow conditions, and the same is true for the next section. For example, the Leslie viscosity ratios are close to those of flow-aligning nematics such as PAA and MBBA. Take MBBA (de Gennes & Prost, 1993): $\bar{\eta} = 7.25 \times 10^{-2}$ Pa·s, $K = 5 \times 10^{-12}$ N (average of the three elastic constants for splay, twist and bend). Then the range of $0.1 \lesssim Er \lesssim 100$ in Figs. 6.6 and 6.7 corresponds to rising velocities from 0.14 to 140 $\mu$m/s for a drop of diameter 100 $\mu$m, which are consistent with the experimental values of Khullar et al. (2007).

### 6.3.4 Rising velocity, drag force and the flow field

In this subsection, we investigate the effect of the nematic microstructure on the flow field, with special attention to the implications of the viscous anisotropy and defect configuration. The geometric setup of the computation is the same as in the last subsection (cf. Fig. 6.5), but some of the parameter values differ. In particular, we will focus on a range of rise velocity that corresponds to zone IV for homeotropic anchoring, with the satellite defect being the sole stable configuration. This range displays the most interesting behavior when a ring defect transforms into a satellite during the rise of the drop. Planar anchoring will be considered as well. Figure 6.9 shows the transient rising velocity of a drop with planar and homeotropic anchoring. To give a sense of the time and velocity scales, a silicone oil drop 100 $\mu$m in diameter rising in MBBA would have $\bar{\eta}/(\Delta \rho ga) = 1.54$ s and $\Delta \rho ga^2/\bar{\eta} = 32.5$ $\mu$m/s, both within the experimental range of Khullar et al. (2007). Within each plot, we examine the effects of viscous anisotropy by
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Figure 6.9: Transient rising velocity of a drop in a nematic liquid crystal with (a) planar anchoring and (b) homeotropic anchoring. $Eo = 0.3$, $Mo = 5.56 \times 10^{-5}$, $A_\sigma = 0.2$ and $A_K = 40$. Time is made dimensionless by $\bar{\eta}/(\Delta \rho g a)$, and velocity by $\Delta \rho g a^2/\bar{\eta}$.

varying the ratio of two Miesowicz viscosities. As explained before, this is achieved by varying $\alpha_2$ and $\alpha_6$ while keeping the characteristic viscosity $\bar{\eta} = (\eta_1 + \eta_2)/2$ and the other Leslie coefficients fixed.

With planar anchoring, the rising velocity $V$ increases monotonically in time toward the terminal velocity $U$. For homeotropic anchoring, on the other hand, $V$ experiences an overshoot. This is caused by the transition from a surface ring to a point defect as explained in the last subsection. Figure 6.10 shows the director and flow fields near the drop with homeotropic anchoring at three times. Initially, $n$ is vertical throughout the domain. A surface ring forms quickly on the equator of the drop and shifts downstream as the drop rises ($t = 6.33$). With the drop accelerating, the flow sweeps the defect ring towards the rear of the drop ($t = 28.4$), and eventually transforms it into a point defect as $V$ attains the terminal velocity ($t = 52.7$). Comparing Fig. 6.10(b) and (c), the $n$ field with the point defect has a larger area—including the wake—in which $n$ are nearly orthogonal to the streamlines. According to Eq. (6.14), the nematic exhibits higher viscosity there than in areas where $n$ is aligned to the flow. Thus, the transformation from surface ring to point defect increases the viscous dissipation in the entire domain and thus the drag on the drop. This explains the overshoot in Fig. 6.9(b). Our recent experiment has confirmed such an overshoot during the ring-to-point defect transformation (Khullar et al., 2007). If the drop has a point defect at the start, or if the steady state falls in zone III, V or VI where the surface ring is stable, there will be no overshoot in $V$. For planar anchoring, two boojums stay at the poles throughout the rise (Fig. 6.10d), and the rising velocity again shows no overshoot. Roughly speaking, the orientation distortion extends into the nematic bulk for a fraction of the drop diameter; within this region the flow is affected by the anisotropic viscosity.
Figure 6.10: Director and flow fields around the drop with homeotropic anchoring at three times: (a) $t = 6.33$, (b) $t = 28.4$, and (c) final steady state at $t = 52.7$, with $Er = 15.8$ and $Re = 6.43$. (d) The steady state for a drop with planar anchoring; $Er = 25.2$ and $Re = 10.3$. These correspond to the curves in Fig. 6.9 with $\eta_1/\eta_2 = 34$. For the streamlines, the reference frame is affixed to the centroid of the drop.
Figure 6.11: Terminal velocity $U$ of the drops in Fig. 6.9 as affected by viscous anisotropy. $U$ is made dimensionless by $\Delta \rho g a^2/\bar{\eta}$. The range of $U$ corresponds to $4.93 < Re < 10.9$ and $12.1 < Er < 26.8$ for planar anchoring, and $4.29 < Re < 6.64$ and $10.5 < Er < 16.3$ for homeotropic anchoring.

With either type of anchoring, the rise velocity increases with viscous anisotropy as measured by $\eta_1/\eta_2$. Figure 6.11 gives a clearer view of this effect in terms of the terminal velocity $U$. Furthermore, planar anchoring produces a higher $U$ than homeotropic anchoring under otherwise identical conditions. This difference can again be explained by the drag as affected by different director fields. With planar anchoring (Fig. 6.10d), $n$ aligns with the streamlines in most of the domain, apparently minimizing the total dissipation (Jadżyn & Czechowski, 2001). This leads to a smaller drag and hence a greater $U$ than the drop with homeotropic anchoring. In both cases, however, alignment between $n$ and $v$ is more prevalent throughout the domain than their being orthogonal, and larger areas experience $\eta_2$ than $\eta_1$. With increasing $\eta_1/\eta_2$, therefore, the overall viscous dissipation diminishes with $\eta_2$ and the rising velocity $U$ increases as in Fig. 6.11, and more significantly for planar anchoring. In fact, for each value of $\eta_1/\eta_2$, the $U$ values for both anchoring types are bounded by the Hadamard-Rybczynski predictions using $\eta_1$ and $\eta_2$. The eddies in the wake of the drop in Fig. 6.10(d) form a vortex ring. It is not expected for Newtonian fluids at $Re = 10.3$ and viscosity ratio $\beta = 0.514$ (Dandy & Leal, 1989), nor does it appear for homeotropic anchoring. The explanation seems to rest with the anisotropic viscosity. The Reynolds number cited above is defined using the characteristic viscosity $\bar{\eta}$. In Fig. 6.10(d), the streamlines align with the director $n$ to varying degrees in the flow field. Thus, the local viscosity may be much below $\bar{\eta}$ in some regions. In particular, the streamlines next to the drop surface follow the $n$ field precisely. If we take the Miesowicz viscosity $\eta_2$ to be the local viscosity, the local Reynolds number will be around 180. The high momentum of this layer of fluid then leads to flow separation in the wake. In contrast, homeotropic anchoring causes $n$ to
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Figure 6.12: The drag coefficient for drops rising in a nematic as a function of $Re$ or $Er$. For homeotropic anchoring, the data correspond to the satellite configuration. $\eta_1/\eta_2 = 3$, $A_\sigma = 0.2$, $A_K = 40$.

be mostly orthogonal to $\mathbf{v}$ near the drop surface. The local Reynolds number is much lower and no separation occurs. We have also noticed that for planar anchoring, the recirculating zone shrinks with decreasing $\eta_1/\eta_2$ and disappears altogether when $\eta_1 = \eta_2$. This is consistent with viscous anisotropy being the cause of the vortex ring.

The drag on the drop can be further analyzed in terms of the drag coefficient

$$C_D = \frac{4\pi}{3} \frac{\Delta \rho g a^3}{\mu_1 U^2 (\pi a^2)}$$

(6.25)
defined from the terminal velocity $U$. The Hadamard-Rybczynski formula gives $C_D \cdot Re = 8(1 + 1.5\beta)/(1 + \beta)$ for a spherical Newtonian drop moving in a Newtonian matrix at vanishing $Re$ (Bachelor, 1980). In view of this formula, we plot the product $C_D Re$ against $Re$ and $Er$ in Fig. 6.12. $U$ and hence $Re$ and $Er$ are varied through the buoyancy force while keeping the viscosity ratio $\beta$ fixed. As noted before, homeotropic anchoring gives a higher drag than planar anchoring. If the matrix were a Newtonian fluid, $C_D Re$ would be constant for small $Re$ and increase with $Re$ for finite inertia. That $C_D Re$ decreases with increasing Reynolds number reflects the enhanced alignment of $\mathbf{n}$ by the flow field. This is better illustrated by $Er$ marked on the upper abscissa. For small Ericksen numbers, say $Er < 1$, the director orientation is hardly affected by the surrounding flow. Thus $C_D Re$ remains roughly constant. As $Er$ exceeds unity, viscous flow effects become comparable to the elastic effects and the flow-alignment of $\mathbf{n}$ reduces $C_D Re$. This decline eventually levels off as the flow-alignment saturates around $Er = 10$.

All prior results in the literature on the drag force are for rigid spheres with homeotropic anchoring at $Re = 0$. Nevertheless, a comparison is interesting. In the limit of vanishing $Er$, Stark & Ventzki (2001) fixed the $\mathbf{n}(r)$ field to the equilibrium solution with a
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Figure 6.13: Non-spherical drop shapes produced by the nearby defects. $Eo = 0.3$, $Mo = 5.56 \times 10^{-5}$, $A_\sigma = 0.5$, $A_K = 15$, $\eta_1/\eta_2 = 4.7$. 

(a) A drop with homeotropic anchoring and a surface ring rising at $Re = 5.54$, $Er = 2.04$. 
(b) A drop with homeotropic anchoring and a point defect. $Re = 3.92$, $Er = 1.44$. 
(c) A drop with planar anchoring and boojums. $Re = 7.16$, $Er = 2.64$. The boojums give the highest rising velocity while the point defect the lowest.

point defect, and computed the drag in terms of an effective viscosity $\eta_{eff}$ defined from the Stokes formula. In our case, a similar $\eta_{eff}$ can be estimated from the Hadamard-Rybczynski formula. At the lowest $Er = 0.109$ for homeotropic anchoring, our data gives $\eta_{eff}/\eta_2 = 2.63$, which is comparable to the results of Stark & Ventzki (2001): 1.83 for MBBA and 2.32 for 5CB. Our somewhat larger drag may have to do with wall confinement in the geometric setup (Fig. 6.5). The decrease of $\eta_{eff}$ with $Er$ is consistent with the findings of Stark & Ventzki (2002). At the highest $Er = 14.1$ in Fig. 6.12, $\eta_{eff}/\eta_2 = 2.22$. Although the Hadamard-Rybczynski formula no longer applies exactly at the finite $Re$ in this case, $\eta_{eff}$ asymptoting to a value significantly larger than $\eta_2$ bespeaks the “orientation boundary layer” on the drop surface due to the homeotropic anchoring (cf. Fig. 6.10c), inside which there is still considerable misalignment between $\mathbf{n}$ and $\mathbf{v}$. With even higher $Er$, the experiment of White et al. (1977) suggests that $\eta_{eff}$ approaches $\eta_2$. For planar anchoring, our data give $\eta_{eff}/\eta_2 = 2.18$ and 1.60 for the low-$Er$ and high-$Er$ limits of Fig. 6.12.

So far we have used relatively large values for the interfacial tension $\sigma$ (or small values of $A_\sigma$) to keep the surface curvature of the drop smooth. At larger $A_\sigma$, drops deform in response to the nearby orientational field, especially the presence of defects. Figure 6.13 illustrates three typical situations with the surface ring, satellite and boojum defects. The proximity of defects causes large curvature on the drop surface as a result of the competition between interfacial tension and anchoring energy. The cost in anchoring energy due to the defects is reduced at the expense of interfacial area such that the total energy is minimized. The lemon shape in Fig. 6.13(c) is well known in nematic drops with planar anchoring, and has also been reported for isotropic drops in nematic medium (Nastishin et al., 2005; Zhou et al., 2007). The drop with boojums rises the fastest while that with the satellite the slowest.
6.4 Summary

This paper presents a computational study of the rise of a Newtonian drop in a nematic liquid crystal. The problem is a rough counterpart of the Hadamard-Rybczynski problem in Newtonian fluids, although the Reynolds number ranges up to about 10 and mild drop deformation occurs. The key physics revealed by the simulation is the two-way coupling between the flow field and the molecular orientation field, and especially the configuration of orientational defects. The results can thus be summarized as follows.

(a) Effect of flow on the orientational field. With either a satellite point defect or a surface ring defect, the flow sweeps the defect downstream. Thus, the surface ring shrinks and moves toward the rear stagnation point, and at high enough Ericksen number may be transformed into a point defect. An initial point defect moves farther downstream with increasing Ericksen number. The stability of the two defect configurations is depicted by a phase diagram in terms of the Ericksen number and the ratio between surface anchoring and bulk elastic energies.

(b) Effect of orientation on the flow field. This is mainly manifested through the viscous anisotropy of the fluid. Drops with planar anchoring rise faster than those with homeotropic anchoring since the director field is better aligned with the streamlines. With homeotropic anchoring, a drop experiences an overshoot in the transient rising velocity when a ring defect changes into a detached point defect. With both types of anchoring, the drag coefficient decreases with the Ericksen number because stronger viscous flow aligns the director to the streamline and reduces frictional dissipation.

Through a systematic examination of the coupling between flow and molecular orientation, we strive to construct a coherent picture for the fluid mechanics of a particle moving in a nematic liquid. So far, the predicted flow effects on defect convection and transformation have been verified experimentally, as has the overshoot in rise velocity accompanying the defect transformation (Khullar et al., 2007). Finally, we point out two limitations in our work. The first is the vectorial nature of the Leslie-Ericksen theory. The original version cannot handle defects as they would constitute singularities. A relaxation of the unit-length requirement on the director allows integer-strength defects to be simulated, but the Saturn ring has to be represented by a surface ring. The latter has fewer degrees of freedom and possibly different stability regimes from an unattached Saturn ring. This restriction can be removed by adopting a tensorial representation of the molecular orientation (Rey & Tsuji, 1998; Feng et al., 2000; Yoneya et al., 2005). Second, the axisymmetric 2D geometry of the computation precludes the interesting scenario of drops rising in a nematic with horizontal far-field orientation.
Bibliography


Bibliography


Chapter 7

Dynamic simulation of droplet interaction and self-assembly in a nematic liquid Crystal *

7.1 Introduction

Common emulsions involve isotropic liquids such as oil and water. When the continuous phase is an anisotropic liquid crystal, the emulsion exhibits unusual microstructures. In their well-known monograph, de Gennes & Prost (1993) described the aggregation of bubbles on the free surface of a cholesteric into strings that delineate the molecular orientation. In nematics, Poulin and coworkers carried out a series of experimental observations on pattern formation of suspended particulates (Poulin et al., 1994, 1997b; Loudet et al., 2000, 2001). Water droplets suspended in the thermotropic liquid crystal pentylcyanobiphenyl (5CB) in the nematic phase form chains with neighboring drops separated by a constant distance, and the chains tend to align with the background nematic orientation (Poulin et al., 1997b). This was later confirmed by experiments using PDMS oil drops in another thermotropic nematic (Loudet et al., 2000, 2001). The formation of parallel chains requires a strong homeotropic anchoring on the drop surfaces, i.e., with the director $n$ normal to the surface. With planar anchoring or weak homeotropic anchoring, the droplets form kinked lines at an angle with the background orientation (Poulin & Weitz, 1998; Mondain-Monval et al., 1999; Poulin et al., 1999; Musevic et al., 2006). Ruhwandl & Terentjev (1996, 1997) obtained analytical solutions in the weak anchoring limit for particles bearing the Saturn ring, and thus provided an explanation for the kinked lines. In the rest of this paper, we limit ourselves to droplets with strong homeotropic anchoring.

Poulin et al. (1997b); Poulin & Weitz (1998) proposed a theoretical framework for understanding the self-assembly of droplets into chains. As the water drop possesses homeotropic anchoring on its surface, its inclusion in an otherwise uniformly oriented liquid crystal necessitates the appearance of defects. In this case, a point defect known as a “hyperbolic hedgehog” accompanies each water droplet, and the two form a dipole when viewed from a great distance. Attraction between such dipoles explains the formation of chains of droplets separated by the satellite point defects. Furthermore, the elastic energy incurred by the point defect prevents the neighboring drops from contact and coalescence. Thus, long-range attraction and short-range repulsion both play roles in the formation and stability of the self-assembled pattern. Poulin et al. (1997b); Poulin & Weitz (1998) and Lubensky et al. (1998) used phenomenological ansatz director fields to

compute the long-range attraction between neighboring particles as due to the interaction among effective dipoles and quadrupoles.

Qualitatively, the above explanation is clear and convincing. But the nature of pairwise interaction needs to be clarified in a more rigorous way. For example, the dipole-dipole interaction accounts for long-range attractions, and predicts $F \sim R^{-4}$ for $R \gg a$, $F$ being the attraction force, $R$ being the center-to-center separation and $a$ being the particle radius. Both experimental measurements (Poulin et al., 1997a; Noël et al., 2006) and numerical computations (Fukuda et al., 2004b) have borne out this long-range scaling. What becomes of the attractive force as the particles move close to each other? Lubensky et al. (1998) used the repulsion between quadrupolar moments to predict a decline of the attraction, but could not produce a repulsive force even when $R \to 2a$. Data of Poulin et al. (1997a) show that the attraction force $F$ starts to fall below the scaling at $R \approx 3a$. Noël et al. (2006) measured $F$ for a wider range of $R$. The decline of the attraction force for short separations is much steeper than predicted by Lubensky et al.’s model. Finally, Fukuda et al. (2004b) computed the repulsion between two “anti-parallel” dipoles, with the two defects on the outer side of the droplets. They found $F \sim r^{-3}$ in the whole range of $r$ from slightly above $2a$ to $9a$, in disagreement with the $r^{-4}$ scaling predicted by dipolar interaction. Thus, there is still much uncertainty about the nature of the pairwise interaction.

More recently, two-dimensional (2D) colloidal crystals have been achieved via nematic-mediated self-assembly (Nazarenko et al., 2001; Musevic et al., 2006). They are of potential importance as a novel way to control the stability and structures of colloids (Loudet & Poulin, 2002) and as templates for novel optical materials (Rudhardt et al., 2003). In particular, Musevic et al. (2006) identified lateral interaction between parallel chains as the key mechanism in governing 2D crystallization. As in Poulin et al. (1997b), particles with the hedgehog defect form chains along the direction of the background nematic orientation. If another particle is in the vicinity of the chain with its dipole parallel and in the same direction as those in the chain, it is repelled by the chain. Conversely, if the single particle’s dipole is opposite to that of the chain (anti-parallel configuration), attraction occurs. Hence, anti-parallel chains aggregate and form a regular and robust hexagonal lattice. Using an energy minimization procedure similar to that of Fukuda et al. (2004b), Musevic et al. (2006) computed the equilibrium arrangement of particles, which turns out to be a periodic pattern similar to observations. But the defect separating particles in the chain is a small ring instead of the observed point defect.

All the above computations are concerned with the static equilibrium position, which has been sought through a straightforward energy minimization procedure. In reality, the particles move as a result of elastic relaxation, and hence the director field is not at equilibrium until the motion ceases in the end. The process cannot be treated as quasi-static in general, and the dynamic pairwise and multi-particle interaction may differ appreciably from predictions based on equilibrium director fields. The dynamic problem is much more difficult than the static one. The motion of the particles is typically driven by an elastic force due to nematic distortion. The fluid flow and evolution of the director field are coupled, and both are in turn dependent on the position and motion of the
Chapter 7. Droplet interaction and self-assembly in a nematic liquid crystal

particle surfaces on which velocity and anchoring boundary conditions are enforced.

This complex task seems to have been first tackled by Stark & Ventzki (2002) using the Leslie-Ericksen theory (de Gennes & Prost, 1993) to model the nematic. Up to now, dynamic simulations have been done on the motion of single particles. Yamamoto (2001) developed a scheme for evolving the position of multiple particles by elastic forces in a quasi-static manner. The director field is equilibrated at every step and no fluid motion is involved. But there have been no dynamic simulation on pairwise and multi-particle interactions in a nematic. Previous experiments and computations on a single particle (Fukuda et al., 2004a; Zhou et al., 2007a; Khullar et al., 2007) have shown rich dynamics in the approach to multiple defect configurations and in the transition among them. For multiple particles, the dynamic evolution will be important to the self-assembly process, and therefore warrants an in-depth study.

In this paper, we present what appears to be the first dynamical simulation of the self-assembly of multiple droplets in a nematic liquid crystal. The numerical methodology is based on a phase-field representation of the interface, and employs finite elements with adaptive meshing to resolve the interfaces as well as defects in the nematic bulk. After describing the numerical methodology and the algorithm, we will report axisymmetric and 2D planar simulations on pairwise interactions and self-assembly of multiple droplets. In particular, we will explore the nature of longitudinal and lateral pairwise interaction forces. In view of prior experimental observations, we will then investigate the formation of chains, chain-chain attraction and repulsion as well as 2D assembly of a cluster of droplets. Where possible, comparisons will be made to experiments as well as previous static computations.

7.2 Theory and numerical methods

Recently, we have developed a general finite-element algorithm AMPHI for simulating interfacial dynamics in two-component rheologically complex fluids (Yue et al., 2006b). The interfaces are treated as having a small but finite thickness with a phase-field variable changing continuously from one phase to the other. Fluid properties, such as density and viscosity, and flow quantities, such as pressure and velocity, change steeply yet continuously across the interfaces. Hence, no discontinuity appears in the system. The phase-field $\phi$, which indicates the position of the interfaces, is governed by a mixing energy consisting of two components, one “hydro”-philic and the other “hydro”-phobic. This energy-based formulation easily incorporates complex rheology as long as the free energy of the microstructures are known. The package has been extensively validated (Yue et al., 2006b), and applied to simulate drop deformation, coalescence and jet breakup in Newtonian and viscoelastic liquids (Yue et al., 2006a; Zhou et al., 2006).

The nematic liquid crystal admits a natural energetic description. Bulk distortions may be described by the Frank energy (de Gennes & Prost, 1993), and surface anchoring by the Rapini-Papoular anchoring energy (Yue et al., 2004; Rapini & Papoular, 1969). Thus, the elastic characteristics are easily incorporated into the phase-field framework of AMPHI. Anisotropic viscosities may be introduced via Leslie coefficients. Thus, we
have recently adapted AMPHI to explore the defect dynamics around a single drop rising in a nematic (Zhou et al., 2007b,a). For the multi-drop simulations to be presented, the code has been generalized to allow periodic boundary conditions in two directions. Details of the theoretical model and computational algorithm can be found in Yue et al. (2004, 2006b) and Zhou et al. (2007a). In the following, we will only summarize the main ideas and give the governing equations.

Consider a two-component immiscible blend of a Newtonian liquid and a nematic liquid crystal. For the problem at hand, we may visualize Newtonian drops of arbitrary shape and size suspended in the nematic medium. The Newtonian bulk is represented by \( \phi = -1 \) and the nematic by \( \phi = 1 \), and the interfaces are simply the level set of \( \phi = 0 \). The governing equations are the continuity and momentum equations, supplemented by the Cahn-Hilliard equation for the transport of the phase field \( \phi \) (Yue et al., 2004) and the Leslie-Ericksen equations for the nematic director \( \mathbf{n} \) (Zhou et al., 2007a):

\[
\nabla \cdot \mathbf{v} = 0, \quad (7.1)
\]

\[
\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \nabla \cdot \mathbf{\sigma}, \quad (7.2)
\]

\[
\frac{\partial \phi}{\partial t} + \mathbf{v} \cdot \nabla \phi = \gamma \lambda \nabla^2 \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\epsilon^2} \right], \quad (7.3)
\]

\[
h = \gamma_1 \mathbf{N} + \gamma_2 \mathbf{D} \cdot \mathbf{n}, \quad (7.4)
\]

where \( \lambda, \epsilon \) and \( \gamma \) are the interfacial energy density, capillary thickness and mobility of the diffuse interface, respectively. The density \( \rho = \frac{1+\phi}{2} \rho_1 + \frac{1-\phi}{2} \rho_2 \) is an average between the two components. The stress tensor \( \mathbf{\sigma} \) in the momentum equation is:

\[
\mathbf{\sigma} = -\lambda \nabla \phi \nabla \phi - K \frac{1+\phi}{2} \nabla \mathbf{n} \cdot (\nabla \mathbf{n})^T - \mathbf{G} + \frac{1+\phi}{2} \mathbf{\sigma}' + \frac{1-\phi}{2} \mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T), \quad (7.5)
\]

where \( \mathbf{G} \) is the anchoring stress of the nematic director on the interface, \( \mathbf{G} = A(\mathbf{n} \cdot \nabla \phi) \mathbf{n} \nabla \phi \) for planar anchoring and \( \mathbf{G} = A[I(\mathbf{n} \cdot \mathbf{n})] \nabla \phi - (\mathbf{n} \cdot \nabla \phi) \mathbf{n} \nabla \phi \) for homeotropic anchoring, \( A \) is the surface anchoring energy density, \( K \) is the bulk elastic constant of the nematics under the one-constant approximation, and \( \mu \) is the Newtonian viscosity. \( \mathbf{\sigma}' \) is the Leslie viscous stress (Leslie, 1966, 1968) in the nematic phase

\[
\mathbf{\sigma}' = \alpha_1 \mathbf{D} : \mathbf{n} \mathbf{n} \mathbf{n} + \alpha_2 \mathbf{N} \mathbf{n} + \alpha_3 \mathbf{N} \mathbf{n} + \alpha_4 \mathbf{D} + \alpha_5 \mathbf{n} \mathbf{n} \cdot \mathbf{D} + \alpha_6 \mathbf{D} \cdot \mathbf{n} \mathbf{n}, \quad (7.6)
\]

where \( \alpha_{1-6} \) are the Leslie viscous coefficients obeying an Onsager relation \( \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \) so five of them are independent (de Gennes & Prost, 1993). \( \mathbf{D} = \frac{1}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right] \) is the strain rate tensor, \( \Omega = \frac{1}{2} \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right] - \nabla \mathbf{v} \) is the vorticity tensor, and \( \mathbf{N} = \frac{\partial \mathbf{v}}{\partial t} - \mathbf{\Omega} \cdot \mathbf{n} \) is the rotation of \( \mathbf{n} \) with respect to the background flow field. The director field \( \mathbf{n} \) evolves in the flow field according to a balance between elastic and viscous torques as given in Eq. (7.4). The molecular field \( \mathbf{h} \), denoting elastic torque in the nematic, derives from the free energies of the system (de Gennes & Prost, 1993):

\[
h = K \left( \nabla \cdot \left( \frac{1+\phi}{2} \nabla \mathbf{n} \right) - \frac{1+\phi(n^2-1)}{2} \right) - g, \quad (7.7)
\]
with $g = A(n \cdot \nabla \phi)\nabla \phi$ for planar anchoring and $g = A[((\nabla \phi \cdot \nabla \phi)n - (n \cdot \nabla \phi)\nabla \phi]$ for homeotropic anchoring. The term involving $\delta$ arises from regularizing the Frank energy to allow defects (Zhou et al., 2007a):

$$f_{\text{reg}}(n) = K \left[ \frac{1}{2} |\nabla n|^2 + \frac{(n^2 - 1)^2}{4\delta^2} \right].$$

(7.8)

Thus, a defect is represented by $|n|$ that falls below unity within a small area of size $\delta$. This regularization is inspired by the Landau-Ginzburg equation (Lin & Liu, 2000; Liu & Walkington, 2000), and amounts to a simplified form of Ericksen’s theory with a variable order parameter (Ericksen, 1991), with $|n|$ acting as the local order parameter. We have used $\delta = 4\epsilon$ since the defect core size is comparable to the interfacial thickness. Note that in the limit of $\epsilon \to 0$, the diffuse interface model reverts to the classic Navier-Stokes sharp-interface hydrodynamics (Yue et al., 2004). In particular, the interfacial tension $\sigma$ and Rapini-Papoular anchoring constant $W$ can be recovered from the diffuse-interface parameters for small $\epsilon$: $\sigma = 2\sqrt{2}/3\epsilon$ and $W = 2\sqrt{2}A/3\epsilon$. We have used $\epsilon = 0.01a$ for most of the calculations, $a$ being the radius of the droplets. Previous computations indicate that such an $\epsilon$ is small enough to approximate the sharp-interface limit in the present simulations (Yue et al., 2006b,a), especially because they involve no small-scale phenomenon such as surface rupture.

In axisymmetric and planar 2D geometries, these equations are discretized on an unstructured grid of triangular elements using the Petrov-Galerkin formulation with streamline upwinding for the constitutive equation (Yue et al., 2006b). A critical ingredient of the algorithm is an adaptive meshing scheme that accurately resolves the drop interfaces as well as the defect cores at a manageable computational cost. As the interface and defects move, the mesh quality is monitored and updated by coarsening and refinement as needed. Time integration is by an implicit second-order scheme with the time step automatically adjusted according to the motion of the interface (Yue et al., 2006b). Typical grid sizes are $h_1 = 0.006a$ on the interface and near defects, $h_2 = 0.2a$ in the bulk of the drop fluid and $h_3 = 0.5a$ in the matrix. The meshing module of the program smooths the transition between different regions. Numerical experiments have shown that these grid sizes and the time step used in the simulations are sufficient for numerical convergence.

As a general numerical algorithm for computing nematic-particle interactions, our package is versatile and powerful. We should perhaps mention some of its features, though not all will be important to the computations reported below. First, our code accounts for several factors that have been largely ignored in the past. These include the drop deformation, which in some cases may interact with the nematic order in the vicinity of the surface (Zhou et al., 2007b), finite anchoring strength that may conceivably be tuned to manipulate the resultant colloidal structure, and the fully anisotropic rheology of the nematic, which plays a major role in the motion of dispersed particulates in a nematic medium (Zhou et al., 2007a). Second, the phase-field formulation has the advantage of simulating topological changes such as interfacial rupture and coalescence naturally under a short-range force resembling the van der Waals force (Yue et al., 2005). There is no need for manual intervention as in sharp-interface models to effect such events.
Finally, the finite-element method with adaptive meshing makes possible simulations of multiple interfaces and defects in complex geometries while maintaining accurate spatial resolution of the large-gradient regions.

We must note that the code is limited at present to two spatial dimensions. Some of the geometric setups to be simulated are axisymmetric and thus can be readily handled by the code. Others, such as the self-assembly of multiple droplets, occur in 3D and we are forced to compute a planar 2D analogy of them. However, this is not as severe a restriction as it might appear. Considerable theoretical and experimental work has been done on particle interaction in freely suspended smectic C films, where the dynamics is essentially 2D. Such results provide direct benchmarking for our computations. Furthermore, their general similarity to observations in 3D nematics suggest that the underlying physics is common, and that our 2D numerical simulations are relevant to 3D reality. More details will be given in the next section.

Some remarks on terminology seem necessary to avoid confusion in discussing the results. The term “2D” has two meanings in this paper. One refers to the 2D patterns formed by particles as opposed to 1D chains. The other refers to the spatial dimensions in the computations. Similarly, we sometime use the term “dipole” to refer to the drop-defect ensemble, with the drop-to-defect vector indicating its orientation. This is to be distinguished from the electrostatic analogy that treats the particle-particle interaction as that between “dipolar” and “quadrupolar” moments (Lubensky et al., 1998). In fact, an important conclusion to be drawn from our simulations is that the pairwise interaction is not of the dipolar nature in general.

7.3 Results and discussion

This section has two main parts. The first deals with pairwise interactions, with each of the droplets bearing a single hyperbolic hedgehog defect. The two droplets are initially arranged so that their line of centers is parallel or perpendicular to the far-field nematic orientation. These will be called, respectively, longitudinal and lateral pairs. In each case, the two drop-to-defect dipoles may be in the same direction (parallel) or opposite to each other (anti-parallel). Special attention will be given to the pairwise interaction forces, in connection with the open questions in the literature regarding the dipolar nature of this interaction. The second part explores the interaction and self-assembly of multiple droplets. We will study the formation of linear chains, interaction between neighboring chains in parallel and anti-parallel orientations, and finally 2D assembly of droplets in a doubly periodic domain.

For a longitudinal pair of droplets, the geometry is axisymmetric. For the other configurations, the real physics is 3D and we are forced to simulate a 2D analogue of it in a planar domain. With axisymmetry, the computational domain is half of the meridian plane, shown in Fig. 7.1. The rectangular domain has a width of $L = 15a$ in the radial direction and length $H = 24a$ along the axis of symmetry, where $a$ is the drop radius. The two droplets are located on the $z$ axis with top-bottom symmetry, at some initial separation. The outer boundary at $r = L$ is a no-slip wall, and periodic
Figure 7.1: The geometry of the computational domain. The radius of the drops is \( a \). With axisymmetry around the \( z \) axis, the domain is half of the meridian plane. For 2D computations, the domain is the entire rectangular box.

boundary conditions are imposed on the top and bottom. The \( z \) axis has symmetric boundary conditions for all the variables: \( \partial / \partial r = 0 \). Note that no boundary conditions are needed on the drop surfaces; velocity and shear-stress continuities occur naturally and the interfacial tension is accounted for by the interfacial stress \(-\lambda \nabla \phi \nabla \phi\) in Eq. (7.5). The 2D domains are rectangles with periodic conditions in the vertical or both directions. For the former, the non-periodic boundaries are non-slip walls with rigid anchoring.

The initial \( n(r) \) field is uniformly vertical everywhere except within a small distance from each drop; in this shell \( n \) aligns radially. Thus, the initial director field has an abrupt jump between the near field and far field orientation. After the simulation starts, there is a rapid rearrangement in the near field, resulting in a point defect near each droplet. For all cases except one (cf. Fig. 7.4), this initial transient is short and insignificant to the ensuing dynamic evolution of the director field. Even though the director does not distinguish between \( n \) and \(-n\) in reality, we have found the direction of \( n \) a convenient means to control the location of the defect. If the far field \( n \) is upward and the near field is radially outward, the point defect will nucleate below the drop. Changing either will put the defect above the drop. This scheme will be used to produce parallel and anti-parallel dipoles in the simulations.
The complete set of dimensionless groups governing our system is:

\[ \alpha = \frac{\rho_2}{\rho_1} \]  

(drop-to-matrix density ratio), \hspace{1cm} (7.9)

\[ \beta = \frac{\mu}{\alpha_4/2} \]  

(drop-to-matrix viscosity ratio), \hspace{1cm} (7.10)

\[ A_K = \frac{Wa}{K} \]  

(anchoring-to-bulk energy ratio), \hspace{1cm} (7.11)

\[ A_\sigma = \frac{W}{\sigma} \]  

(anchoring-to-interfacial tension ratio), \hspace{1cm} (7.12)

\[ Re = \frac{\rho_1 U a}{\eta} \]  

(Reynolds number), \hspace{1cm} (7.13)

\[ Ca = \frac{U \eta}{\sigma} \]  

(capillary number), \hspace{1cm} (7.14)

along with the various length ratios of the geometry and ratios between the Leslie viscous coefficients. \( Re \) and \( Ca \) are defined using a characteristic velocity \( U = \frac{K}{\eta a} \) and the viscosity \( \eta = (\alpha_3 + \alpha_4 + \alpha_5)/2 \) that is the average between the largest and smallest Miesowicz viscosities (de Gennes & Prost, 1993). The ratio \( \alpha_3/\alpha_2 \) distinguishes “flow-aligning” nematics from “tumbling” ones in simple shear flows. In the complex flows due to droplet self-assembly, this distinction is insignificant. Experiments have also used a wide range of thermotropic and lyotropic liquid crystals of both aligning and tumbling types. We have adopted the Leslie viscosities of a common nematic MBBA at 25°C for all computations (de Gennes & Prost, 1993): \( \alpha_1 = 6.5 \) centipoise (cp), \( \alpha_2 = -77.5 \) cp, \( \alpha_3 = -1.2 \) cp, \( \alpha_4 = 83.2 \) cp, \( \alpha_5 = 46.3 \) cp, \( \alpha_6 = -32.4 \) cp. Furthermore, we have assumed that the isotropic drop phase has the same density as the nematic and the same viscosity as the isotropic part of the nematic viscosity: \( \alpha = 1, \beta = 1 \). For the anchoring energy \( W \), prior experiments cited “strong anchoring” without giving a value (Poulin & Weitz, 1998) while computations typically assumed rigid anchoring (Lubensky et al., 1998). In all the computations, we have used a large \( A_K = 100 \). In addition, \( W \) is typically much smaller than the interfacial tension \( \sigma \) (Sonin, 1995). We have used \( A_\sigma = 0.2 \). This, along with a small \( Ca = O(10^{-3}) \), ensures that the droplets never deviate visibly from the spherical shape. The Reynolds number \( Re = O(10^{-2}) \) for all the computations and inertia is negligible.

In presenting the results, we have used two different methods to visualize the nematic orientation (Fig. 7.2). The first is a computed light intensity map through crossed polarizers, which would correspond to birefringent images recorded in the experiments. This will be used for the longitudinal pairs in axisymmetric geometry. The numerical scheme is detailed by Han & Rey (1995). For a satellite point defect near a drop, Fig. 7.2(a) shows the light intensity map along with vector lines for the director field \( \mathbf{n}(\mathbf{r}) \). The pattern of two bright lobes separated by a darker line, with the point defect at the tip, closely resembles experimental pictures in the literature (Poulin et al., 1997a; Noël et al., 2006; Khullar et al., 2007). The second presentation (Fig. 7.2b) uses contours of \( (n_x^2 - 1/2)^2 \) in a 2D planar domain, where \( n_x \) is the horizontal component of \( \mathbf{n} \) (Yamamoto, 2001; Yamamoto et al., 2004). Thus, bright areas indicate a horizontal or vertical \( \mathbf{n} \), while dark
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Figure 7.2: Representation of the director field. (a) Birefringent pattern for an axisymmetric $n$ field through crossed polarizers; (b) Grayscale representation of $n$ in 2D geometries with contours of $(n_x^2 - 1/2)^2$. White indicates a vertical or horizontal $n$, while black means a $45^\circ$ tilt.

areas have $n$ at a $45^\circ$ angle. The point defect is clearly marked by the focal point from which four dark brushes emanate. The gradient of the grayscale indicates the degree of elastic distortion, which reaches a maximum at the point defect and dies off in the far field.

### 7.3.1 Pairwise interactions

#### 1. Longitudinal pairs

Consider first the interaction of two particles in the parallel configuration, with a center-to-center distance of $R$. The defects are on the line of centers, which is parallel to the far-field director orientation. Representing the long-range force by the interaction of dipolar and quadrupolar moments, Lubensky et al. (1998) constructed a phenomenological formula for the attraction force $F_P$ between the particles:

$$
\frac{F_P}{4\pi K} = -24.97 \left( \frac{a}{R} \right)^4 + 62.21 \left( \frac{a}{R} \right)^6 .
$$

Note that the dipolar attraction (the first term) dominates the quadrupolar repulsion (the second term) at large distances. Mathematically, the repulsive force becomes significant for smaller $R$, but the formula is supposed to be used only for $R \gg a$. In the rest of the paper, we will use the same sign convention, i.e., repulsion being positive and attraction being negative.
Figure 7.3: Attraction between a longitudinal pair of drops in the parallel configuration. Time is made dimensionless by the elastic relaxation time \( \tau_e = \eta a^2 / K \), length by \( a \) and force by \( 4\pi K \). The same non-dimensionalization is used for all later plots. (a) The center-to-center distance \( R \) as a function of time. The insets show the defect configuration, visualized as in Fig. 7.2(a), at time \( t = 56.1 \) and 145.1. (b) The attraction force \( F(R) \), computed by integrating the elastic stress around the drop, compared with prior experimental data (symbols) and theoretical results (lines). The dash line is the drag force estimated from Eq. (7.16), and the dash-dot line is the phenomenological \( F_P \) of Eq. (7.15). The long-dash line indicates the \( R^{-4} \) scaling.

In our dynamic simulation in the axisymmetric computational domain of Fig. 7.1, the two droplets indeed attract each other, and their separation decreases in time from an initial \( 7a \) to a final equilibrium value \( R_e = 2.45a \) (Fig. 7.3a). The speed of approach increases initially as \( R \) shrinks, and reaches a maximum around \( R = 3.5a \). Afterwards, the speed quick drops to zero. In the equilibrium state, one point defect is roughly midway between the two drops, a distance of \( 1.22a \) from either drop center. Compared with the position of the point defect near a single drop (Zhou et al., 2007a), the defect between the droplets is “compressed”. The other defect is at a greater distance of \( 1.32a \), close to that near a single drop. Note that the equilibrium separation of \( 2.45a \) agrees with prior experimental (Noël et al., 2006) and numerical results (Fukuda et al., 2004a) to within 3%. The \( R(t) \) curve closely resembles that of Poulin et al. (1997a) In the experiment, the particles’ approach takes about 5 seconds, which corresponds to a dimensionless time of 136, comparable to that in Fig. 7.3(a).

We have also computed the instantaneous attractive force \( F \) between the droplets, by integrating the elastic stress components over the drop surface, and this is plotted in Fig. 7.3(b). To extract an attractive force from the particle trajectory, Poulin et al. (1997a) calculated a Stokes drag with an “effective viscosity” \( \mu_e \) measured from a capillary tube:

\[
F_D = 6\pi\mu_e aV
\]  

(7.16)
where $V$ is the instantaneous velocity of the particles. Then $F$ is equated to $F_D$ by assuming zero inertia for the particles. In our computations, $Re \sim 10^{-2}$ and inertia is negligible. But strictly speaking, the idea of a constant effective viscosity is suspect since the anisotropic viscosity may vary significantly depending on the flow field (Zhou et al., 2007a). As a test of Eq. (7.16), we have computed $F_D$ by taking $\mu_e$ to be $\eta$, the average between the largest and smallest of the Miesowicz viscosities. This turns out to be a reasonable approximation of $F$; it is some 12% smaller in magnitude but follows the same trend. The discrepancy comes from the choice of $\mu_e$. Since the nematic director is mostly normal to the drop surface, it is no surprise that $\mu_e$ underestimates the local viscosity and hence the drag force $F_D$.

For large separations ($R > 5a$), all computations and measurements agree that the attraction force $F$ obeys the $R^{-4}$ scaling. This is consistent with the dipolar attraction in Eq. (7.15). The magnitude of our $F$ is slightly below Lubensky et al.’s formula and Noël et al.’s data. Poulin et al.’s data, however, are lower by a factor of about 4. This may be due to their using a $\mu_e$ in Eq. (7.16) that is too low. Prior studies (Poulin et al., 1997a; Fukuda et al., 2004a; Noël et al., 2006) put the lower bound of $R$ for the $R^{-4}$ scaling between $3a$ and $4a$, whereas our $F$ starts to fall below the power-law at $R \approx 5a$. The reason for this difference is unclear at present. Our $F$ reaches a maximum near $R = 3.6a$ and then declines with decreasing $R$. The data of Noël et al. show a much stronger attraction for smaller $R$, followed by a precipitous drop within $R \approx 2.5a$. Thus, their interaction is much more “hard-sphere-like”, with a shorter range than in our case. Equation (7.15) is a poor approximation for short-range interaction, as expected. The quadrupolar repulsion is far too weak to represent the decline of attractive force with decreasing $R$. In fact, the formula never predicts much reduction in the attraction before the drops touch.

If the drops are initially closer than the equilibrium separation $R_e$, they are expected to repel each other. To explore this scenario, we simulated the separation of two droplets from an initial separation of $2.37a$. Upon start of the simulation, the $n$ field relaxes into one with two point defects, similar to the insets of Fig. 7.3(a). This elastic relaxation, an artifact due to the initial condition, produces the anomalous behavior in Fig. 7.4 for the initial period of the simulation ($t \lesssim 2$). At the beginning, $R$ decreases momentarily ($t \lesssim 0.5$) before increasing with time. Then the droplets separate from each other with increasing velocity until $t \approx 2$. With negligible inertia, the acceleration reflects the changing forces on the droplets. Indeed, the repulsive force $F$ also increases with $R$ in this period, which is counterintuitive. Since time $t$ is scaled by the elastic relaxation time $\tau_e = \eta a^2 / K$, the duration of this initial transient ($t \approx 2$) being of order one is reasonable. Only afterwards does $F$ decrease with increasing $R$ as expected. The motion ceases at an equilibrium separation of $R_e = 2.45a$, the same value as reached in the pairwise attraction simulation of Fig. 7.3. Therefore, only the latter part of the simulation, with $t > 2$ and $R > 2.4$, can be meaningfully compared with static measurements of $F(R)$ (Fig. 7.4b). The numerical result parallels the trend of the experimental data (Noël et al., 2006), although shifted to larger $R$, again indicating longer-range interaction in our computation than in the experiment. Incidentally, Noël et al. (2006) reported that
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Figure 7.4: Interaction between a parallel longitudinal pair of droplets with an initial separation smaller than the equilibrium value. (a) Temporal evolution of the center-to-center distance $R(t)$ and elastic force $F(t)$. $F$ is computed by integrating the elastic stress, and positive values denote repulsion. (b) Comparison between the computed $F(R)$ and measurements by Noël et al. (2006)

Figure 7.5: The repulsion between an anti-parallel longitudinal pair. (a) The separation $R(t)$ increases from an initial value of 2.5$a$. (b) The repulsion force $F$ has a long range and decays slowly with $R$.

pushing the two particles too close will result in the point defect opening into a ring. Our simulations show the same transition for initial separations below 2.37$a$.

We turn our attention now to two droplets in the anti-parallel configuration, with the two point defects lying outside of the pair, one on the top of the upper drop and the other below the lower drop. The initial center-to-center separation between the drops

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Figure 7.6: Experimental observation of the repulsion between an anti-parallel pair of droplets. The insets are images through crossed polarizers. The drop on top is at the end of a vertical chain (not shown) with upward dipolar orientation. \( R \) and \( t \) are made dimensionless by the drop radius \( a \) and \( \tau_e = \eta a^2 / K \), with \( \eta = 0.0765 \) Pa·s, \( a = 50 \) μm and \( K = 10^{-11} \) N.

is 2.5a. There is a rapid elastic relaxation at the beginning of the run, but unlike in Fig. 7.4, this transient is insignificant compared with the length of the simulation. The two droplets separate in time with a slowly decreasing velocity (Fig. 7.5a). The simulation is terminated as \( R \) approached 10a and the droplets get close to the top and bottom of the computational domain (cf. Fig. 7.1). At that time the two are still moving apart very slowly. As before, we plot the repulsion force \( F \) as a function of \( R \) in Fig. 7.4(b). For \( R \) up to 6a, \( F \) decays as \( R^{-1/3} \). For larger separations, the decline of \( F \) becomes even milder.

Fukuda et al. (2004a) computed the static repulsion between two anti-parallel dipoles fixed in space. Their results show the scaling \( F \sim R^{-3} \), in disagreement with the \( R^{-4} \) scaling expected, at least for large \( R \), from dipolar interactions. Why does our \( F \) exhibit an even slower decay? For the last part of the simulation, say \( R > 6a \), one can imagine that the periodic boundary conditions on the top and bottom of the domain have introduced interference. A plausible explanation for the mild \( R^{-1/3} \) initial decay is the dynamic nature of our simulation. As the droplets move apart, the surrounding director field is continuously evolving. This will produce a different elastic force on the droplets than if the latter are fixed in space. Even though the total simulation lasts more than 100\( \tau_e \), the drops move an appreciable 0.1a apart within \( \tau_e \). Therefore, the velocity of separation is too high for the process to be considered quasi-static.

To probe the anti-parallel repulsion further, we have conducted an experiment on the interaction among droplets of silicone oil in the nematic 5CB. Occasionally the anti-parallel configuration appears and repulsion is observed. We present one such scenario in Fig. 7.6, where a single droplet (at bottom) is repelled by another (at top) with an
opposite dipolar direction, the latter being the end of a chain of particles with upward dipoles. Over the entire period of observation, the separation $R$ increases almost linearly in time. If we ignore the later portion of the data (say $R > 3.5a$) because nearby droplets may have interfered, there does appear to be a weak power-law decay of the velocity $v \sim R^{-0.5}$ for the range of $2.6a < R < 3.5a$. This implies that the repulsion force also decays weakly according to $F \sim R^{-0.5}$. That this power law is much closer to our dynamic computation than prior static computations lends support to our argument above.

2. Lateral pairs

When a pair of droplets are placed side by side, with their line-of-centers orthogonal to the far-field nematic orientation, the geometry is no longer axisymmetric. Therefore, we resort to 2D planar simulations for lateral pairwise interactions. The same is true for the multiple particle interactions in the next section. Fortunately, essentially 2D dynamics can be realized experimentally by incorporating relatively large particles or droplets into freely suspended smectic-C and smectic-C\* films (Cluzeau et al., 2001). In fact, considerable research has been devoted to this special setup as a rare opportunity to study “anisotropic, two-dimensional emulsions” (Völtz & Stannarius, 2004). The 2D character greatly simplifies theoretical analysis (Pettey et al., 1998; Cluzeau et al., 2004) and facilitates experimental observations (Dolganov et al., 2003). For example, in a smectic-C\* film of thickness smaller than the helical pitch, the droplets are observed to interact through the accompanying point defect and form chains, in qualitatively the same fashion as in 3D nematics (Cluzeau et al., 2001). Therefore, our 2D simulations enjoy greater relevance to reality than can be generally expected.

Consider first the parallel configuration for a lateral pair, with their dipole direction initially in parallel (Fig. 7.7). The rectangular computational domain has a horizontal width of $17a$ and a height of $10a$, and the two drops are initially placed side by side in the middle with a separation of $3.33a$. Upon start of the simulation, there is again a very brief transient caused by the initial $n(r)$ field relaxing to lower the elastic distortional energy. As the two hedgehog defects take shape, they move inward toward each other. There is no rotation of the drops in this process. Then the two droplets repel each other and move apart laterally (Fig. 7.7a). This motion slows down in time and eventually stops at a dimensionless time $t \approx 80$. The apparent steady-state has a drop separation $R_e = 4.02a$ and an angle between the two dipoles of $46.9^\circ$.

Musevic et al. (2006) measured the interaction potential for a single particle when it is placed beside a chain of particles in 5CB, with the dipole of the single particle parallel to that of the chain. Although their result may have involved contributions from multiple particles in the chain, we have estimated their repulsion force $F$ and compared it with our numerical result in Fig. 7.7(b). Two differences stand out. Our $F$ is several times smaller, and it drops to zero rather abruptly at a relatively short separation. The larger $F$ in Musevic et al.’s measurement is probably due to repulsion from neighboring particles in the chain. The short range of our $F$ may have to do with the side walls on which fixed vertical anchoring is imposed. Besides, the drop-to-defect vectors tilt toward each
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Figure 7.7: The interaction between a lateral pair of droplets in the parallel arrangement. (a) The center-to-center distance $R(t)$ increases as the droplets repel each other. The $n$ field is visualized as in Fig. 7.2(b) in the insets. (b) The repulsion force $F$ as a function of $R$ in the dynamic simulation. The data of Musevic et al. (2006) are also shown for comparison.

other as the drops separate. This configuration promotes attraction between drops (cf. Fig. 7.10), which may have shortened the range of repulsion relative to that for parallel dipoles. Note also that the simulation is dynamic in a 2D geometry, while the experiment is static in 3D next to a substrate. It is difficult to speculate on the implications of such factors for $F$.

Additional measurements of Musevic et al. (2006) suggested that a lateral pair with their dipoles in anti-parallel arrangement will attract each other. We have simulated such a scenario in the same computational domain as above, with the droplets initially side by side at a separation of $2.62a$ (Fig. 7.8). The droplets not only approach each other laterally, but also shift vertically so as to move the two point defects closer (see insets). As the line of centers makes an angle of roughly $23^\circ$ with the vertical far-field nematic orientation ($t = 125$), the two point defects sit on opposite sides of the line of centers instead of moving into the gap between the droplets. Soon afterwards, the two drops coalesce at $t = 136$. In this process, the attractive force $F$ varies non-monotonically with the separate $R$, with a peak at $R = 2.3a$ (Fig. 7.8b). With decreasing $R$, the attraction initially increases as one would expect. Then the relative rotation between the droplets changes the defect configuration and the nature of the attraction. This causes the decline of the attraction force for $R < 2.3a$.

In the static measurements of Musevic et al. (2006), a single particle is placed beside a chain of particles, with its dipole anti-parallel to that of the chain. The single particle is not abreast with one in the chain, but rather is staggered between two neighboring ones (cf. Fig. 7.11a). Thus, the measured $F$ comes from two or more particles in the chain, and there is no relative rotation among the particles as exhibited by our doublet. Subject
Figure 7.8: The interaction between a lateral pair of droplets in the anti-parallel arrangement. (a) The center-to-center distance $R(t)$ decreases as the drops approach each other. Their line of centers also rotates clockwise. In the end, the two droplets coalesce. (b) The attractive force $F$ as a function of $R$ in the dynamic simulation. The data of Musevic et al. (2006) are also shown for comparison.

to these complications, perhaps only the initial portion of our result, say $R > 2.4$ in Fig. 7.8(b), are comparable with the experimental data. Similar to the repulsion between a parallel pair (Fig. 7.7b), our force is smaller in magnitude, and also occurs in a much shorter range than in the experiment. The apparent agreement in the humped shape of the curves is probably fortuitous. In the experiment, the attraction dies down when the single particle is pushed too close to the chain. In our simulation, on the other hand, the two drops maneuver in two dimensions. The downturn in the attraction force with shrinking $R$ is due to the evolving defect pattern toward the end.

To summarize the results and discussion in this subsection, our simulations reproduce the characteristics of pairwise interactions as measured in experiments and predicted by ad hoc models. For longitudinal doublets, a parallel pair tend to attract each other while an anti-parallel pair repel, unless their initial separation is very small. For lateral pairs, parallel pairs repel while anti-parallel ones attract. Besides, computations and measurements exhibit common trends in the magnitude of the forces. For example, longitudinal interactions are stronger than lateral ones. For longitudinal pairs, the parallel attraction is greater than the anti-parallel repulsion, whereas for lateral pairs, the parallel repulsion and the anti-parallel attraction have comparable magnitudes. These can be rationalized by the relative position of the point defects as it determines the elastic distortion surrounding the droplets.

Quantitatively, the long-range longitudinal attraction between parallel pairs is the only situation with a well-established scaling ($F \sim R^{-4}$), which is consistent with the simple picture of dipole-dipole attraction. For closer ranges, the inter-particle force shows considerable divergence among different computational and experimental studies. To a
large extent, this discrepancy reflects the dynamic nature of the interaction when the particles are allowed to move. However, a clearer understanding requires more careful computations as well as measurements that account for complicating factors such as differences in spatial dimensionality and the presence of substrates.

### 7.3.2 Multi-drop interactions

1. **Chain formation**

Among experimental observations, the most prominent feature of self-assembly is the formation of chains parallel to the far-field director orientation (Poulin & Weitz, 1998). We simulate this by arranging 4 droplets in a regular zig-zag pattern in a rectangular domain (Fig. 7.9 inset), with initial center-to-center separation of $3a$ and the line of centers making an angle of 39° with the vertical. The width of the domain is $20a$, and its height is $12.5a$. The director is fixed in the vertical direction on the side walls, where the velocity vanishes. Periodic boundary conditions are used for the upper and lower boundary. As before, the initial director field has a thin ribbon of radially outward orientation around each drop, outside of which $n$ points uniformly upward.

Upon start of the simulation, the director field near each droplet quickly rearranges itself and produces a satellite point defect. These defects are not directly above or below the drop, as one would expect for a single droplet in an otherwise vertically oriented nematic. Rather, the droplet-defect dipole points toward the neighboring drop below it (Fig. 7.9). Then each drop experiences attraction from both neighbors, according to the pairwise attraction force of Fig. 7.3. The net effect is to pull the drops into a straight line. Since this horizontal force is proportional to $\sin \theta$, where $\theta$ is the angle between the line-of-centers and the vertical, the motion is fast initially when $\theta$ is large, and slows down toward the end as $\theta \to 0$.

The process of chain formation is qualitatively the same as observed in 3D nematics (Poulin et al., 1997b; Poulin & Weitz, 1998) and 2D smectic C* films (Cluzeau et al., 2001). However, the periodicity of the computational domain in the vertical direction introduces an artifact. As the four-particle array is repeated above and below, the equilibrium inter-particle separation $R_e$ is predetermined as 1/4 of the height of the domain, independent of the physical parameters of the system. In this case, $R_e = 3.125a$ is somewhat higher than the 2D observation of $2.6a$ (Cluzeau et al., 2001). Note also that we have used the regular zig-zag initial configuration for ease of analyzing the forces in the droplets. Similar chains should form from a more random initial configuration. We will explore such a scenario toward the end.

2. **Chain-chain interactions**

Experiments indicate that chain-chain interaction is central to the formation of regular 2D arrays (Musevic et al., 2006). From a fundamental viewpoint, chain-chain interaction is more complex than pairwise interactions since it involves the collective motion of multiple particles and defects. Motivated by the experiment of Musevic et al. (2006), we
Figure 7.9: Four droplets assemble into a vertical chain in a vertically aligned nematic. The height of the domain is $12.5a$ with periodic conditions in the vertical direction. The side walls are $20a$ apart and are not shown in the plots. The angle $\theta$, between the neighboring drops and the vertical axis, decreases from $39^\circ$ toward zero.

Figure 7.10: Interaction between two chains in the parallel arrangement. (a) Separation between the second drops from the top. (b) Repulsion force on the second drop from the top of the right chain.

We have simulated the interaction between two chains, each consisting of four droplets, in the parallel and anti-parallel configuration.

The computation domain has a width of $18a$ and a height of $13.3a$, and the boundary conditions are the same as in Fig. 7.9. The parallel chains are initially separated by a center-to-center distance of $R = 3.2a$ (Fig. 7.10(a)). The defects are directly below the
droplet and the chains are parallel to the far-field director orientation. Upon start of
the simulation, the two defects at the bottom of the chains quickly move inward toward
each other (Fig. 7.10a). This is reminiscent of the defect motion in the lateral pair of
Fig. 7.7. Meanwhile, the other three pairs of defects are confined between the neighboring
droplets and are not free to move. In view of the pairwise repulsion, one expects the two
chains to move laterally away from each other in time. This is largely true, except for
the two droplets at the bottom. Breaking the mirror symmetry, the left droplet moves
downward while the right one upward, the two forming an attractive doublet similar to
that in Fig. 7.3. At this point, the motion of the droplets has practically stopped, and
a steady-state configuration emerges. The symmetry breaking may have been triggered
by numerical noise such as asymmetry in the unstructured grid, but is indicative of
the instability of the symmetry pattern. The branched conformation closely resembles
experimentally observed patterns for water droplets in a 3D nematic, e.g., Fig. 11 of

We have also computed the repulsive force $F$ on one of the upper particles and plotted
$F(R)$ in Fig. 7.10(b). Based on the pairwise repulsion of Fig. 7.7, we expect $F$ to decline
monotonically with $R$. The curious rise for $3.2a < R < 3.5a$ is not due to the initial
elastic relaxation, since its duration is roughly 20 times the elastic time scale $\tau_e$. Rather
it is the result of the complex dynamic interaction between the chains. As the two
bottom drops attract each other, their attraction force “propagates” up the chains as
if along a string. This amounts to an additional attraction on the upper drops, which
weakens the repulsion force for the initial period. As the two bottom particles approach,
their attraction dies out and so does this effect. Then the repulsion force $F$ assumes its
normal decay with $R$. The magnitude of $F$ is between that of our pairwise repulsion and
Musevic et al.’s measurement in Fig. 7.7. Therefore, interaction with multiple particles
is responsible, partly at least, for the larger repulsion force here and in Musevic et al.’s
experiment than our pairwise repulsion. Note also that $F$ decays over a longer range
than the pairwise repulsion, and the steady separation is larger. These are consistent
with the idea that for the pairwise interaction in Fig. 7.7, the tilting of the drop-defect
vectors toward each other promotes attraction and suppresses repulsion.

The attraction between anti-parallel chains turns out to be simpler as it does not
greatly distort the conformation of each chain (Fig. 7.11). The initial condition is similar
to that of Fig. 7.10(a), but the right chain is flipped vertically so that the point defect
is on top of each droplet. The two chains are also offset vertically by a distance of $a$.
The initial separation between the lines of centers is 2.9a. This setup approximates what
Musevic et al. (2006) used experimentally. The two chains approach each other with a
velocity that is roughly constant up to $t = 900$. Afterwards, the motion slows down and
at $t \approx 1300$, the chains approach an equilibrium state with a separation of 2.44a between
the centerlines (Fig. 7.11a). This is reasonably close to the experimental value of 2.31a
(Musevic et al., 2006).

The chain-chain attraction $F$, plotted in Fig. 7.11(b), differs markedly from the pair-
wise attraction in Fig. 7.8(b). First, $F(R)$ does not show the humped shape. The decline
with shrinking $R$ should be compared with similar decline in Musevic et al.’s data (Mu-
Figure 7.11: Interaction between two chains of droplets in the anti-parallel arrangement. (a) The separation between the chains $R(t)$ decreases from an initial value of $2.9a$ to an equilibrium one of $2.44a$. (b) The attractive force $F$, averaged among the droplets, as a function of $R$ in the dynamic simulation.

Sevic et al., 2006) in Fig. 7.8(b) rather than our computed pairwise attraction, as the latter is due to the rotation of the doublet that is absent here. Perhaps because our initial separation is too small, $F$ in Fig. 7.11(b) does not exhibit the experimentally recorded long-range regime where the attraction decays with the chain-chain separation. Starting from an initial separation of $4a$, the chains barely move in thousands of time units, indicating $F \approx 0$ for $R \geq 4a$. Furthermore, $F$ is some two orders of magnitude smaller than the numerical and experimental data in Fig. 7.8(b). This is because two anti-parallel chains vertically offset by $a$ induce an $n$ field that is nearly left-right symmetric about the line of centers for each chain. This is apparent when contrasting the insets in Fig. 7.11(a) with those in Fig. 7.8(a). In the former, the dark brushes are confined within the gap between neighboring particles in the chain, while in the latter they extend to the other particle. Thus, the anti-parallel chain-chain interaction is much weaker than that between two individual particles. Such symmetry does not exist for the parallel chains in Fig. 7.10, and thus the chain-chain repulsion is comparable to the pairwise repulsion.

3. Multidrop self-assembly

We simulate the self-organization of eight droplets in a square domain of dimensions $14a \times 14a$. Periodic boundary conditions are imposed in both directions; the lack of a Dirichlet condition for $n$ implies that the director field will evolve under the influence of the anchoring on the droplets rather than a far-field alignment. Initially, the droplets are randomly positioned in the periodic domain (Fig. 7.12a). Similar to the preceding simulations, the initial director field is such that $n$ is radial within a thin ribbon surrounding
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Figure 7.12: Self-assembly of 8 drops in a doubly periodic domain. Note that the time is made dimensionless by $\eta a^2/K$.

Each droplet and uniformly vertical outside. After the simulation begins, a point defect immediately nucleates near each particle (Fig. 7.12a), visualized by the intersection of four dark brushes.

The ensuing self-assembly seems to be driven by the pairwise interactions discussed in Section 7.3.1. The point defects quickly move toward the nearest neighbor so the drop-defect dipole points to the latter, similar to Fig. 7.9. This is seen in Fig. 7.12(a) for drop 8 (toward drop 6) and drop 1 (toward drop 4). This is followed, in Fig. 7.12(b), by attraction between longitudinal pairs (drops 1 and 4, 5 and 6, and 6 and 8) as well as repulsion between lateral pairs (drops 3 and 5, 5 and 7). The repulsion between 3 and...
5 is short-lived, however, as the drop-to-defect dipole for drop 5 rotates clockwise until it points toward drop 3. Afterwards the two attract in a similar way to the two bottom droplets of Fig 7.10(a). Toward the end of the simulation ($t = 547.8$), a predominant chain has taken shape, consisting of drops 8, 6, 5, 3, and possibly 1 (Fig. 7.12d), oriented diagonally. Drops 1, 4 and 2 are forming a minor chain along the vertical direction. Drop 7 is the only “free” droplet at this moment, but may eventually be absorbed into the diagonal chain by attractions from drop 1 and 3. Because of the double-periodicity of the computational domain, the interaction among the droplets are not guided by a fixed far-field orientation, and the assembly proceeds slowly, especially in the late stage. Because of the modest number of droplets, chain-chain interaction is absent and the formation of 2D arrays cannot be simulated.

Qualitatively, the self-assembly of droplets into chains is in agreement with experimental observations in 3D nematics (Poulin et al., 1997b; Loudet et al., 2000; Musevic et al., 2006) and 2D smectic-C films (Cluzeau et al., 2001, 2004). Quantitatively, we can compare the time required for the self-assembly and the equilibrium drop spacing in the chain. Cluzeau et al. (2001) reported chain formation in 2.8 seconds in their experiment, which translates to a dimensionless time of roughly 110. This is comparable to the time scale of chain formation in Fig. 7.12. In the diagonal chain of Fig. 7.12(d), the point defect is more or less midway between the neighboring particles, with a distance of $1.37a$ to the drop center. Thus, the drop spacing is $R_e = 2.74a$. This is in reasonable agreement with experimental measurements for chains both in 3D nematic ($R_e = 2.6a$) (Poulin et al., 1997b) and in 2D smectic-C films ($R_e = 2.6a \pm 0.2a$) (Cluzeau et al., 2001).

The most comparable computational study seems to be that of Yamamoto and coworkers (Yamamoto, 2001; Yamamoto et al., 2004). As mentioned in the Introduction, their scheme is quasi-static and ignores hydrodynamic effects. It amounts to assuming that the flow is much slower than elastic relaxation, and thus decouples the particle motion from flow in the limit of a vanishing Ericksen number. This is perhaps justifiable in the final stage of self-assembly, but the dynamics can be important early on as shown by our simulation of pairwise interactions. There is a second and perhaps more significant difference. The theoretical model of Yamamoto (2001) is such that the satellite point defect is unstable in 2D, and the pairwise interaction is of the “quadrupolar” type rather than the “dipolar” type seen here and in most experiments. Consequently, the particles aggregate into clusters that tend to assume an angle with the far-field orientation, which is fixed in his computation. These clusters should be compared with the “kinked chains” formed of droplets bearing Saturn rings (Musevic et al., 2006) or particles with planar anchoring (Poulin & Weitz, 1998). The straight chains linked by point defects, prevalent in experiments with 3D nematics as well as 2D smectic-C films, cannot be realized using his theoretical model. In more recent work, Yamamoto et al. (2004) presented results for a smectic-C film. The free energy appears slightly different and a stronger anchoring parameter is used. This produces satellite point defects near individual particles, which assemble into chains that are similar to ours in Fig. 7.12. The final center-to-center separation $R_e = 2.88a$ is somewhat larger than ours and prior experimental values. The time scale of self-assembly cannot be compared because of the quasi-static nature of their
7.4 Summary

Through dynamic simulations, we have explored the interaction of particles in a nematic using a more or less rigorous theory of nematohydrodynamics. The goal is to gain a more rational understanding of the self-assembly process than previously achieved through analogies and ad hoc models. The results on pairwise and multi-particle interactions can be summarized as follows.

(a) The long-range attraction force between pairs of droplets, each having a point defect that is on the line-of-centers of the droplets and facing the same direction, obeys a scaling $F \sim R^{-4}$ with the drop separation $R$. This is the most well-established fact about pairwise interaction, and is consistent with the idea of attraction between dipoles.

(b) Pairwise interaction in shorter range is poorly documented and there is considerable discrepancy among the few theoretical and experimental studies. We have examined several configurations for the drop-defect ensemble in which the droplets attract or repel each other. The dynamic nature of the interaction is important, especially in the early stage, and the force between droplets cannot be represented by that between dipolar and quadrupolar moments.

(c) Multiple droplets form linear chains via pairwise attraction and repulsion between neighboring droplets. Preformed parallel chains repel each other if their drop-to-defect vectors are in the same direction. They attract if their orientations are reversed.

We have compared our simulations with prior static calculations and experiments to the greatest extent possible. There is qualitative, and sometimes semi-quantitative, agreement. More detailed comparison is hampered by experimental complications such as the presence of substrates and difficulties in quantifying anchoring strength, as well as two limitations in our simulations: two-dimensionality and the small number of particles. On a more fundamental level, a vector-based theory such as the Leslie-Ericksen model cannot describe the structure of the defect core, which may play a role in the interaction between particles in close proximity (Musevic et al., 2006). Clearly, more carefully designed experiments and sophisticated computations are needed to establish a coherent and detailed understanding of particle interaction and assembly in nematics.
Bibliography


Bibliography


Chapter 8

Dynamic simulation of capillary breakup of nematic fibers: molecular orientation and interfacial rupture *

8.1 Introduction

Immiscible blends of nematic liquid crystals (LCs) and isotropic liquids occur in several contexts. In optical applications such as polymer-dispersed liquid crystals (Mucha, 2003), the desirable phase morphology is liquid crystal droplets suspended in a polymer matrix. In liquid-crystalline polymer (LCP) composites, on the other hand, it is essential to have the minor LCP phase stretched into thin fibers with strong molecular alignment in the axial direction (Dutta et al., 1990; Kernick & Wagner, 1999). If the composite is rapidly frozen to retain the fibrous morphology in the solid state, the LCP fibers act as ultra-strong in-situ reinforcement (Acierno & Collyer, 1996). In addition, LCP nanofibers (Srinivasan & Reneker, 1995), with diameters on the order of tens of nanometers, form an essential building block in many areas of nanotechnology. Although these are typically electrospun in a gaseous medium, the fiber surface morphology is a central concern as well (Reneker & Chun, 1996). More recently, LC filament breakup has been used in microfluidic devices for making monodisperse nematic droplets (Hamlington et al., 2007).

The nematic order is a significant determinant of the speed of drop pinchoff and the drop size. Therefore, it is important to understand the capillary stability of the LC fiber and its breakup process.

From a fundamental viewpoint, the breakup of a nematic LC fiber is an interesting process. As the physical dimension of the fiber narrows down to the micro- or nanometer scale, interfacial effects become increasingly dominant (Stone et al., 2004). Aside from the conventional isotropic interfacial tension, the anchoring of LC molecules on the interface contributes in effect an anisotropic part to the interface tension, which may play a significant role in the phase morphology and fluid dynamics of nematic-isotropic two-phase systems (Yue et al., 2005b; Nastishin et al., 2005). This has been illustrated by recent work on bubble and drop behavior in a nematic matrix (Zhou et al., 2007b,a; Khullar et al., 2007). Typically the coupling between surface anchoring and fluid flow is mediated by bulk elasticity of the LC. For example, enforcing the anchoring condition leads to bulk distortion that modifies the anisotropic rheology of the LC bulk. Evidently, surface anchoring and bulk elasticity are the two major factors governing the energetics of LC-isotropic interfaces. When considering the dissipative dynamics of interfacial

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deformation and flow, a third factor—anisotropic viscosity—must be considered as well.

Previous experimental work on nematic fiber breakup seems to consist of two qualitative observations of the evolving interface and the birefringent pattern inside the fiber. For a lyotropic liquid-crystalline polymer fiber about 50 μm in initial diameter, Tsakalos et al. (1996) reported Rayleigh instability that proceeds much as for Newtonian fluids. Birefringent patterns do reflect effects of the flow field, however, with the uniaxial elongation at the neck producing strong orientational order. Eventually, fiber breakup gives rise to bipolar droplets with a range of sizes. Machiels et al. (1997) observed similar breakup of thermotropic liquid-crystalline polymer fibers. Neither study was able to shed much light on the coupling between capillary breakup and molecular orientation, and polydomains may have complicated the microstructural order.

Theoretical studies are limited to linear instability analysis based on simplified models. Rey (1997) did the first linear analysis on an infinite nematic fiber. The nematic director field \( \mathbf{n}(r) \) is uniform and fixed along the axis of the fiber, unperturbed by the capillary waves. But undulation of the interface forces \( \mathbf{n} \) to deviate from the planar easy direction and is penalized by a Rapini-Papoular anchoring energy (Rapini & Papoular, 1969). Thus, surface anchoring is accounted for in the weak anchoring limit, since it does not modify the bulk orientation. But in the bulk, Ericksen’s transversely isotropic fluid (TIF) model is used that does not allow distortional elasticity. Results show that the anchoring tends to stabilize the fiber against capillary waves; the threshold for unstable wavelengths is raised and the growth rate of the fastest growing mode is damped when compared with Newtonian fibers of the same viscosity. Similar conclusions were reached by Wang (2001) using the Doi theory. Bulk elasticity is omitted, and anchoring is accounted for by an anisotropic surface energy. More recently, Cheong & Rey (2001, 2002, 2004) have extended linear analysis to “onion” and radial director fields and non-axisymmetric instability modes.

In spite of the progress made, our theoretical understanding of capillary breakup of nematic fibers suffers from several limitations. First, only linear instability modes have been analyzed, and we have no knowledge of nonlinear growth of capillary waves and the eventual breakup. Second, theoretical analysis has necessitated the use of drastically simplified models. These may capture one or two of the key factors: surface anchoring, bulk elasticity or anisotropic viscosity, but not all three. Finally, the flow field and director field are almost always decoupled to simplify analysis. The motivation for our work is to carry out a fully coupled fluid-dynamic simulation of nematic fiber breakup using the Leslie-Ericksen theory of nemato-hydrodynamics.

The complex rheology of LCs and the need to capture an evolving interface make this a challenging computation. We overcome these difficulties using a finite-element algorithm based on a diffuse-interface model (Yue et al., 2006b). The methodology was developed for simulating interfacial flows of complex fluids in general. In the current application, we will analyze the effects of surface anchoring, bulk elasticity and anisotropic viscosity separately, with an emphasis on the coupling between nano-scale molecular order and micro-scale fiber morphology.
8.2 Theory and numerical methods

We treat the nematic-isotropic interface as a thin diffuse layer across which physical properties change rapidly but continuously. The diffuse-interface theory uses a variational formulation based on the free energy of the two-phase system. This is most convenient for the current application where bulk distortion of LCs can be represented by the Frank energy (de Gennes & Prost, 1993), and surface anchoring by the Rapini-Papoular anchoring energy (Rapini & Papoular, 1969). Finally, anisotropic viscosity is incorporated by Leslie’s viscous stress tensor. Thus, our algorithm integrates the Leslie-Ericksen theory naturally into an interface-capturing flow solver, bridging the gap between molecular orientation and macroscopic hydrodynamics. Another advantage of the diffuse-interface model, essential to the current simulation, is that it handles topological changes such as interfacial rupture and coalescence rationally via a short-range force resembling the van der Waals force. There is no need for manual intervention as in sharp-interface models to effect such events. The numerical package has been extensively validated (Yue et al., 2006b), and applied to simulate drop deformation, breakup and coalescence in polymeric and nematic liquids (Yue et al., 2004, 2005a,b, 2006a; Zhou et al., 2006, 2007a). Thus, we will briefly summarize the main ideas in the following, and refer the reader to prior publications for details of the theoretical model and computational algorithm.

We employ a scalar phase field \( \phi(r) \) to represent the composition of a Newtonian-nematic two-component system. The Newtonian bulk is represented by \( \phi = -1 \) and the nematic by \( \phi = 1 \), and the interfaces are simply the level set of \( \phi = 0 \). The governing equations are the continuity and momentum equations, supplemented by the Cahn-Hilliard equation for the transport of the phase field \( \phi \) and the Leslie-Ericksen equations of nematohydrodynamics (Yue et al., 2004; Zhou et al., 2007a):

\[
\nabla \cdot v = 0, \tag{8.1}
\]

\[
\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \nabla \cdot \sigma, \tag{8.2}
\]

\[
\frac{\partial \phi}{\partial t} + v \cdot \nabla \phi = \gamma \lambda \nabla^2 \left[ -\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\epsilon^2} \right], \tag{8.3}
\]

\[
h = \gamma_1 N + \gamma_2 D \cdot n, \tag{8.4}
\]

where \( \lambda, \epsilon \) and \( \gamma \) are the interfacial energy density, capillary thickness and mobility of the diffuse interface, respectively. The density \( \rho = \frac{1+\phi}{2} \rho_1 + \frac{1-\phi}{2} \rho_2 \) is an average between the two components. The stress tensor \( \sigma \) in the momentum equation is:

\[
\sigma = -\lambda \nabla \phi \nabla \phi - K \frac{1+\phi}{2} \nabla n \cdot (\nabla n)^T - G + \frac{1+\phi}{2} \sigma' + \frac{1-\phi}{2} \mu [\nabla v + (\nabla v)^T], \tag{8.5}
\]

where \( K \) is the Frank elastic constant of the bulk nematic under the one-constant approximation, and \( \mu \) is the Newtonian viscosity. \( G \) is the anchoring stress of the nematic director on the interface, \( G = A(n \cdot \nabla \phi) n \nabla \phi \) for planar anchoring, \( A \) being the surface anchoring energy density. Homeotropic anchoring can be readily modeled but is not as
relevant here since stretched LC fibers tend to have $n$ aligned axially (Tsakalos et al., 1996; Rey, 1997). $\sigma'$ is the Leslie viscous stress (Leslie, 1966) in the nematic phase

$$\sigma' = \alpha_1 D : nnn + \alpha_2 nN + \alpha_3 NN + \alpha_4 D + \alpha_5 nn \cdot D + \alpha_6 D \cdot nn, \quad (8.6)$$

where $\alpha_1-6$ are the Leslie viscous coefficients obeying an Onsager relation $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$ so five of them are independent (de Gennes & Prost, 1993). $D = \frac{1}{2}[(\nabla v + (\nabla v)^T]$ is the strain rate tensor, $\Omega = \frac{1}{2}[(\nabla v)^T - \nabla v]$ is the vorticity tensor, and $N = \frac{dn}{dt} - \Omega \cdot n$ is the rotation of $n$ with respect to the background flow field. The director field $n$ evolves in the flow field according to a balance between elastic and viscous torques as given in Eq. (8.4). The molecular field $h$, denoting elastic torque in the nematic, derives from the free energies of the system (de Gennes & Prost, 1993):

$$h = K \left[ \nabla \cdot \left( \frac{1 + \phi}{2} \nabla n \right) - \frac{1 + \phi (n^2 - 1)}{2} \frac{n}{\delta^2} \right] - g, \quad (8.7)$$

with $g = A(n \cdot \nabla \phi)\nabla \phi$ for planar anchoring. The term involving $\delta$ arises from an energy penalty added to the Frank energy to allow defects to be represented by reduced $|n|$ values within a small area of size $\delta$ (Liu & Walkington, 2000). Thus, $|n|$ acts like a local order parameter, and the model closely resembles Ericksen’s generalization of the Leslie-Ericksen theory by a variable order parameter (Ericksen, 1991). We have used $\delta = 4\epsilon$ since the defect core size is comparable to the interfacial thickness. Note that in the limit of $\epsilon \to 0$, the diffuse interface model reduces to the classic sharp-interface hydrodynamics (Yue et al., 2004). In particular, the interfacial tension $\sigma$ and Rapini-Papoular anchoring constant $W$ can be recovered from the diffuse-interface parameters for small $\epsilon$: $\sigma = 2\sqrt{2}\lambda/3\epsilon$ and $W = 2\sqrt{2}A/3\epsilon$. To faithfully approximate the sharp-interface limit, $\epsilon$ needs to be $O(10^{-2}a)$, $a$ being the macroscopic length scale of typical problems.

Although non-axisymmetric instability modes have been considered before (Cheong & Rey, 2002), experiments have shown only axisymmetric capillary waves and drop pinchoff (Tsakalos et al., 1996; Machiels et al., 1997; Hamlington et al., 2007). Thus, we will assume axisymmetry throughout this study. The governing equations are discretized on a unstructured grid of triangular elements using the Petrov-Galerkin formulation (Yue et al., 2006b). A critical ingredient of the algorithm is an adaptive meshing scheme that accurately resolves the evolving interface and any orientational defects. Typical grid sizes are $h_1 = 0.006a$ at the interface and near defects, $h_2 = 0.2a$ inside the fiber and $h_3 = 0.5a$ in the matrix, with smooth transitions between different regions. Time integration is by an implicit second-order scheme with the time step automatically adjusted according to the motion of the interface. Numerical experiments have shown that the grid sizes and the time step used in the simulations are sufficient for numerical convergence.

### 8.3 Results and discussion

The geometry of the axisymmetric computational domain is shown in Fig. 8.1, with the nematic LC fiber surrounded by a quiescent Newtonian fluid. We apply periodic
boundary conditions along the $z$ direction, and no slip boundary conditions on the outer boundary ($r = R$). On the axis of symmetry $r = 0$, $n$ is in the $z$ direction and the radial velocity vanishes. Note that the velocity, stress and anchoring conditions on the nematic-isotropic interface have been embedded into the diffuse-interface formulation and do not constitute boundary conditions. Initially both phases are at rest, the interface is a perfect cylinder and the molecular orientation is uniform and axial inside the fiber. Surface disturbances arise spontaneously from numerical noise.

Most results presented are for a domain length $H = 25a$ and width $R = 3.33a$. Since the dominant capillary wavelength is not known \textit{a priori}, and in any event varies with the physical parameters, imposing periodicity over a finite $H$ necessarily introduces errors to the result. Comparison with simulations in longer domains, with $H$ up to 60a, shows that $H$ affects the results quantitatively but does not modify the qualitative trend. Thus, $H = 25a$ represents a tradeoff between computational cost and accuracy. For Newtonian fluids, the confinement effect of the outer boundary on capillary instability of a filament has been studied by Mikami & Mason (1975). For $R = 3.33a$, the growth rate of the dominant mode should decrease by approximately 10%. For our nematic fiber, comparing the result with that in a wider domain with $R = 10a$ shows that the confinement reduces the growth rate by 4.6%. Therefore, the finite size of the computational domain, while exerting a quantitative influence, does not hinder the main purpose of the simulations.
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The complete set of dimensionless groups governing our system is:

\[
\alpha = \frac{\rho_1}{\rho_2} \quad \text{(nematic-to-matrix density ratio),} \quad (8.8)
\]

\[
\beta = \frac{\alpha_4/2}{\mu} \quad \text{(nematic-to-matrix viscosity ratio),} \quad (8.9)
\]

\[
A_K = \frac{K}{\sigma a} \quad \text{(bulk elasticity-to-interfacial tension ratio),} \quad (8.10)
\]

\[
A_W = \frac{W}{\sigma} \quad \text{(anchoring-to-interfacial tension ratio),} \quad (8.11)
\]

\[
Ca = \frac{\eta U}{\sigma} \quad \text{(capillary number),} \quad (8.12)
\]

\[
Re = \frac{\rho_1 U a}{\eta} \quad \text{(Reynolds number),} \quad (8.13)
\]

along with the various length ratios of the geometry and ratios between the Leslie viscous coefficients. \(Re\) and \(Ca\) are defined using the visco-capillary velocity \(U = \sigma/\eta\). Therefore the capillary number is 1, and the Reynolds number is kept at 150 throughout this study. Note that the typical velocity during the fiber breakup is roughly 1% of \(U\), and the actual \(Ca\) and \(Re\) are much smaller. The viscosity \(\eta = (\alpha_3 + \alpha_4 + \alpha_5)/2\) is the average between the largest and smallest Miesowicz viscosities (de Gennes & Prost, 1993). The ratio \(\alpha_3/\alpha_2\) determines whether the nematic “tumbles” or “flow-aligns” in simple shear flows. But the distinction is unimportant here as fiber breakup engenders predominantly elongational flows. Thus we adopt the Leslie viscosities of a common nematic MBBA at 25°C as the basis for the computations (de Gennes & Prost, 1993): \(\alpha_1 = 6.5\) centipoise (cp), \(\alpha_2 = -77.5\) cp, \(\alpha_3 = -1.2\) cp, \(\alpha_4 = 83.2\) cp, \(\alpha_5 = 46.3\) cp, \(\alpha_6 = -32.4\) cp. Furthermore, we match the density and isotropic viscosity of the nematic with the surrounding fluid: \(\alpha = 1\), \(\beta = 1\). In the following subsections, we study the effects of the bulk elasticity, interface anchoring and anisotropic viscosity in turn, by varying \(A_K\), \(A_W\) and the viscosity ratios, respectively.

### 8.3.1 Bulk elasticity

With the anchoring energy fixed at \(A_W = 1\), Fig. 8.2 compares the development of capillary waves at different strengths of bulk elasticity. Note that the baseline case (Fig. 8.2a) is not for a Newtonian fluid; the fiber still retains the same anisotropic viscosity and surface anchoring. In our periodic domain of length 25a, the dominant mode has three wave forms, with a wavelength of 8.33a. In comparison, an infinitely long Newtonian fiber of the same viscosity would have a fastest growing wavelength of 9.66a according to Mikami and Mason’s model (Mikami & Mason, 1975). For a nematic fiber with a weak bulk elasticity, \(A_K = 0.0167\), the modification to the dominant wavelength is too small to be manifested, and the three wave forms persist (Fig. 8.2b). At \(A_K = 0.833\), however, the dominant wavelength has lengthened to 12.5a with two wave forms (Fig. 8.2c). Further doubling the bulk elasticity to \(A_K = 1.67\) does not change the wavelength in Fig. 8.2(d).
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Figure 8.2: Effect of bulk elasticity on capillary waves on a nematic fiber. The domain is $25a$ in length and $6.66a$ in width. The viscosity coefficients are those of MBBA, and surface anchoring is fixed at $A_W = 1$. The bulk elasticity $K$ increases from left to right: (a) $A_K = 0, t = 491$; (b) $A_K = 0.0167, t = 497$; (c) $A_K = 0.833, t = 547$; (d) $A_K = 1.67, t = 575$. Time is made dimensionless by $\eta a/\sigma$.

One observation is that bulk elasticity tends to increase the wavelength of the capillary waves. This is in qualitative agreement with the predictions of linear stability analysis. Cheong & Rey (2004) showed that the fastest growing wavelength on an infinitely long inviscid nematic fiber is

$$\lambda_{\text{max}} = 2\sqrt{2\pi a}\sqrt{1 + 2A_K}, \quad (8.14)$$

which reduces to Rayleigh’s classical result for an inviscid fiber at $K = 0$. This formula predicts that the bulk elasticity would increase $\lambda_{\text{max}}$ by 1.7%, 63% and 108% for the three cases in Fig. 8.2(b–d), which is consistent with the numerical results considering the constraint of the forced periodicity over $H = 25a$. However, further increasing $A_K$ up to 10 does not produce a single wave form in our domain, as expected from the linear formula above. We will return to this discrepancy shortly. A second observation is that the bulk elasticity tends to dampen the growth of the capillary waves. The four panels in Fig. 8.2 correspond to roughly the same wave amplitude. The time needed for reaching this amplitude increases with increasing $A_K$. Again, this may be compared with the linear growth rate on an inviscid nematic fiber (Cheong & Rey, 2004):

$$\alpha_{\text{max}} = \frac{\sqrt{\frac{\sigma}{8\rho a^3}}}{\sqrt{1 + 2A_K}}. \quad (8.15)$$

For our three cases (Fig. 8.2b–d), this predicts a reduction in $\alpha_{\text{max}}$ of 2%, 39% and 52%, respectively. The actual damping of the growth rate in the simulations is smaller in magnitude: 1.2%, 10% and 15% for the three cases.

It is perhaps unreasonable to expect a closer correspondence between our numerical results and Eqs. (8.14) and (8.15). Besides the aforementioned constraints of $H = 25a$,
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\( R = 3.33a \) and the nonlinear nature of our results, the physical models differ in that Cheong & Rey (2004) assumed inviscid fibers and rigid anchoring on the interface. Rigid anchoring tends to amplify the effects of bulk elasticity since it couples the interfacial deformation to bulk distortion more directly, without the “buffering” effect of the anchoring energy. Therefore, it is not surprising that in our simulations using a finite \( W = \sigma \), the dominant wavelength does not increase as much as predicted by Eq. (8.14), and the growth rate does not decrease as much as predicted by Eq. (8.15).

A nonlinear feature of Fig. 8.2 is that the waves are not precisely periodic along the axial direction. The thinning of the fiber proceeds more rapidly at the upper “neck” than the lower. This can be easily understood from the capillary pressure in the fiber. Let us assume that two neighboring wave forms are initially identical. The high capillary pressure at the neck drives the fluid toward the crest of the wave. If some small disturbance should slightly delay the thinning of one neck relative to the next, the thinner neck experiences a greater capillary pressure that more effectively pumps fluid away, thereby further widening the difference between the two necks. Thus, the uneven growth among the waveforms is a natural outcome of capillary instability. This behavior has been observed in Newtonian (Kowalewski, 1996) and nematic fiber breakup experiments (Tsakalos et al., 1996; Machiels et al., 1997), and is related to “volume scavenging” between coupled spherical-cap droplets (Theisen et al., 2007). As a result, polydisperse drops are produced. To produce monodisperse droplets, one can resort to strongly elongational flows, as have been used in microfluidic devices (Zhou et al., 2006; Hamlington et al., 2007).

Figure 8.3 depicts the late stage of fiber breakup for a nematic fiber with \( A_K = 0.0167 \) and \( A_W = 1 \). Since \( A_W/A_K = Wa/K \gg 1 \), one expects the anchoring effect to dominate the bulk elasticity in determining the director field (Zhou et al., 2007b). Indeed, throughout the breakup process, \( n \) follows the undulation of the interface except near the centerline, where the elongational flow aligns \( n \) axially. The same elongational flow stretches the neck into a thread (Fig. 8.3b), which then pinches off at both ends to form a satellite drop between the two daughter drops (Fig. 8.3c-d). The pinchoff produces pointed tips where the director field converges. The high curvature there induces a large capillary force that pulls the tips back sharply, giving rise to flat ends (Fig. 8.3d) or even flattened drops (Fig. 8.3e). In the meantime, the converging director field develops “boojums” defects at the ends. Finally, the thread breaks up into three primary droplets and three satellite droplets. The drops display a bipolar configuration (Fig. 8.3f) with two boojums at the poles. The shape is nearly spherical in this case, but becomes more prolate with increasing \( A_W \) and \( A_K \), similar to previous observations (Yue et al., 2005b). As anticipated earlier, the primary drops are not monodisperse; the bottom drop is some 5.7% smaller than the other two. Note also that the satellite drops shrink in time and eventually disappear owing to the Cahn-Hilliard diffusion. The implications of this diffuse-interface phenomenon has been examined at length (Yue et al., 2007).

The nematic fiber breakup process, as simulated and discussed above, may be compared with experimental observations (Tsakalos et al., 1996; Machiels et al., 1997). First, the simulation and experiments agree in that the breakup of a nematic fiber does not
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Figure 8.3: Evolution of the interface and the director field during breakup. $A_W = 1.0$, $A_K = 0.0167$. The snapshots are at different times: (a) $t = 476$, (b) 502, (c) 507, (d) 512, (e) 566, (f) 658. Note that $\mathbf{n}$ is shown only on a small number of interpolation points; the finite-element mesh is much denser.

Differ markedly from that of a Newtonian fiber. The uneven wave growth, the pinchoff at the neck and even the formation of satellite drops are qualitatively the same as in Newtonian fluids (Notz et al., 2001). There is nothing as spectacular as, say, the bead-on-string morphology for highly viscoelastic polymeric threads (Christanti & Walker, 2001). Quantitatively, the nematic order makes the breakup proceed more slowly, and we will amplify this point shortly in connection to the thinning of the neck. Second, the general features of the experiments are captured by the simulations, including the highly aligned $\mathbf{n}$ field at the necks, the formation of satellite drops, the bipolar configuration and the polydispersity of the primary drops (Tsakalos et al., 1996). Finally, there are a few observations that the computation fails to reproduce. For instance, a “banded structure”, visible through crossed polarizers, sometimes emerges prior to capillary instability (Tsakalos et al., 1996). This is probably due to the relaxation of the molecular order that has been elevated during the formation of the fibers by stretching. Our Leslie-Ericksen theory does not account for such molecular relaxation. Furthermore, thermotropic LCP fibers often break up into spherical drops containing polydomains whose disordered orientation renders the drop essentially isotropic on the whole (Machiels et al., 1997; Yu et al., 2004). The origin of defects and polydomains is a long-standing problem in LCP dynamics, and requires more sophisticated models than that used here.

To examine more quantitatively the effect of bulk elasticity on the breakup process, we plot in Fig. 8.4 the minimum neck radius $R_n$ for several values of $A_K$, which decreases in time until pinchoff. Interestingly, the initial growth of the capillary waves ($t < 300$) is little influenced by the differing bulk elasticity. At the beginning of the simulations,
the nematic director $n$ is aligned axially in the bulk and tangentially on the interface, which induces neither bulk elastic energy nor surface anchoring energy. As the capillary wave develops, surface undulation causes both surface and bulk distortion and the energy penalties amount to an elastic force that resists the growth of the capillary wave. This is the explanation for the stabilizing effects of the nematic order. As a reaction to interfacial deformation, however, the effect only becomes significant as the capillary wave reaches a certain amplitude. As measured in Fig. 8.4, the amplitude is only about 0.05$a$ at $t = 300$, and thus the director field has yet to exert a significant effect on the capillary wave development. Later, with growing capillary waves, the interfacial and bulk distortion continue to absorb some of the energy released from interfacial area reduction. As a result, less is available to drive capillary breakup against viscous dissipation and inertia. This explains the longer pinchoff time for larger $A_K$ values in Fig. 8.4.

Finally, it is important to note that real liquid crystals typically have a weak $K \sim 10^{-11}$ N (de Gennes & Prost, 1993). With a surface tension $\sigma \sim 10^{-3}$ N/m (Kim et al., 2004; Wu & Mather, 2005), for example, $A_K = 0.01$ for a fiber 1 $\mu$m in radius. Thus, LC bulk elasticity plays a significant role only for nanofibers, such as produced by electrospining (Srinivasan & Reneker, 1995; Reneker & Chun, 1996). However, certain lyotropic systems possess exceedingly low interfacial tensions (Kaznacheev et al., 2003), for which bulk elasticity effect may be manifested at larger length scales.

### 8.3.2 Interface anchoring

We have chosen to discuss bulk elasticity and surface anchoring separately, but obviously the two must cooperate for either to have an effect. It is perhaps appropriate to say that the surface anchoring communicates interfacial deformation to the director field in the bulk. In previous linear instability analyses, Rey (1997) isolated the effect of surface anchoring by making the bulk elasticity infinitely strong, and Cheong & Rey
Table 8.1: Wavelength and pinchoff time at various surface anchoring energies, with $A_K = 0.833$, $Ca = 1$ and $Re = 150$. Time is made dimensionless by $\eta a / \sigma$. The last column, for an isotropic Newtonian fluid with a viscosity equal to the average viscosity $\eta$ of the LC’s, will be cited in the next subsection.

(2004) isolated the effect of bulk elasticity by making surface anchoring rigid. In this subsection, we fix bulk elasticity at $A_K = K / \sigma a = 0.833$, and vary the anchoring strength through $A_W = W / \sigma$.

The effect of $A_W$ is illustrated by Table 8.1 that compares the wavelength and pinchoff time for $A_W$ values ranging from 0 to 10. Thus, the surface anchoring tends to raise the threshold wavelength for unstable modes, and reduce their growth rates. In terms of hindering the growth of capillary instability, $A_W$ is similar to $A_K$. This is no surprise because, as we alluded to above, the surface anchoring and bulk distortion are allied in bringing about the stabilizing effect on capillary waves.

For an infinite nematic fiber with $A_K = \infty$ but a finite $A_W$, Rey’s analysis (Rey, 1997) gives the fastest growth wavelength

$$\lambda = 2\sqrt{2} \pi a \sqrt{1 + A_W + 2 \sqrt{\frac{Ca}{Re} \sqrt{1 + A_W}}}$$

and the fastest growth rate

$$\alpha_{max} = \sqrt{\frac{\sigma}{8 \rho a^3}} \frac{1}{\sqrt{1 + A_W + \sqrt{\frac{Ca}{Re}}}}$$

For $Ca = 1$, $Re = 150$ and $A_W = 1$, for example, the above formulae predict a 49% increase of the fastest-growing wavelength due to the interface anchoring, and a 34% decrease of its growth rate. Table 1 gives, for the corresponding conditions, a 50% lengthening of the wavelength and 7.1% decrease in the growth rate (estimated from the inverse of the total pinchoff time). Considering the differences in the physical models, parameters and geometric setup, the qualitative agreement is reasonable. Wang (2001) carried out a similar normal mode analysis using the Doi theory for liquid-crystalline polymers in the limit of vanishing bulk elasticity. At a capillary number of unity, with $A_W$ increasing from 0 to 10, the most dangerous wavelength is roughly doubled, and its grow rate decreases by 40%. These numbers are again consistent with our results in Table 1.

The later stage of the fiber breakup process does not vary qualitatively for the $A_W$ range simulated. Necking, drop pinchoff and satellite drop formation are similar to those depicted in Fig. 8.3. In fact, these features are basically the same as in Newtonian
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Figure 8.5: Effect of $A_W$ on the director field $(a)$ inside the fiber during breakup and $(b)$ inside a daughter drop. The radial dimension in $(a)$ is amplified by a factor of 3 for a clearer view. In each plot, the left image corresponds to weak anchoring at $A_W = 0.1$, with time $t = 113$ in $(a)$ and $t = 694$ in $(b)$, while the right to $A_W = 6$ with $t = 170$ in $(a)$ and $t = 780$ in $(b)$. All other parameters are the same as in Table 1.

fiber breakup, as noted in previous experimental observations (Tsakalos et al., 1996; Machiels et al., 1997). But the molecular orientation inside the fiber and later inside the drops does reflect the anchoring strength as shown in Fig. 8.5. For weak anchoring, $n$ readily deviates from the easy direction on the interface so as to avoid comparatively expensive bulk distortions. During the growth of capillary waves (Fig. 8.5a), therefore, the interfacial undulation only affects the outer layer of the nematic. In the daughter drops that result from the breakup (Fig. 8.5b), $n$ does not nucleate boojum defects on the surface but maintains a relatively uniform orientation. For strong anchoring, the interfacial contour has a much greater impact on the bulk $n$ field, both in the fiber and the final bipolar daughter drops.

8.3.3 Anisotropic viscosity

The foregoing discussion on anchoring and bulk elasticity concern energetic interactions. In the later stage of breakup, fluid flow introduces considerable dissipation into the system. Thus, anisotropic viscosity, a key rheological feature of nematic LCs, becomes a factor in the development of finite-amplitude capillary waves and final breakup. In fact, that is why in the preceding subsections, we compared the nematic fibers not against an isotropic Newtonian baseline, but one with nil bulk or anchoring energy and the same anisotropic viscosity. The latter being kept the same, the effects of $A_K$ and $A_W$ were thus isolated. For a truly Newtonian fiber with an isotropic viscosity matching the LC average viscosity $\eta$, the pinchoff time is 686 in Table 1. Comparing this with the
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Figure 8.6: Effect of viscous anisotropy on the thinning of the neck during the breakup of nematic fibers. The average LC viscosity $\eta$ is fixed such that $Ca = 1$, $Re = 150$. In addition, $A_W = 1$, $A_K = 0.833$. (a) Varying $\alpha_2$; (b) varying $\alpha_3$.

nematic fibers having $A_W = 0$ and $A_W = 10$ in the same table, it is apparent that the viscous anisotropy may have as great an effect on LC fiber breakup as $A_W$ (and $A_K$). To quantify this systematically, we fix the surface anchoring and bulk elasticity at $A_\sigma = 1$ and $A_K = 0.833$ and vary the degree of viscous anisotropy through the Leslie coefficients. Note that this is essentially a nonlinear effect in that it does not affect the initial stages of linear instability.

Given the five independent Leslie coefficients, it is not obvious how to quantify viscous anisotropy. In simple shear flows, a convenient gauge is the Miesowicz viscosities measured with the director $\mathbf{n}$ uniformly fixed perpendicular or parallel to the flow direction (de Gennes & Prost, 1993; Zhou et al., 2007a):

\[ \eta_\perp = -\frac{\alpha_2 + \alpha_4 + \alpha_5}{2}, \quad (8.18) \]
\[ \eta_\parallel = \frac{\alpha_3 + \alpha_4 + \alpha_6}{2}. \quad (8.19) \]

Borrowing the same idea to the fiber breakup problem, we have kept the average LC viscosity $\eta = (\eta_\perp + \eta_\parallel)/2$ constant, and varied the viscous anisotropy via the ratio $\nu = \eta_\perp/\eta_\parallel$. Using the Onsager relationship $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$, we rewrite $\nu$ as

\[ \nu = \frac{2\eta - \alpha_2 - \alpha_3}{2\eta + \alpha_2 + \alpha_3} = \frac{4\eta}{2\eta + \alpha_2 + \alpha_3} - 1, \quad (8.20) \]

which shows that $\nu$ can be manipulated via either $\alpha_2$ or $\alpha_3$. To keep $\eta$ constant, $\alpha_6$ or $\alpha_5$ have to be adjusted accordingly. In the following, we vary $\alpha_2$ or $\alpha_3$ on the basis of the Leslie coefficients of MBBA, which has $\eta = 64.15$ cp and $\nu = 4.34$. 157
Chapter 8. Dynamic simulation of capillary breakup of nematic fibers

Figure 8.7: Axial velocity profiles $v_z(z)$ at two radial positions $r = 0.2a$ and $0.65a$ at dimensionless time $t = 499$. $A_W = 1$, $A_K = 0.833$, and the viscosities correspond to $\nu = 4.34$ in Fig. 8.6(a). The velocity is made dimensionless by $\sigma/\eta$, and the outline of the fiber at this instant is also shown.

Figure 8.6 plots thinning of the neck radius for various degrees of viscous anisotropy. First, note that in the parameter ranges explored, the effect of $\nu$ on the pinch-off time is comparable to that of $A_K$ (Fig. 8.4) and $A_W$ (Table 1). With varying $\alpha_2$, Fig. 8.6(a) shows a monotonic trend, with the fiber breaking up faster for larger $\nu$ (or smaller $\alpha_2$). Naively, one might rationalize this by the fact that in the neck region, the LC molecules are predominantly aligned to the fiber axis. Thus, the viscosity $\eta_\parallel$ should matter much more than $\eta_\perp$. Increasing the viscosity ratio $\nu$ then amounts to reducing $\eta_\parallel$ and consequently the “effective viscosity” of the ordered LC. The same argument fails for Fig. 8.6(b), however, where the pinch-off time does not depend on $\nu$ or $\alpha_3$ monotonically.

The solution to this puzzle is that the flow within the fiber has both elongation and shear components. While the former dominates at the thinning neck, the higher capillary pressure there drives the fluid toward the wave crest, creating a shear flow that may be likened to the Poiseuille flow. This is illustrated by the axial velocity profiles in Fig. 8.7. The radial variation $\partial v_z/\partial r$ gives the degree of shear while the axial one $\partial v_z/\partial z$ indicates the stretching or compression. Therefore, it is necessary to consider the elongational viscosity of the nematic as well. Assuming a uniform director field perfectly aligned with the stretching direction, $\mathbf{n} = (0, 0, 1)$ in cylindrical coordinates, the stress tensor in the nematic undergoing uniaxial elongation along $z$ can be calculated from Eq. (8.6):

$$\sigma' = \text{diag} \left[ -\frac{\alpha_4 \dot{\epsilon}}{2}, -\frac{\alpha_4 \dot{\epsilon}}{2}, \frac{(\alpha_1 + \alpha_4 + \alpha_5 + \alpha_6) \dot{\epsilon}}{2} \right],$$

(8.21)

where $\dot{\epsilon}$ is the strain rate. Note that $\alpha_2$ and $\alpha_3$ represent rotational friction and do not appear here. Thus, an elongational viscosity can be defined from the normal stress
\[\eta_e^\parallel = \alpha_1 + \frac{3}{2}\alpha_4 + \alpha_5 + \alpha_6 = \left(4\eta + \alpha_1 - \frac{\alpha_4}{2}\right) + \alpha_2 - \alpha_3, \quad (8.22)\]

where we have invoked the average shear viscosity \(\eta\) and the Onsager relation. When we increase \(\nu\) by decreasing \(\alpha_2\) in Fig. 8.6(a), the elongational viscosity \(\eta_e^\parallel\) decreases together with the “effective shear viscosity” mentioned above. The consequence is unequivocal: the fiber breaks up more rapidly. In Fig. 8.6(b), on the other hand, increasing \(\nu\) by decreasing \(\alpha_3\) tends to reduce the effective shear viscosity, but in the meantime raises the elongational viscosity. The non-monotonic effect on the breakup of the nematic fiber, therefore, can be interpreted as the outcome of the competition between these two mechanisms.

### 8.4 Summary

In this paper we have investigated the breakup of nematic fibers with planar anchoring on the surface and initially axial molecular orientation in the bulk. The process is simulated from the onset of linear disturbances to nonlinear growth and finally to formation of drops. The main findings can be summarized as follows:

(a) Interface anchoring and bulk elasticity conspire to dampen the growth of capillary waves and the breakup process. In particular, the threshold wavelength for instability is raised and the growth rate of unstable modes is suppressed.

(b) Anisotropic viscosity plays a significant role in the growth of the capillary wave. The effect of individual Leslie coefficients depends on how it changes the elongational and shear viscosities of the nematic liquid crystal separately since both types of flow are involved in the breakup.

(c) The nonlinear growth of the capillary waves leads to the loss of axial periodicity and eventually the formation of polydisperse daughter drops. The nematic order within the fiber does not change the main features of the breakup, besides the quantitative effect of slowing down the process. On the other hand, the interfacial deformation and fluid flow do have a direct effect on the molecular orientation: the nematic is highly aligned in the neck region, and typically displays the bipolar configuration in the daughter drops.

(d) The numerical results are in reasonable agreement with prior work in the literature where comparisons can be made. Specifically, the effect of bulk elasticity and anchoring in suppressing capillary instability is in qualitative agreement with linear analysis. The numerically predicted breakup process captures the main features of experimental observations, and agrees with the latter in that nematic fibers break up in basically the same way as Newtonian ones.

In comparison with linear instability analysis, numerical simulations have the advantage of accessing the later stage of the breakup process. A disadvantage, however, is that the finite domain size tends to influence the wavelength that emerges. Comparison with linear analysis shows quantitative differences because of this restriction. Besides, this work leaves out several physical factors, including homeotropic or more general anchoring directions, bulk textures (radial or onion), non-axisymmetric modes of instability and
finally the role of molecular order parameter. The first 3 have been analyzed in the linear limit (Cheong & Rey, 2004). The last is known to be relevant to the banded textures observed in nematic fiber breakup (Tsakalos et al., 1996). These are open issues that future work should explore.

Nevertheless, this study appears to be the first to explore the nonlinear stage of the capillary breakup and drop pinchoff, and to include all the three factors—anchoring, bulk elasticity and viscous anisotropy—in a self-contained nemato-hydrodynamic theoretical framework. The results will be particularly relevant to the processing and manipulation of nano-scale nematic fibers whose small dimension accentuates distortional elasticity relative to interfacial tension.
Bibliography


Bibliography


Chapter 9

Conclusions and recommendation

We developed the diffuse interface based numerical toolkit, AMPHI, to simulate interfacial dynamics in complex fluids, and applied it to a number of physical problems. The numerical algorithm has two major elements: an efficient finite-element flow solver and an adaptive meshing scheme. The flow solver was originally developed for solving Navier-Stokes systems, and the adaptive meshing deploys a fine grid near the moving interface and a coarse grid away from the interface to achieve high numerical accuracy at a reasonable computational cost. The phase-field parameter \( \phi \) obviates the need to track the moving and deforming interface, and allows discretization and numerical solution within an Eulerian framework. Moreover, its gradient \( \nabla \phi \) supplies a convenient criterion for the meshing scheme to determine the local mesh size. In this thesis, two types of complex fluids have been investigated: viscoelastic fluid and nematic liquid crystal. The viscoelastic fluid is described by the Oldroyd-B model, and the liquid crystal is modeled by the Leslie-Ericksen theory. For each simulation, the numerical results have been summarized at the end the preceding chapters. In this chapter, we conclude the thesis by offering a more general view of the theoretical model, the numerical method and physical insights gained from this work, and by suggesting further research to be undertaken in the area of interfacial dynamics in complex fluids.

9.1 Theoretical model and numerical algorithm

For the problems of interest here, the diffuse interface model proves to be a convenient and uniquely revealing theoretical framework. In terms of interface capturing on a Eulerian grid, the method is comparable to level set and volume-of-fluid methods. However, it is unique in that the theoretical formulation is rooted in a physically meaningful idea: the free energy of the mixing between the species. This endows the resulting model several desirable features. (a) Complex rheology can be included along with interfacial dynamics in a unified variational procedure. (b) The model incorporates coarse-grained molecular interactions in the form of a disjoining potential comparable to the van der Waals potential. (c) The variational formulation ensures an energy law for the two-phase system and facilitates analysis of the convergence and regularity of the numerical solution (Lin & Liu, 2000; Liu et al., 2005; Feng et al., 2005).

In terms of numerical efficiency, AMPHI represents a major improvement over a previous spectral algorithms (Yue et al., 2004). Adaptive meshing results in considerable savings in grid numbers, thus making it possible to simulate thinner interfaces with better resolution. This also opens up opportunities for tackling larger-scale flow problems, especially in 3D. Moreover, the finite-element method easily accommodates complex flow geometry and various boundary conditions. The theoretical model and numerical schemes have been validated extensively in various flow conditions and the numerical accuracy
has been demonstrated (Yue et al., 2004, 2006b, a). The implicit scheme fully couples the flow equations and interface Cahn-Hilliard equations, and computes flows dominated by large interfacial tension accurately with robust numerical stability. The convergence with the interfacial thickness and mesh size has been established. Note also that the adaptive meshing can be viewed as a compromise between fixed Eulerian grid and moving Lagrangian grid; our grid remains fixed for a certain number of time steps and then adapts to the moving interface.

9.2 Physical insights

One may summarize the findings of the whole thesis by one insight: interfaces of complex fluids behave differently than those of Newtonian fluids. The ultimate cause of the “anomalous” behavior is the coupling among several factors: the microstructural conformation in the bulk fluids, the interfacial morphology, and the hydrodynamics of the flow field. These can be viewed as pertaining, respectively, to the micro-, meso- and macroscopic length scales of the problem, and all the analysis in the preceding chapters was devoted to unraveling the interplay among these length scales.

The insights gained in this exercise are not only of scientific interest, but also important to engineering applications. For example, multi-layer coextrusion of polymer films depends critically on maintaining the interfacial shape and position, and these in turn depends on the rheology of each component on the one hand, and the overall flow field on the other. Another example is polymer dispersed liquid crystals, where the drop shape depends on the microstructure of the mesogenic phase and the bulk deformation that the mixture undergoes during processing.

9.3 Theoretical and numerical limitations

We must point out the limitations of our theoretical model and numerical scheme. First, resolving the interfacial layer constitutes a formidable numerical challenge. Physical systems typically have an interfacial thickness of nanometers and a macroscopic length scale ranging from micrometers to millimeters. This disparity in length scales is a generic conundrum for numerical resolution. Thus, one has to use as thin an interface as computationally affordable while still deploying enough grid points within this layer to ensure accurate evaluation of the interfacial tension. This is the main motivation for our adaptive meshing scheme. Even with it, interfacial resolution remains the bottleneck for our scheme. Thus, the advantage of having a physically meaningful treatment of the interfacial profile comes at the price of computing the 4th-order Cahn-Hilliard equation. There are physical problems, such as the moving contact line (Jacqmin, 2000), where the former is essential. Then 3D simulation will require parallel computation. We will return to this point when discussing future work. Second, the phase-field model is not easily generalized to more than two fluid components. A three-component system entails multiple order parameters and interaction energies; such phase-field models have appeared in the
literature but their complexity makes numerical computation difficult (Kim et al., 2004).

Finally, the Leslie-Ericksen theory for the nematic liquid crystals is the simplest that couples molecular orientation and hydrodynamics. Its vectorial nature is inadequate for several aspects of the microstructure. The original version (de Gennes & Prost, 1993) cannot handle defects as they would constitute singularities. A relaxation of the unit-length requirement on the director allows integer-strength defects to be simulated, but the Saturn ring has to be represented by a surface ring. The latter has fewer degrees of freedom and possibly different stability from an unattached Saturn ring. This restriction can be removed by adopting a tensorial representation of the molecular orientation (Rey & Tsuji, 1998; Feng et al., 2000; Yoneya et al., 2005).

9.4 Recommendations for future work

The work described in this thesis may be extended along two directions. One is to upgrade the numerical toolkit to 3D and to incorporate more features, and the other is to apply the tools to other interesting physical problems. Upgrading the numerical code may include the following aspects.

(a) Extending the current 2D code (AMPHI-2D) into a full 3D version AMPHI-3D. Both the current adaptive mesh generator and the Navier-Stokes flow solver are available in 3D already. One will need to generalize the diffuse-interface solver (for the Cahn-Hilliard equations) to 3D. This will greatly expand the range of problems that can be investigated using AMPHI, a few examples of which are given below.

(b) Extending the current two-component diffuse-interface formulation to allow three components. This feature will allow us to model compound drops, double emulsions, and eukaryotic cells more realistically. Up to now, we have had to make the innermost fluid identical to the outermost one. This is a poor representation of the cell nucleus, for instance, which is much more viscous and stiffer than the cytoplasm. Phase-field formulations for three-component systems are available in the literature, and the main challenge will be to solve the more complex equations efficiently.

(c) Generalizing the wetting conditions on solid walls to allow a wide range of contact angles. This can be achieved by adding a surface energy functional to the current formulation (Jacqmin, 2000). With the freedom to define varying degrees of wettability on different parts of the domain boundary, one will be able to investigate the control of interfacial motion through substrate patterning. The microfluidic device with a T-junction, for one, uses alternating hydrophobicity and philicity in different branches to create double emulsions. The role of wettability can then be elucidated systematically by simulations.

(d) Incorporating thermocapillary flows. This consists in adding a heat transfer equation into the solver and allowing the interfacial energy to be temperature-dependent. The motivation is to control and manipulate microscopic droplets by temperature gradients. This is a common strategy in thermo-capillary flows that depends on Marangoni forces. Furthermore, thermal gradients may provide a convenient means for moving particles and droplets in liquid crystals by way of modifying the temperature-dependent bulk elasticity.
The upgraded numerical code can be applied fruitfully to a wide range of physical problems, three of which are outlined below.

(a) **Drop formation in microfluidic devices.** One may extend the studies of drop formation in the microfluidic flow-focusing device from axisymmetric geometries into full 3-dimensional ones. Experiments have almost always used rectangular micro-channels since they are easier to fabricate than ones with circular cross sections. In addition, one may investigate asymmetric microfluidic devices such as the T-junction (Thorsen et al., 2001). In this geometry, the confluence of two immiscible flows, possibly water and oil, yields micro-droplets. Surface wettability is a key player in the process, especially in compound drop formation. The numerical simulations will quantify a variety of parametric effects to guide the microfabrication of the devices, the selection the fluid properties and the control of flow conditions in the experiments.

(b) **Drop migration and manipulation.** Drop migration in 3D channels and channel bifurcations has potential applications in drop-size-based separation, emulsion densifications and separation of blood cells (Shevkoplyas et al., 2005) (see item c below). Moreover, the introduction of temperature gradients gives an additional means of manipulating the drops, and possibly separating them according to size. The induced Marangoni flow inside the drop would also enhance the internal mixing and facilitate chemical reactions (Bringer et al., 2004).

(c) **Biological applications.** There is a close resemblance between liquid drops and blood cells, and simple and compound drop models may be used to simulate the motion and deformation of leukocytes in narrow capillaries. The cytoplasm can be either Newtonian or viscoelastic, and the nucleus can be represented by an inner drop of higher viscosity and interfacial tension. Three processes are of particular interest: entry of neutrophils into pulmonary capillaries that have smaller size than the blood cells under a constant pressure drop; migration of cells in blood vessels (the Fähræus and Fähræus-Lindqvist effects (Popel & Johnson, 2005)); and the separation of blood cells at bifurcations (the “bifurcation law” (Pries et al., 1996; Popel & Johnson, 2005)). Interestingly, the last effect has been exploited to extract white cells from blood using a microfluidic device (Shevkoplyas et al., 2005).
Bibliography


