Notes on Complex Fluids: Kinetic Theory

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Chapter 1

Introduction

1.1 What are Complex Fluids?

Complex fluids include polymeric liquids, colloidal suspensions (gels, sols, and emulsions), liquid crystalline materials, foams, powders, and granular materials. These non-Newtonian fluids are ubiquitous: milk, ketchup, mustard, molten chocolate, ice cream, shampoo, toothpaste, blood, saliva, etc. For an illustrative introduction see the book by Larson [5] From the technological point of view, complex fluids have significant relevance as they are precursors of advanced materials. Many of these materials are processed in liquid form and as such they are complex fluids, for example all plastics and resins and liquid crystalline polymers (LCPs).

Complex fluids have peculiar rheology due to the presence of a microstructure formed by long-chain molecules (macro-molecules) or other types of microscopic or nanoscopic particles which interact with a flow. These microstructures have long relaxation time scales to equilibrium and consequently a flow can induce in them large changes which in turn affect the overall macroscopic properties of the system. For example, a notorious property of polymeric liquids is their viscoelasticity which gives them a ”rubber-like” behavior. We will look later at some of the many other behaviors of complex fluids that are not exhibited by Newtonian fluids like water.

We will focus on a molecular description of polymeric liquids, known as *Kinetic Theory*. Polymers are formed by chemically coupling a large quantity of small reactive molecules called monomers. The chains are typically very long with thousands or millions of monomer units. These macromolecules come in different architectures; they could be flexible or rigid, branched, closed-ring, or star-shaped. The large size of these molecules justifies a modeling simplification in which the details of the individual monomer molecules are neglected. With that spirit, the Kinetic

Theory of polymers focuses on the construction of coarse mechanical models which attempt to capture the macroscopic behavior of the macromolecules (polymers). In addition, because the macromolecules tend to pack in large numbers, they typically interact with many other molecules. Each of these interactions has a small effect to the extent that we can concentrate our efforts on the study of individual molecules. Much of the material of these notes is contained in the treatise on the subject by Bird, Curtiss, Armstrong, and Hassager [2], in the book of Doi and Edwards [3].

1.2 A Two-Scale Problem

Complex fluids are characterized by two disparate length scales and two distinctive time scales. A typical length scale ℓ of the microstructure is on the order of 1 μm whereas a macro length scale L could be anything from a few millimeters to several centimeters. We will assume from the outset that there is a separation of length scales and $\epsilon = \ell/L$ can be considered a small parameter.

There are two different time scales as well: a macromolecular relaxation time scale t_{micro} describing the slowest molecular motions and a characteristic (macro) time for the flow t_{macro}. The *Deborah number De* is defined as the ratio of these two time scales

$$De = \frac{t_{\text{micro}}}{t_{\text{macro}}} \tag{1.1}$$

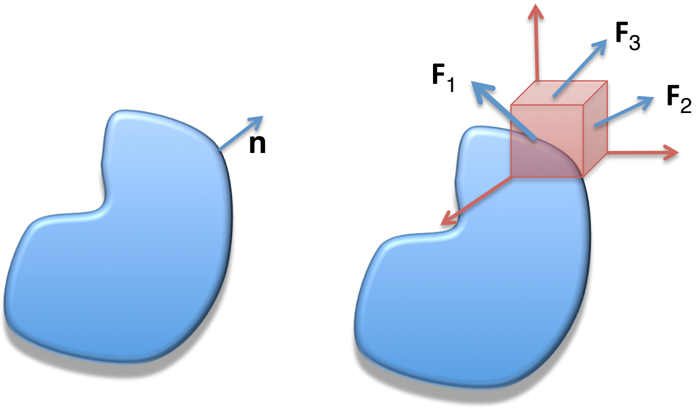
If $De \ll 1$ thermal fluctuations will relax the flow-distorted macromolecules and the fluid will behave largely like a Newtonian one. If, on the other hand $De \gg 1$ the flow-affected macromolecules will not have time to fully relax and as a result the fluid will show some solid-behavior characteristics.

1.3 The Equations of Motion of the Flow

Consider an arbitrary fixed element of fluid Ω_0 as in Fig. 1.1(a), with surface $\partial\Omega_0$. Then the rate of change of the total mass contained in that fluid element is equal to the flux of mass across the surface $\partial\Omega_0$, in the absence of sinks or sources inside Ω_0:

$$\frac{d}{dt}\int_{\Omega_0} \rho\, dV = -\int_{\partial\Omega_0} \rho\mathbf{v}\cdot\mathbf{n}\, dS. \tag{1.2}$$

Here ρ is the mass density, $\mathbf{v}$ is the flow's velocity field, and $\mathbf{n}$ is the unit normal pointing outward of $\partial\Omega_0$. This is the principle of conservation of mass. Using the



(a) Fluid element (b) Stress forces

Figure 1.1: Stress forces on a element. $\mathbf{T} = [\mathbf{F}_1 \quad \mathbf{F}_2 \quad \mathbf{F}_3]$.

Gauss' s Divergence Theorem, (1.2) becomes

$$\int_{\Omega_0} \frac{\partial \rho}{\partial t}\, dV = -\int_{\Omega_0} \nabla \cdot (\rho \mathbf{v})\, dV \tag{1.3}$$

and because Ω_0 is arbitrary we obtain the *Continuity Equation*

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{1.4}$$

For constant density flows we get the incompressibility condition

$$\boxed{\nabla \cdot \mathbf{v} = 0.} \tag{1.5}$$

We can apply Newton's second law to Ω_0 to obtain a statement of conservation of momentum. The momentum of Ω_0 will change due to three sources: flux of momentum across $\partial\Omega_0$, external (body) forces $\rho \mathbf{f}_{\text{ext}}$ (e.g. gravity), internal forces $\mathbf{S}$ of molecular nature acting on $\partial\Omega_0$:

$$\frac{d}{dt}\int_{\Omega_0} \rho \mathbf{v}\, dV = -\int_{\partial\Omega_0} (\rho \mathbf{v} \otimes \mathbf{v})\, \mathbf{n}\, dS + \int_{\Omega_0} \rho \mathbf{f}_{\text{ext}}\, dV + \int_{\partial\Omega_0} \mathbf{S}\, dS. \tag{1.6}$$

Here, $\mathbf{v} \otimes \mathbf{v}$ is the tensor product of $\mathbf{v}$ with itself and $(\mathbf{v} \otimes \mathbf{v})_{ij} = v_i v_j$. Cauchy's Theorem states that these stress forces are linear in $\mathbf{n}$ and

$$\mathbf{S} = \mathbf{T}\mathbf{n}. \tag{1.7}$$

where **T** is a second order tensor called the *stress tensor* and we will represent it as a matrix. Thus, T_{ij} is the i-th component of the force per unit area in a plane normal to the j-th direction (see Fig. 1.1(b)). Substituting (1.7 into (1.6) and applying the Gauss's Theorem we have

$$\int_{\Omega_0} \frac{\partial(\rho\mathbf{v})}{\partial t}\, dV = -\int_{\Omega_0} \nabla\cdot(\rho\mathbf{v}\otimes\mathbf{v})\, dS + \int_{\Omega_0} \rho\mathbf{f}_{\text{ext}}\, dV + \int_{\Omega_0} \nabla\cdot\mathbf{T}\, dV. \tag{1.8}$$

The divergence of the tensors $\rho\mathbf{v}\otimes\mathbf{v}$ and $\mathbf{T}$ are the vectors with components

$$[\nabla\cdot(\rho\mathbf{v}\otimes\mathbf{v})]_i = \sum_{j=1}^{3} \frac{\partial(\rho v_i v_j)}{\partial x_j}, \qquad (\nabla\cdot\mathbf{T})_i = \sum_{j=1}^{3} \frac{\partial T_{ij}}{\partial x_j}, \tag{1.9}$$

respectively. Thus, in differential form the conservation of momentum reads

$$\frac{\partial(\rho\mathbf{v})}{\partial t} + \nabla\cdot(\rho\mathbf{v}\otimes\mathbf{v}) = \nabla\cdot\mathbf{T} + \rho\mathbf{f}_{\text{ext}}. \tag{1.10}$$

Upon using the Continuity Equation (1.4), we obtain the following equation in non-conservative form:

$$\rho\left[\frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v}\right] = \nabla\cdot\mathbf{T} + \rho\mathbf{f}_{\text{ext}}, \tag{1.11}$$

where

$$(\mathbf{v}\cdot\nabla)v_i = \sum_{j=1}^{3} v_j \frac{\partial v_i}{\partial x_j}. \tag{1.12}$$

The bracketed term in (1.11) is the *material or substantial derivative* of $\mathbf{v}$:

$$\frac{D\mathbf{v}}{Dt} = \frac{\partial\mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} \tag{1.13}$$

and thus the conservation of momentum can be written more succinctly as

$$\boxed{\rho\frac{D\mathbf{v}}{Dt} = \nabla\cdot\mathbf{T} + \rho\mathbf{f}_{\text{ext}}.} \tag{1.14}$$

Equations (1.5) and (1.14), supplemented with appropriate boundary and initial conditions, are the relevant equations to describe the motion of an incompressible fluid. However, the system is not closed until we provide a mechanism to compute the stress tensor **T**. It is convenient to write **T** as

$$\mathbf{T} = -p\mathbf{I} + \boldsymbol{\sigma}, \tag{1.15}$$

where $-p\mathbf{I}$ represents the isotropic part due to hydrostatic pressure p and $\boldsymbol{\sigma}$ is the *deviatoric or excess stress.* Often in continuum models of fluids, $\boldsymbol{\sigma}$ is taken to be a function of the velocity gradient, $\boldsymbol{\sigma} = \boldsymbol{\sigma}(\nabla\mathbf{v})$. Here, $\nabla\mathbf{v}$ is the matrix given by

$$(\nabla\mathbf{v})_{ij} = \frac{\partial v_i}{\partial x_j}. \tag{1.16}$$

For a large class of fluids, so called *Newtonian*, $\boldsymbol{\sigma}$ obeys a simple constitutive equation:

$$\boldsymbol{\sigma} = \mu\left(\nabla\mathbf{v} + \nabla\mathbf{v}^T\right) + \left(\kappa - \frac{2}{3}\mu\right)\mathrm{tr}(\nabla\mathbf{v})\,\mathbf{I}, \tag{1.17}$$

where μ is the fluid viscosity, $\nabla\mathbf{v}^T$ denotes the transpose of the velocity gradient (1.16), κ is the *dilatational viscosity*, and $\mathrm{tr}(\nabla\mathbf{v}) = \nabla\cdot\mathbf{v}$ is the trace of $\nabla\mathbf{v}$. Thus, for a Newtonian, incompressible fluid

$$\mathbf{T} = -p\mathbf{I} + \mu\left(\nabla\mathbf{v} + \nabla\mathbf{v}^T\right). \tag{1.18}$$

Often, in rheology literature $\nabla\mathbf{v}$ denotes the transpose of (1.16). Here, we will retain the mathematical meaning given in (1.16) as the derivative matrix of $\mathbf{v}$. Note that with the constitutive equation for the stress, Eq. (1.18), we have a close system given by (1.5), (1.14), (1.18). The system constitutes the *Navier-Stokes* equations for the dynamics of an incompressible *Newtonian* fluid.

It is convenient to decompose $\nabla\mathbf{v}$ into its symmetric and anti-symmetric parts, $\nabla\mathbf{v} = \mathbf{D} + \boldsymbol{\Omega}$ where

$$\mathbf{D} = \frac{1}{2}\left[\nabla\mathbf{v} + \nabla\mathbf{v}^T\right], \tag{1.19}$$

$$\boldsymbol{\Omega} = \frac{1}{2}\left[\nabla\mathbf{v} - \nabla\mathbf{v}^T\right]. \tag{1.20}$$

$\mathbf{D}$ is called the *deformation* or *rate of strain* tensor and $\boldsymbol{\Omega}$ the *vorticity* tensor. Note that $\mathrm{tr}(\mathbf{D}) = \nabla\cdot\mathbf{v}$ and thus for an incompressible fluid $\mathbf{D}$ is traceless.

We are particularly interested in polymer solutions with an incompressible, Newtonian solvent. In such cases it is convenient to write the stress tensor as

$$\mathbf{T} = -p\mathbf{I} + 2\mu\mathbf{D} + \boldsymbol{\sigma}_p, \tag{1.21}$$

where $\boldsymbol{\sigma}_p$ is the stress caused by the macromolecules.

The main task of the theory and of the computations of complex fluids is to obtain $\boldsymbol{\sigma}_p$.

Like the Newtonian $\boldsymbol{\sigma}$, the microstructural stress $\boldsymbol{\sigma}_p$ is symmetric for most models. This follows from the assumption of isotropy (when the fluid is at rest) and the conservation of angular momentum.

1.4 Creeping Flow: Stokes Approximation

In the absence of external forces, the Navier-Stokes equations (1.5), (1.14), and (1.18) for an incompressible, Newtonian fluid can be written as

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}\right)=-\nabla p+\mu\nabla^2\mathbf{v}, \tag{1.22}$$

$$\nabla\cdot\mathbf{v}=0. \tag{1.23}$$

These equations may be non-dimensionalized by introducing a characteristic length scale L_c, a characteristic velocity U_c, and a characteristic time scale T_c. Let us select $T_c = L_c/U_c$. Introducing the following dimensionless variables

$$\mathbf{x}'=\frac{\mathbf{x}}{L_c}, \tag{1.24}$$

$$\mathbf{v}'=\frac{\mathbf{v}}{U_c}, \tag{1.25}$$

$$t'=\frac{t}{\left(\frac{L_c}{U_c}\right)}, \tag{1.26}$$

$$p'=\frac{p}{\left(\frac{\mu U_c}{L_c}\right)}, \tag{1.27}$$

we get the non-dimensionalized Navier-Stokes equations:

$$Re\left(\frac{\partial \mathbf{v}'}{\partial t'}+\mathbf{v}'\cdot\nabla'\mathbf{v}'\right)=-\nabla' p'+\nabla'^2\mathbf{v}', \tag{1.28}$$

$$\nabla'\cdot\mathbf{v}'=0, \tag{1.29}$$

where

$$Re=\frac{\rho U_c L_c}{\mu}, \tag{1.30}$$

is a dimensionless parameter known as the *Reynolds number*. Equations (1.28) and (1.29) as well as corresponding, *non-dimensionalized* boundary and initial conditions define a one-parameter family of solutions (depending only on Re). All flows which satisfy the same non-dimensionalized boundary and initial conditions and whose combination of μ, ρ, L_c, and U_c yield the same Re will be described by the same solution of (1.28) and (1.29). This is the principle of *Dynamic Similarity*.

This Reynolds number can be interpreted as the ratio of inertial forces to viscous forces. Indeed

$$Re=\frac{\left(\frac{\rho U_c^2}{L_c}\right)}{\left(\frac{\mu U_c}{L_c^2}\right)}. \tag{1.31}$$

When inertial effects are small compared to viscous forces, i.e. $Re \ll 1$, a useful approximation is to take formally the limit $Re \to 0$ in the momentum equation (1.28). For these *creeping flows*m we get the (steady) *Stokes approximation*:

$$-\nabla p + \nabla^2 \mathbf{v} = \mathbf{0}, \tag{1.32}$$

$$\nabla \cdot \mathbf{v} = 0, \tag{1.33}$$

where the primes have been dropped in all dimensionless variables to simplify the notation.

For many complex fluid solutions $Re \ll 1$ and thus it is appropriate to describe their dynamics with the Stokes approximation. Going back to (1.14) and (1.21) and reintroducing the dimensioned variables we have the Stokes approximation for an incompressible, non-Newtonian solution:

$$-\nabla p + \mu \nabla^2 \mathbf{v} + \nabla \cdot \boldsymbol{\sigma}_p = \mathbf{0}, \tag{1.34}$$

$$\nabla \cdot \mathbf{v} = 0. \tag{1.35}$$

Given the two-scale nature of complex fluids we call also speak of a *microscopic Reynolds number*, Re_{micro}. However, to maintain a separation of macro and micro scales, we must assume that also $Re_{\text{micro}} \ll 1$ for otherwise the complex flow system could develop *macroscopic* boundary layers of characteristic length smaller than ℓ.

1.5 Two Important Simple Flows

A *simple shear flow* is given by the velocity gradient

$$\nabla \mathbf{v} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{1.36}$$

where the scalar $\dot{\gamma}$ is the *shear rate*. It could be produced by the sliding motion of two parallel plates with a relative velocity V, separated by a fluid-filled gap L as in Fig. 1.2(circular and cone-and-plate geometries can also be employed to produce shear flows). In this case $\dot{\gamma} = V/L$. Note that the *streamlines* $\mathbf{X}(t)$, defined by

$$\frac{d\mathbf{X}(t)}{dt} = \mathbf{v}\left(\mathbf{X}(t)\right), \tag{1.37}$$

$$\mathbf{X}(t_0) = \mathbf{x}_0, \tag{1.38}$$

trace a family of sliding planes.

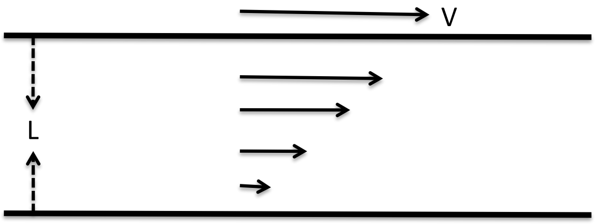


Figure 1.2: Planar shear flow geometry.

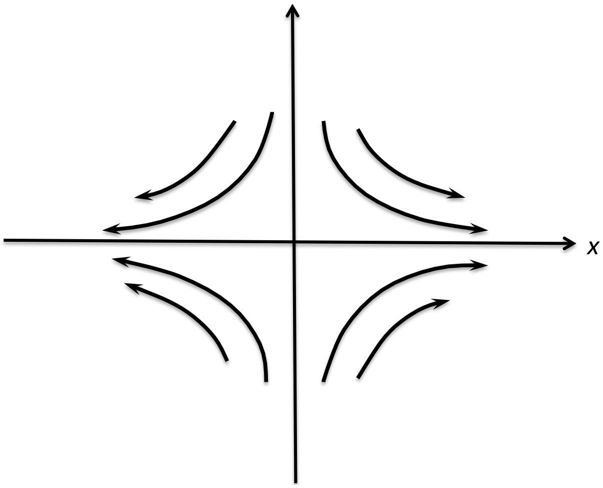


Figure 1.3: Uniaxial extensional flow.

A second important, simple flow which is useful in the characterization of complex fluids is an *extensional or elongational flow*, given by

$$\nabla \mathbf{v} = \begin{bmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon}/2 & 0 \\ 0 & 0 & -\dot{\epsilon}/2 \end{bmatrix}, \tag{1.39}$$

where the scalar $\dot{\epsilon}$ is the *magnitude of the strain* (Fig. 1.3). In Cartesian coordinates, the streamlines are

$$X(t) = x_0 e^{\dot{\epsilon}(t-t_0)}, \tag{1.40}$$

$$Y(t) = y_0 e^{-\frac{1}{2}\dot{\epsilon}(t-t_0)}, \tag{1.41}$$

$$Z(t) = z_0 e^{-\frac{1}{2}\dot{\epsilon}(t-t_0)}. \tag{1.42}$$

Hence, if $\dot{\epsilon} > 0$ there is a *uniaxial* exponential stretching of fluid elements in the x-direction and if $\dot{\epsilon} < 0$ the stretching is *bi-axial.*

When $\dot{\gamma}$ and $\dot{\epsilon}$ are constant the corresponding flows are steady and are called *viscometric flows.*

1.6 Material Functions

1.6.1 Shear Flows

In a shear flow of a Newtonian fluid only the *shear stress* $\sigma_{12} = \sigma_{21} = \mu\dot{\gamma}$ is non-zero. In general, for an *isotropic*, incompressible non-Newtonian fluid, the stress tensor has the form

$$\mathbf{T} = \begin{bmatrix} -p + \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & -p + \sigma_{22} & 0 \\ 0 & 0 & -p + \sigma_{33} \end{bmatrix}. \tag{1.43}$$

The off-diagonal entries $\sigma_{13} = \sigma_{31}$, and $\sigma_{23} = \sigma_{32}$ are zero due to symmetry; a rotation of π around the x_3-axis leaves the velocity field invariant and assuming the fluid is isotropic the stress inherits this symmetry.

Because the pressure is defined up to an additive constant, only differences of the diagonal terms of $\mathbf{T}$ can be measured. Two such *normal stress differences* are defined as:

$$N_1 = \sigma_{11} - \sigma_{22}, \tag{1.44}$$

$$N_2 = \sigma_{33} - \sigma_{22}. \tag{1.45}$$

Usually, $N_1 > 0$ while $N_2 < 0$ and $|N_2| < N_1$. For steady shear flow, i.e. $\dot{\gamma}$ time-independent, the *shear viscosity* η is defined, like in the Newtonian case, by

$$\eta(\dot{\gamma}) = \frac{\sigma_{12}(\dot{\gamma})}{\dot{\gamma}}. \tag{1.46}$$

Note that, in contrast to Newtonian fluids, the shear viscosity depends on the shear rate.

The normal stress differences N_1 and N_2 are also dependent on the shear rate, typically at a higher than linear rate. To characterize that dependence two *viscometric functions* are defined as:

$$\Psi_1(\dot{\gamma}) = \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2}, \tag{1.47}$$

$$\Psi_2(\dot{\gamma}) = \frac{N_2(\dot{\gamma})}{\dot{\gamma}^2}. \tag{1.48}$$

Ψ_1 and Ψ_2 are called the *first and second normal stress coefficients.* Note that for a Newtonian fluid both normal coefficients are zero.

In addition to steady flows, small amplitude shear flows are used experimentally to study the response of the microstructure to unsteady flows. In these non-steady flows the shear rate is sinusoidal:

$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos \omega t, \tag{1.49}$$

where $\dot{\gamma}_0 \ll 1$. Then, the stress varies also sinusoidal but not necessarily in phase with the shear rate. This motion is expressed as

$$\sigma_{12} = \dot{\gamma}_0 \left[\eta'(\omega) \cos \omega t + \eta''(\omega) \sin \omega t \right]. \tag{1.50}$$

This expression defines two viscosity functions η' and η'' or alternatively a "complex" viscosity function $\eta^* = \eta' - i\eta''$. Note that for a Newtonian fluid $\eta'' = 0$. The function η' is called the *dynamic viscosity.* A complex *modulus* G^* is defined through the relation $G^* = i\omega\eta^* = G' + iG''$. G' and G'' are called the *loss modulus* and *storage modulus*, respectively.

1.6.2 Extensional Flows

Due to symmetry with respect to all the axes, the stress for simple extensional flows has a very simple form:

$$\mathbf{T} = \begin{bmatrix} -p + \sigma_{11} & 0 & 0 \\ 0 & -p + \sigma_{22} & 0 \\ 0 & 0 & -p + \sigma_{33} \end{bmatrix}. \tag{1.51}$$

Because the x_2 and x_3 directions are indistinguishable for this geometry, only the first normal stress difference N_1 is relevant ($N_2 = 0$). A viscosity function $\eta(\dot{\epsilon})$ is defined to characterize the dependence of N_1 on the magnitude of the strain $\dot{\epsilon}$ for steady flows:

$$\eta_(\dot{\epsilon}) = \frac{N_1(\dot{\epsilon})}{\dot{\epsilon}}. \tag{1.52}$$

1.7 Distinctive Phenomena in Complex Fluids

A characteristic feature of complex fluids under shear flows is that, in contrast to Newtonian fluids, the viscosity depends on the shear rate. For the majority of complex fluids, the viscosity decreases with increasing shear rate. Fluids with this behavior are called *shear thinning.* Blood, paint, syrup, and molasses are familiar examples of this type of non-Newtonian fluids. It is more unusual to have complex fluids whose viscosity increases with increasing shear rate. One example of this *shear thickening* fluid is quicksand (i.e. sand in water).

There are some complex fluids that would only start to flow for shear rates higher than a certain threshold, like ketchup and toothpaste. These are called *yield fluids.*

The imbedded microstructure interacting with the flow gives rise to a variety of fascinating non-linear phenomena. Generally, there is a strong resistance of non-Newtonian fluid elements to stretching, i.e. a *high extensional viscosity.* As a result, even a few parts per million of polymers in a solution can lead to a strong inhibition of drop break-up and jet formation which are important in several industrial applications. This high resistance to stretching is also responsible for the cusp formation observed at the trailing edge of an ascending bubble in a polymeric fluid to avoid the large extensional flow flowing out of the rear stagnation point (see Fig. 1.4)

(a) (b) (c)

Figure 1.4: Ascending air bubble in (a) a Newtonian fluid and (b)-(c) a non-Newtonian fluid (front and side view) .

Another distinctive non-linear behavior of many complex fluids is elastic effects. When subject to straining these fluids can store energy. Silly Putty® and Slime® offer dramatic examples of this type. They can be stretched and cut like rubber but can also flow and fill up a container (Fig. 1.5).

There are several other interesting non-linear behaviors of complex fluids, see [1] Chapter 2. One of the more distinctive is the presence of *normal stresses* to shear flows. For Newtonian fluids the normal stress differences defined in (1.44) and (1.45) are exactly zero. These normal stresses can be interpreted as *tension along the streamlines* and can be used to explain the *rod climbing* effect observed when a non-Newtonian fluid is stirred by a rotating rod. The free surface has an upward deflection in contrast to the flat surface observed in a Newtonian fluid for comparable rotations. The shear caused by the rotating rod produces in the circular streamlines. This “circular” stress balances the hydrostatic pressure of a column of fluid above it inducing the fluid to climb (Fig. 1.6).

Figure 1.5: Slime

1.8 General Framework

As we will see, KT models for polymeric fluids vary in complexity depending on the mechanical structures employed to represent the macromolecules. These coarse-grained models could be linear *rod-bead* chains or *bead-spring* chains as illustrated in Fig. 1.7.

Despite their differences, there is a common mathematical framework that they all share [4]. Let us focus on the case in which we have an incompressible Newtonian solvent. At very low Reynolds numbers, as is the case in these polymeric systems, the Stokes approximation for the conservation of momentum (in dimensionless form) and the condition of incompressibility give

$$-\nabla p + \nabla^2 \mathbf{v} + \nabla \cdot \boldsymbol{\sigma}_p = \mathbf{0}, \tag{1.53}$$

$$\nabla \cdot \mathbf{v} = 0. \tag{1.54}$$

This system would be closed if σ_p were a function of $\mathbf{x}$, t, and $\nabla \mathbf{v}$ alone. However, $\boldsymbol{\sigma}_p$ depends strongly on the flow as wells as on the history of average configurations of the macromolecules. Consequently, we need an additional mechanism to determine $\boldsymbol{\sigma}_p$. For concreteness, let us describe the configuration of these "macromolecules" in a very coarse fashion by looking at the end-to-end vector $\mathbf{Q}$ of the chains. Thus, configuration is space Ω_C for this case is three-dimensional. The microscopic description can be accomplished with either an *evolution equation* for a probability density function (PDF) $\psi(t, x, \mathbf{Q})$ which describes the probability of finding a macromolecule in a given configuration (specified by $\mathbf{Q}$) at time t and in the position $\mathbf{x}$ or with a simulation of *stochastic processes* for the macromolecule

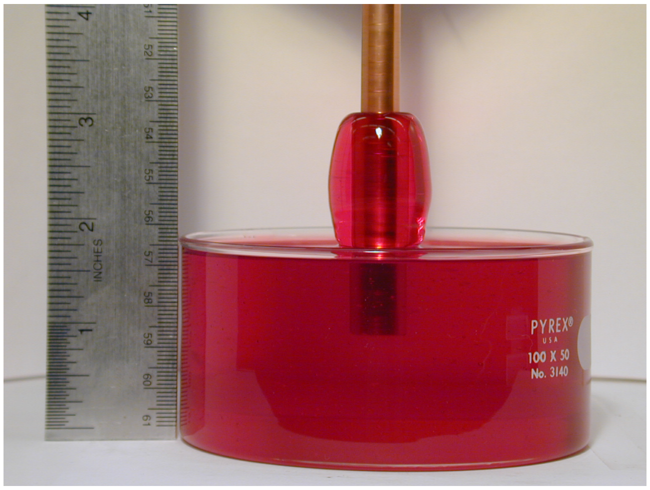
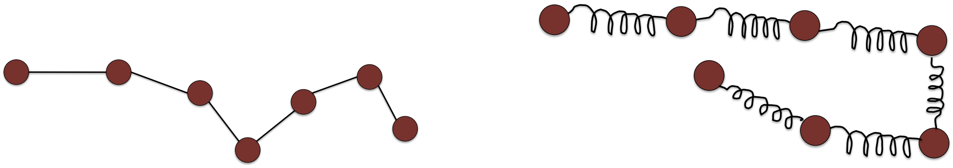


Figure 1.6: Rod climbing effect.



(a) Bead-rod chain (b) Bead-spring chain

Figure 1.7: Typical Kinetic Theory mechanical models for the macromolecules.

dynamics. We write these two options generically as

$$\frac{D\psi}{Dt} = -\nabla_{\mathbf{Q}} \cdot \{\mathbf{a}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v})\psi\} + \frac{1}{2}\nabla_{\mathbf{Q}}\nabla_{\mathbf{Q}} : \{\mathbf{D}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v})\psi\}, \tag{1.55a}$$

$$d\mathbf{Q} = \mathbf{a}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v})\ dt + \mathbf{b}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v}) \cdot d\mathbf{W}_{\mathbf{Q}}(t), \tag{1.55b}$$

where D/Dt is the material derivative (1.13), $\mathbf{A}$ is a “drift” vector in configuration space and $\mathbf{D} = \mathbf{b}\mathbf{b}^T$ is a diffusion (symmetric) matrix, and $W_{\mathbf{Q}}(t)$ is a Weiner process. In (1.55a), $\nabla_{\mathbf{Q}}\nabla_{\mathbf{Q}} : \{\mathbf{D}\psi\} = \sum_i \sum_j \partial_{Q_i}\partial_{Q_j}(D_{ij}\psi)$. Equation (1.55b) is often called a em Langevin-type equation whereas (1.55a)is known as the *Fokker-Planck* or *Smoluchowski* equation. Both approaches are mathematically equivalent. We will spend some time discussing the computational aspects of both option later. The polymeric stress $\boldsymbol{\sigma}_p$ is an average in configuration space which we can express generically as

$$\boldsymbol{\sigma}_p = \int_{\Omega_c} \mathbf{g}(\mathbf{Q})\psi d\mathbf{Q} := \langle \mathbf{g}(\mathbf{Q}) \rangle_{\psi}\,. \tag{1.56}$$

The generic model (1.53)-(1.56) is deceivably simple. The devil is in the details and these will come from the particular KT mechanical models one employs to describe the macromolecules. Even though these models are already coarse-grained, the large number of degrees of freedom makes this flow-structure interaction problem a formidable computational challenge.

1.8.1 The Closure Problem

Alternatively, one could try to compute $\boldsymbol{\sigma}_p$ as follows. Assume $\boldsymbol{\sigma}_p = \mathbf{F}(t, \mathbf{x}; \langle \mathbf{Q}\mathbf{Q} \rangle_\psi)$. Multiply the Fokker-Plank equation (1.55a) by $\mathbf{QQ}$ and integrate with respect to $\mathbf{Q}$ in configuration space

$$\begin{aligned} \int_{\Omega_C} \mathbf{QQ} \frac{D\psi}{Dt} d\mathbf{Q} = &- \int_{\Omega_C} \mathbf{QQ} \, \nabla_{\mathbf{Q}} \cdot \{ \mathbf{a}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v}) \psi \} \, d\mathbf{Q} \\ &+ \frac{1}{2} \int_{\Omega_C} \mathbf{QQ} \, \nabla_{\mathbf{Q}} \nabla_{\mathbf{Q}} : \{ \mathbf{D}(t, \mathbf{x}, \mathbf{Q}; \nabla \mathbf{v}) \psi \} \end{aligned} \tag{1.57}$$

The left hand side of (1.57) is just the material derivative of the second moment $\langle \mathbf{QQ} \rangle_\psi$. However, the right hand side, with counted exceptions, will depend on higher moments as well. Suppose it also depends on the fourth moment, so that (1.57) is an equation of the form

$$\frac{D}{Dt} \langle \mathbf{QQ} \rangle_\psi = \mathbf{G}(t, \mathbf{x}; \langle \mathbf{QQ} \rangle_\psi, \langle \mathbf{QQQQ} \rangle_\psi). \tag{1.58}$$

If we now derive an equation for the fourth moment its right hand side will depend on it and on the *sixth moment* as well. We have a *closure problem.* We are "mathematically tempted" to approximate the high order moments using the low order ones. For example, we can postulate that $\langle \mathbf{QQQQ} \rangle_\psi \approx \mathbf{f}(\langle \mathbf{QQ} \rangle_\psi)$, for some "physically inspired" function $\mathbf{f}$. Closure approximations are appealing because they reduce the dimensionality of the problem by eliminating the configuration space. However, the price paid can be substantial; a closure approximation can produce solutions that depart significantly from the expected physical behavior. Also troubling is the fact that closure approximations can change the type and structure of the coupled system of partial differential equations describing the flow-structure interaction.

1.9 Computational Challenges

In classical Computational Fluid Dynamics (CFD) of Newtonian flows we only needs to compute the velocity field $\mathbf{v}$ and the pressure p. In the computation of KT models of complex fluids we must also compute the evolution of a microstructure. More precisely, at every in time and space $(t, \mathbf{x})$ we need to evaluate the fluid stress induced by the microstructure (macromolecules).

Computationally, it would be ideal if we had a time-evolution equation for the stress $\boldsymbol{\sigma}_p$, a so called *constitutive equation*, and solve this coupled to the Stokes system (1.53)-(1.54) in our $(t, \mathbf{x})$ computational domain. We could attempt to derive such an equation by getting evolution equations for the moments from (1.55a) as explain in the preceding section. Unfortunately, only in very few simple cases of KT models (Oldroyd B model being a notable example) can we obtain a closed, constitutive equation for $\boldsymbol{\sigma}_p$. Hence, we are left to work with either (1.55b) or (1.55a). If we are inclined to work within a deterministic framework and use (1.55a) then we need to solve this equation in configuration space (i.e. in $\mathbf{Q}$) for each point $(t, \mathbf{x})$ of our computational time-space grid. Even in the simplest model of a rigid-like molecule where need only need two degrees of freedom to describe its configuration (the angles of rotation, i.e configuration space is the unit sphere), the total number of dimensions would be $1 + 3 + 2 = 6$! Clearly, this approach quickly becomes computationally intractable as the number of degrees of freedom to describe the macromolecules increases. The stochastic approach (1.55b) represents an attractive alternative to deal with such high dimensionality [6] but the overall flow-structure problem is still a daunting challenge where significant advances in computational methodologies are much needed.

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