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Derivation and Applications of a Generalized Oldroyd Constitutive Model

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Derivation and Applications of a Generalized Oldroyd Constitutive Model

by

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B.S., Brigham Young University, 2009
M.S., University of Colorado, 2016

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Department of Chemical and Biological Engineering

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Date: ________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Martin, Richard M. (Ph.D., Chemical Engineering)

Derivation and Applications of a Generalized Oldroyd Constitutive Model

Thesis directed by Prof. Robert H. Davis

Abstract

The search for relevant constitutive models valid for a broad variety of non-Newtonian fluids is an urgent problem in rheology. These constitutive models must accurately capture many of the non-Newtonian behaviors of the fluids and be valid for arbitrary kinematics. Many constitutive models have been proposed, but are sometimes limited in their scope of application. Some constitutive models are only valid for a specific type of fluid, and other models have many material parameters that cannot be readily evaluated. In this work, a generalized Oldroyd model is developed that can be applied to a broad range of complex, non-Newtonian fluids. The generalized Oldroyd model consists of five material parameters, that can be evaluated based on the rheological functions of two base flows—simple shear and planar extension. The material parameters are allowed to be functions of an invariant of the flow, which is chosen to be the energy dissipation rate in this work.

The generalized Oldroyd equation is applied to three non-Newtonian suspensions: dilute emulsions, suspensions of rigid spheroids subject to Brownian rotations, and dilute emulsions in the presence of surfactants. A variety of kinematics is explored to validate the effectiveness of the generalized Oldroyd equation, including calculation of the stress components in planar mixed flows and uniaxial extension/compression. A number of Lagrangian-unsteady flows are also explored to test the generalized Oldroyd method in nontrivial time-dependent flows. The Lagrangian-unsteady flows that are explored in this work include: flow in a rectangular cavity with a moving wall; flow around a macroscopic sphere; time-dependent planar extension; flow around a macroscopic sphere at a finite Reynolds number; and flow between two eccentric spheres. For these Lagrangian-unsteady cases, a material fluid element is advected along
one of the streamlines in the flow, and the stress is calculated along the streamline. The generalized Oldroyd model is shown in all cases to accurately predict the stresses, with greater accuracy in slower flows. The generalized Oldroyd equation in this work is shown to be a broad constitutive model that can be applied to a variety of complex fluids in arbitrary kinematics.
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Chapter 1: Introduction

The study of suspensions is pertinent to a range of fluids found in industry, biology, and the environment. There is a large variety of suspensions, consisting of liquid or solid particles dispersed in liquid, gaseous, or solid media, or gases dispersed in liquids or solids [1]. Industrial applications include pharmaceuticals, oil extraction and transport, and food and beverage processing. Biological suspensions include blood and bacteria present in aqueous solutions. In the environment, suspensions of solid particles in liquid or gases are often present, such as sediment dispersed in a flowing river and solid particulates in the atmosphere. The suspensions that are most relevant to this dissertation are mixtures of two immiscible liquids (emulsions) and solid particulates dispersed in a liquid. In suspensions, the liquid drops or solid particles in a suspension are referred to as the dispersed phase, and the suspending medium is referred to as the continuous phase.

The suspensions studied herein are subject to a variety of flow conditions, where the continuous-phase fluid applies a viscous force to the suspended drops or solid particulates. The flows are in the low Reynolds number regime; thus the inertial terms in the Navier-Stokes equation can be neglected, which results in the Stokes equation. The total stress present in the system is a sum of the continuous-phase contribution and the dispersed-phase contribution to the stress. Even when the continuous-phase fluid is Newtonian, the addition of a dispersed phase (whether a solid or another Newtonian liquid) may cause the bulk fluid to behave in a non-Newtonian fashion. The study of non-Newtonian behavior is a branch of fluid mechanics known as rheology (meaning “the study of flow”, derived from the Greek root rheos for stream). A major interest in rheology is the development of constitutive equations
that can predict the stress of a non-Newtonian fluid in arbitrary kinematics. There are many different characteristics of non-Newtonian fluids that are observed in nature, among which are fluids with a fading “memory”, where the stress tensor depends on the past kinematic history of the fluid. Many constitutive models have been proposed, but are sometimes limited in their scope of application. Some constitutive models are only valid for a specific type of fluid, and other models have many material parameters that cannot be readily evaluated. In this work, a generalized Oldroyd model is developed that can be applied to a broad range of complex, non-Newtonian fluids. This model requires the determination of the rheology for a variety of complex fluids.

The proceeding sections are organized as follows: Section 1.1 explores the fundamental equations for solving fluid flow problems in the low-Reynolds-number regime. In Sec. 1.2, constitutive equations and different approaches to modeling non-Newtonian fluids are described. Section 1.3 gives a summary of the chapters contained in this dissertation. For incompressible fluid flows, the fundamental equations required for calculating the velocity, stress, and pressure fields involve the conservation equations of mass and momentum, which are manifest in the continuity and Navier-Stokes equations, respectively. These equations are presented in the following section.

1.1. The Stokes and continuity equations

One of the fundamental equations in fluid mechanics is the Cauchy momentum equation, which is derived based on the principle of conservation of momentum (see Çengel and Cimbala [2] for details). The Cauchy momentum equation is given as:

\[
\frac{Du}{Dt} = \frac{1}{\rho} \nabla \cdot \tau + b,
\] (1.1)

where \(Du/Dt\) is the material derivative of the velocity \(u\), \(\rho\) is the fluid density, \(\tau\) is the Cauchy stress tensor, and \(b\) is the sum of body forces acting on the fluid. When the shear
stress is taken to be linearly proportional to the shear strain rate (i.e., a Newtonian fluid),
and the fluid is taken as incompressible, the Navier-Stokes equation follows from the Cauchy
Eq. (1.1) as [2]
\[
\rho \frac{Du}{Dt} = -\nabla p + \mu \nabla^2 u ,
\]
where \(\mu\) is the fluid viscosity and \(p\) is the dynamic pressure. The dynamic pressure is defined
as \(p = p_{tot} - \rho gz\), where \(p_{tot}\) is the total pressure, \(g\) is the gravitational acceleration constant,
and \(z\) is the depth of the fluid at a point [3]. In this work, we are concerned primarily with
flows at low Reynolds number. The Reynolds number \(Re\) is a dimensionless number which
gives the ratio of the inertial and viscous effects:
\[
Re = \frac{\rho VL}{\mu} ,
\]
where \(V\) is the characteristic velocity of the flow and \(L\) is the characteristic length scale of
the flow. At low Reynolds numbers, the inertial effects in the Navier-Stokes Eq. (1.2) are
neglected. This reduces Eq. (1.2) to the Stokes equation:
\[
-\nabla p + \mu \nabla^2 u = 0 .
\]
The Stokes equation is valid for Newtonian fluids in slow or viscous flows, or when the density
or length scale is small.

The continuity equation is often used in conjunction with Eq. (1.4). The continuity
equation is derived from the conservation of fluid mass, and written as
\[
\frac{1}{\rho} \frac{D\rho}{Dt} + \nabla \cdot u = 0 .
\]
For incompressible fluid flows, Eq. (1.5) is simplified to
\[
\nabla \cdot u = 0 .
\]
Equations (1.4) and (1.6) are the fundamental equations used to calculate the flow properties in a given system at low Reynolds number. Although these equations are written for Newtonian fluids, when a suspension consists of either two Newtonian fluids or solid particulates in a Newtonian fluid, the bulk fluid can display non-Newtonian characteristics. The differences between Newtonian and non-Newtonian fluids are further explained in the following section.

1.2. Constitutive equations

The search for practical and broadly applicable constitutive equations continues to be a main goal in rheology. Generally, constitutive equations relate the flow properties and other material parameters of a fluid to the bulk stress of the fluid. A basic case would be a constitutive equation that relates the strain rate to the stress of a fluid. Figure 1.1 shows various relations and examples of non-Newtonian behavior. A Newtonian fluid has a linearly proportional relationship between the stress and strain rate. Three types of non-Newtonian fluids are shown in Fig. 1.1. A shear thinning or pseudoplastic fluid becomes easier to shear as more stress is applied. The opposite effect is apparent in shear thickening or dilatant fluids, where increased stress makes the fluid more difficult to shear further. A Bingham plastic resists flow up to a certain amount of applied stress, known as the yield stress.

The total Cauchy stress $\boldsymbol{\tau}$ on a Newtonian fluid is characterized by

$$\boldsymbol{\tau} = -p_{iso} I + 2\mu \boldsymbol{E},$$  \hspace{1cm} (1.7)

where $\boldsymbol{E} = [\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T]/2$ is the rate-of-strain tensor, $p_{iso} I$ is the isotropic pressure term, and $I$ is the identity matrix. When describing the total stress of a suspension, the particle contribution to the stress is added to Eq. (1.7), giving

$$\boldsymbol{\tau} = -p_{iso} I + 2\mu \boldsymbol{E} + \phi \boldsymbol{\tau}^p,$$  \hspace{1cm} (1.8)
where $\phi$ is the particle volume fraction and $\tau^p$ is the particle contribution to the stress (or the intrinsic stress). Rheological (or constitutive) models seek to determine $\tau$ or $\tau^p$ based on the rate-of-strain tensor and other flow parameters. Equation (1.8) is valid for dilute suspensions, and it becomes less accurate as the concentration of the suspension increases. In the current work, only dilute suspensions are considered, where the particle contribution to the stress can be determined from the response of single particles or droplets. There are two main approaches to develop constitutive models for fluids. One approach is to model complex fluids as generalized Newtonian fluids [1]. This approach is based on phenomenological or empirical models that are found to agree well with common behavior of non-Newtonian fluids. For example, in the x-y plane, a power law model seeks to model both shear-thinning and shear-thickening behaviors through the equation

$$\tau_{xy} = K \left( \frac{\partial u_x}{\partial y} \right)^n,$$  \hspace{1cm} (1.9)

where $K$ is the flow consistency index and $n$ is the power law index [1]. Other similar equations have been developed to provide relationships which model different types of non-Newtonian fluid behavior.

The other main approach to rheology seeks to include “memory” effects to determine the stress, where the history of deformations affects the local strain rate. Viscoelastic fluids are one type of fluid that have a fading “memory”, and can fully or partially relax to a previous state [2]. This branch of rheology is most relevant to the studies conducted in this dissertation. Constitutive models in this approach are sought by developing different tensorial and rate-based methods to rheology. Hand’s model [4] is an important example of a general approach. In Hand’s model, the stress tensor is a function of the rate-of-strain tensor $E$ and another tensor $a$, where $a$ is a symmetric tensor describing the microstructure of the fluid. Hand postulates a constitutive model where the stress tensor $\tau$ is written in
Figure 1.1: The rheological behavior of fluids based on the relation of shear stress to the shear strain rate. Adapted from Çengel and Cimbala [2].

terms of the rate-of-strain tensor \( \mathbf{E} \) and the symmetric tensor \( \mathbf{a} \):

\[
\mathbf{\tau} = \beta_0 \mathbf{I} + \beta_1 \mathbf{a} + \beta_2 \mathbf{E} + \beta_3 \mathbf{a}^2 + \beta_4 (\mathbf{a} \cdot \mathbf{E} + \mathbf{E} \cdot \mathbf{a}) \\
+ \beta_5 (\mathbf{a} \cdot \mathbf{E} + \mathbf{E} \cdot \mathbf{a}) + \beta_6 (\mathbf{a}^2 \cdot \mathbf{E} + \mathbf{E}^2 \cdot \mathbf{a}) + \beta_7 (\mathbf{a}^2 \cdot \mathbf{E}^2 + \mathbf{E}^2 \cdot \mathbf{a}^2) ,
\]

(1.10)

where \( \mathbf{a}^2 = \mathbf{a} \cdot \mathbf{a}, \mathbf{E}^2 = \mathbf{E} \cdot \mathbf{E} \), and the material parameters \( \beta_i \) are functions of flow invariants of \( \mathbf{E} \) and \( \mathbf{a} \). The material parameters are functions of flow invariants since the tensor invariants remain the same upon any rotation of the coordinate system. The first invariant of a tensor is its trace and the second invariant for a tensor \( \mathbf{B} \) is defined as \( I_2(\mathbf{B}) = B_{ij}B_{ji} \), which can be written as \( I_2(\mathbf{B}) = B_{ij}B_{ij} \) for a symmetric tensor. The third invariant is the determinant of a tensor. In another tensor-based approach, Rivlin-Ericksen tensors are used to model complex fluids. The Rivlin-Ericksen models calculate the Cauchy stress as [5]:

\[
\mathbf{\tau} + p_{iso} \mathbf{I} = f(A_1, A_2, \ldots)
\]

(1.11)
and the Rivlin-Ericksen tensors are defined as:

\[
A_1 = \nabla u + (\nabla u)^T ,
\]

\[
A_{n+1} = \frac{DA_n}{Dt} + A_n \nabla u + (\nabla u)^T A_n .
\] (1.12)

Similar to these approaches, the model proposed by Oldroyd [6] also uses tensors to predict the stress. The Oldroyd model, which is the focus of this dissertation, is:

\[
\left(1 + \lambda_1 \frac{D}{Dt}\right) \tau + \mu_o \text{tr}(\tau)\mathbf{E} - \mu_1 (\tau \cdot \mathbf{E} + \mathbf{E} \cdot \tau) + \nu_1 (\tau : \mathbf{E})\mathbf{I}
\]

\[
= 2\eta \left[ \mathbf{E} + \lambda_2 \frac{D\mathbf{E}}{Dt} - 2\mu_2 \mathbf{E} \cdot \mathbf{E} + \nu_2 (\mathbf{E} : \mathbf{E})\mathbf{I} \right] .
\] (1.13)

The Oldroyd Eq. (1.13) is a time-dependent, nonlinear equation with eight material parameters: \(\lambda_1, \lambda_2, \mu_o, \mu_1, \mu_2, \nu_1, \nu_2,\) and \(\eta\). This equation consists of mixed order terms of the stress tensor and the rate-of-strain tensor, and second-order contributions from the rate-of-strain tensor. The time derivative \(\frac{D}{Dt}\) is the Jaumann (or corotational) derivative, which operates on any tensor \(\mathbf{B}\) as

\[
\frac{D\mathbf{B}}{Dt} = \frac{D\mathbf{B}}{Dt} + \mathbf{B} \cdot \Omega + \Omega^T \cdot \mathbf{B} ,
\] (1.14)

where \(\Omega = (\nabla u - \nabla u^T)/2\) and \(\frac{D\mathbf{B}}{Dt}\) is the material derivative of \(\mathbf{B}\). A simplified model of the Oldroyd Eq. (1.13) is often employed in the literature, and referred to as the Oldroyd-B model:

\[
\left(1 + \lambda_1 \frac{D}{Dt}\right) \tau = 2\eta \left(1 + \lambda_2 \frac{D}{Dt}\right) \mathbf{E} .
\] (1.15)

An example of using Eq. (1.15) is found in Hayat et al. [7]. This model is adequate at times, but the complete model (1.13) allows more degrees of freedom and versatility in constitutive modeling.

There still exists the need for a general constitutive model that is valid for a wide range of
non-Newtonian fluids. Many existing constitutive equations are only applicable to a specific non-Newtonian fluid, or they cannot capture many important non-Newtonian phenomena, such as viscoelasticity. For the non-Newtonian fluids considered in this dissertation (dilute emulsions of deformable drops, dilute suspensions of rigid spheroids, and dilute emulsions in the presence of surfactants), there have been various constitutive models proposed in the literature. For emulsions, Schowalter et al. [8] and Frankel and Acrivos [9] have developed small-deformation constitutive models. These models work well in the weak-flow limits, where drop deformations are minimal, but are less accurate as drop deformations become significant. Vlahovska et al. [10, 11] have developed a third-order perturbation theory in $\epsilon$, where $\epsilon$ is equivalent to the capillary number in weak flows. They also extended their analysis to drops covered in surfactants. This constitutive model is more accurate than the small-deformation models, but is difficult to extend to arbitrary flows because of its complexity, and is still limited to small deformations. Evidently, constitutive models valid for a wider range of flow strengths are needed.

There have also been many constitutive models for dilute suspensions of rigid spheroids. These models are termed closure approximations, from which the stress can be evaluated for a variety of aspect ratios of the spheroids. The closure approximations can be readily applied in arbitrary kinematics. In Chapter 3, these closure approximations are shown to be accurate in a wide range of flow fields. Although these constitutive models are useful, they are specific for dilute suspensions of rigid spheroids. They cannot be easily extended to flows of concentrated suspensions, where particle-particle interactions become significant, and where there are strong hydrodynamical interactions.

In this dissertation, a general constitutive model is sought that can be applied to a variety of non-Newtonian fluids. This general constitutive approach should also be able to predict many non-Newtonian phenomena, such as normal stress differences, relaxation times, and “memory” effects. This general constitutive model should also be accurate in arbitrary kinematics. Equation (1.13) is used as a starting point to develop this rheological model,
referred to herein as the generalized Oldroyd model. In this dissertation, this model is applied to three types of suspensions: dilute emulsions of deformable drops, dilute suspensions of rigid spheroids subject to Brownian rotations, and dilute emulsions in the presence of surfactants. The generalized Oldroyd model requires calculating the stress for two canonical flows—simple shear and planar extension (referred to as “base flows” herein), from which the necessary parameters of the Oldroyd equation are determined. These stress functions are obtained either through numerical simulations (as the approach adopted in this dissertation does) or through experiments. The accuracy of the generalized Oldroyd model is then evaluated for the three types of suspensions in a variety of flow fields. The generalized Oldroyd model (as described more fully in Chapter 2) allows the researcher to calculate the stress for many complex fluids in any arbitrary flow environment. The approach is very general and can be extended to a number of rheologically complex fluids beyond the ones considered in this dissertation. Although not explored herein, the stress calculated from the generalized Oldroyd model can be used in conjunction with the Cauchy Eq. (1.1) to solve boundary-value problems for any given geometry.

1.3. Chapter summaries

Each chapter of this dissertation presents the rheology of a specific type of suspension, and describes the development of a constitutive model (the generalized Oldroyd model) to predict the particle contribution to the stress in the suspension. Chapter 2 contains a study of dilute emulsions of deformable drops. The dilute emulsion is modeled using the boundary-integral (BI) equation and the resulting stress is calculated. The generalized Oldroyd model is presented and applied to the case of dilute emulsions. To validate the theory, the generalized Oldroyd model is evaluated in a variety of different kinematical conditions. The Frankel and Acrivos [9] constitutive model for dilute emulsions is solved and compared to the predictions of the generalized Oldroyd model. The test cases include planar
mixed flow, uniaxial extension/compression, Stokes flow around a macroscopic sphere, and flow in a rectangular cavity with a moving wall. The stresses predicted by the generalized Oldroyd model are compared to both the exact BI equation and the Frankel and Acrivos model. The results show that the generalized Oldroyd model yields accurate predictions for the rheological stress components of a dilute emulsion. The work in Chapter 2 was originally published in the *Journal of Rheology* [12].

In Chapter 3, the generalized Oldroyd model is extended to the case of a suspension of rigid spheroids subject to Brownian rotations. The rigid spheroids are either prolate (rodlike) or oblate (disklike) particles in suspension. The suspension of rigid spheroids is first modeled from first principles following the work of Jeffery [13]. Spherical harmonics are used to solve the Fokker-Planck-Smulochowski equation, and the stress of the system is solved from this solution. Once the rheological functions are calculated, the generalized Oldroyd constitutive model is applied to a range of different arbitrary kinematic conditions. The test cases include planar mixed flow, uniaxial extension/compression, time-dependent planar extension, and flow around a macroscopic sphere at a moderate Reynolds number. To serve as a comparison, two closure approximations (constitutive models for suspensions of spheroids) are solved in the same conditions—the Hinch and Leal [14] and the Bingham closure [15] models. The results demonstrate the accuracy of the generalized Oldroyd equation to the case of solid spheroids in suspension. The work in Chapter 3 was originally published in the *Journal of Rheology* [16].

In Chapter 4, the rheology of dilute emulsions in the presence of surfactants is studied. Surfactants lower the local interfacial tension on the drops; since the surfactant concentration can vary over the surface of each drop, regions of both high and low interfacial tension can be present. The BI equation is used to simulate the drop deformation and the resulting stress of the drop. Singularities in the BI equation are present due to the variation in the local interfacial tension on the surface of the drop; these singularities are regularized using the method of Klaseboer *et al.* [17]. A surface equation of state is also required that relates
the local surfactant concentration to the local interfacial tension; three different equations of state are evaluated. The generalized Oldroyd model is again employed in this case. In order to validate the model, test cases are presented for planar mixed flow and flow between eccentric spheres, where the inner sphere is rotating at a constant rate. The work presented in Chapter 4 is currently being prepared for publication. Chapter 5 includes concluding remarks and possible paths for future research.

1.4. References


Chapter 2: A Generalized Oldroyd’s Model for Non-Newtonian Liquids with Applications to a Dilute Emulsion of Deformable Drops

This work was originally published in the *Journal of Rheology*, vol. 58, pp. 759–777 (2014) with co-authors Alexander Zinchenko and Robert Davis [1].

Synopsis

A new, general approach to constitutive modeling for non-Newtonian liquids (i.e., formulating an equation for the stress tensor in flows with arbitrary kinematics) is proposed and tested, with a particular application to a dilute emulsion of deformable drops. A generalized traceless Oldroyd model is used for the drop-phase contribution to the stress tensor, with five material parameters allowed to be functions of one instantaneous flow invariant. Two choices for this invariant are explored (i) the second invariant $I_2$ of the rate-of-strain tensor and (ii) the energy dissipation rate. In both versions, all five parameters are found from simultaneously fitting the Oldroyd model to viscometric and extensiometric functions for steady shear and planar extension (PE), respectively, at arbitrary flow intensities. The model predictions are compared to precise (but computationally intensive) results from boundary-integral simulations for several flows different from simple shear or PE. The energy dissipation rate is found to be generally a much better choice for the invariant than $I_2$, especially for comparable drop and continuous-phase viscosities, and it provides very good accuracy in a wide range of conditions (away from drop breakup). Test examples include mixed planar flow,
uniaxial/biaxial extension, flow in a cavity with a moving wall, and flow past a macro-
scopic sphere. Unlike small-deformation theories, the present approach can be extended to
large-strain flows of highly concentrated emulsions.

2.1. Introduction

The study of emulsions has been a topic of active interest for many years, due to their
importance and complex, non-Newtonian rheology. Emulsions, consisting of small immiscible
drops freely suspended in another, continuous fluid, are found in a wide range of applications,
including beverage processing, oil recovery and transport, cosmetics, and pharmaceutical
manufacturing. Even for Newtonian, surfactant-free constituents, non-Newtonian emulsion
behavior results from drop deformation and interactions. Early small-deformation theories
[2, 3, 4, 5] were able to produce constitutive models for dilute emulsions of noninteracting
drops in flows with arbitrary kinematics, but the range of deformations covered by these
theories is limited. It was not until the works of Vlahovska et al. [6] and Vlahovska et
al. [7] that the complete $O(\epsilon^3)$ theory for small drop deformation was developed, where
$\epsilon \ll 1$ is a ratio of the deformation and drop radius. This theory is capable of much greater
accuracy, but, unfortunately, the complexity of the analysis has restricted the rheological
applications so far. For surfactant-free drops, steady-shear viscometric functions were derived
for matching viscosities only, and no constitutive equation has resulted yet from the complete
$O(\epsilon^3)$ theory. As opposed to asymptotic small-deformation theories based on expansions,
the approach of Wu et al. [8] approximates a drop as a 3D ellipsoid at finite deformations
to calculate the drop-phase rheological response in flows with arbitrary kinematics. The
ellipsoid-fitting technique in Wu et al. [8] was found to give surprisingly accurate results in
several tests.

It is not clear, even in principle, how any of the above single-drop theories could be
extended in a satisfactory way to large-strain flows of concentrated emulsions. The initial
computer simulations at small-to-moderate emulsion concentrations [9, 10] and subsequent large-scale multidrop simulations for highly concentrated emulsions [11] are for steady-shear flow only, and they do not offer a constitutive model. An early effort [12] to include the effect of finite drop volume fraction in constitutive modeling was based on a cell model; by modern standards, such an approach to hydrodynamical interactions is an oversimplification. In particular, at high concentrations, true interactions of slightly deformable drops result in sharp variation of rheological functions (e.g., shear viscosity) with the capillary number [11]. Such a behavior cannot be captured by cell models with artificial interactions between a drop and the cell boundary.

In the present work, we explore instead, in a pragmatic fashion, a new general approach to constitutive modeling for non-Newtonian liquids, with a particular application to a dilute emulsion of deformable drops (where precise, although computationally intensive results can be obtained by the boundary-integral (BI) method for validation). We employ the generalized traceless Oldroyd model, where five material parameters are allowed to be functions of one instantaneous flow invariant. Such a possibility is embraced, of course, by a very general, phenomenological Hand’s model [13], where material parameters can depend on up to nine flow invariants; obviously, Hand’s model is too flexible. The essence of our method is to find all five material functions by simultaneously fitting the Oldroyd equation to viscometric and extensiometric functions in simple shear and planar extension (PE), respectively, at arbitrary flow intensities. The inclusion of PE greatly extends the range of kinematics that can be realistically modeled, since many practical flows have an extensional component.

The plan of the paper is as follows. In Sec. 2.2, the small-deformation constitutive model of Frankel and Acrivos [3] is outlined, since it is later used for systematic comparisons with our model. Section 2.3 describes our general approach to constitutive modeling, which is not limited to emulsions but can be applied, in principle, to any non-Newtonian liquid with known viscometric and extensiometric functions at arbitrary flow intensities. Two versions of modeling are considered, based on the choice of the flow invariant as the argument of
Oldroyd’s material parameters. In Sec. 2.4, we outline the single-drop BI method and the precise rheological functions it provides for simple shear and PE, both for matching and arbitrary phase viscosities. Based on these results, generalized Oldroyd coefficients are calculated and discussed in Sec. 2.5. Section 2.6 is devoted to validation of our constitutive modeling. Namely, the predicted rheological response of the drop is compared with exact results from single-drop BI simulations for several flows (both Lagrangian-steady and unsteady) that differ from simple shear or PE. Examples include (1) planar mixed flow, (2) uniaxial/biaxial extension, (3) flow in a cavity driven by a moving wall at finite Reynolds number, and (4) Stokes flow past a macroscopic sphere. Our approach does not assume small deformations (although drop breakup is a limitation). The present constitutive model can be used to compute the effect of the drop phase on the emulsion flow in various geometries as the first-order perturbation in the drop volume fraction, although this task was not pursued herein. Most important, though, is possible extension of our constitutive modeling to large-strain flows of concentrated emulsions, as discussed in Summary (Sec. 2.7). Such an extension critically depends on reproducible periodic lattices of Kraynik and Reinelt [14] for planar-extensional flow simulations. Unlike the present methodology, small-deformation theories appear to not have this potential and are essentially limited to dilute emulsions of noninteracting drops.

2.2. The Frankel-Acrivos constitutive model

The constitutive model for a dilute emulsion of Frankel and Acrivos [3] (FA in what follows) will be used as a comparison to the present method. The FA model was derived for Stokes flow conditions on the microscale and using a first-order perturbation in the capillary number in the limit of small droplet deformations. The total deviatoric stress for an emulsion is written as

\[ \mathbf{\tau} = 2\mu_e \mathbf{E} + \phi \mathbf{\tau}^d, \]  

(2.1)
where \( \mu_e \) is the viscosity of the continuous phase, \( E \) is the local average rate-of-strain tensor, \( \phi \ll 1 \) is the drop volume fraction, and \( \tau^d \) is the droplet contribution to the stress (called the intrinsic stress tensor) which arises from the presence and deformation of the drops.

The FA model predicts the intrinsic stress as

\[
\tau^d = \mu_e \left\{ \frac{10(\lambda - 1)}{2\lambda + 3} E + \frac{24}{2\lambda + 3} F + \frac{360(\lambda - 1)^2}{7(2\lambda + 3)^2} \beta \mathcal{L}_d [F \cdot E] + \frac{288(\lambda - 6)}{7(2\lambda + 3)^2} \beta \mathcal{L}_d (F^2) \right\} ,
\]

with the evolution equation for the symmetric second-rank tensor \( F \) given by

\[
F + c_1 \beta \frac{D F}{D t} = c_2 E + c_3 \beta \mathcal{L}_d [F \cdot E] + c_4 \beta \mathcal{L}_d [F^2] .
\]

Equations (2.2) and (2.3) correspond to (3.4) and (3.5), respectively, in Frankel and Acrivos [3]. Here, \( \beta = a \mu_e / \sigma \), \( a \) is the undeformed drop radius, \( \sigma \) is the surface tension, and \( \lambda = \mu_d / \mu_e \) is the drop-to-medium viscosity ratio. The coefficients in Eq. (2.3) are

\[
c_1 = \frac{(2\lambda + 3)(19\lambda + 16)}{40(\lambda + 1)} , \quad c_2 = \frac{19\lambda + 16}{24(\lambda + 1)} ,
\]

\[
c_3 = \frac{(4\lambda - 9)(19\lambda + 16)}{28(2\lambda + 3)(\lambda + 1)} , \quad c_4 = \frac{36(137\lambda^3 + 624\lambda^2 + 741\lambda + 248)}{35(2\lambda + 3)(19\lambda + 16)(\lambda + 1)} .
\]

The Jaumann or corotational derivative \( \mathcal{D}/\mathcal{D}t \) can be calculated in fixed Cartesian axes for any tensor \( A \) as

\[
\left( \frac{\mathcal{D}A}{\mathcal{D}t} \right)_{ij} = \left( \frac{DA}{Dt} \right)_{ij} + \frac{1}{2} (\nabla_i v_k - \nabla_k v_i) A_{kj} + \frac{1}{2} (\nabla_j v_k - \nabla_k v_j) A_{ik} ,
\]

where \( D/Dt \) is the material derivative, \( \mathbf{v} = (v_1, v_2, v_3) \) is the velocity of a material element, and \( \nabla_i = \partial / \partial x_i \). Operator \( \mathcal{L}_d \) acts on tensor \( b \) according to

\[
\mathcal{L}_d [b] = \frac{1}{2} \left[ b + b^T - \frac{2}{3} \text{tr}(b) I \right] ,
\]

17
where $\text{tr}(b)$ is the trace of $b$, $I$ is the identity tensor, and the superscript $T$ stands for the transpose. Frankel and Acrivos [3] also include a simplified version of their constitutive model [Eq. (3.12) therein]

$$
\tau^d + \Lambda \frac{D\tau^d}{Dt} = 2\mu_e a_1 \left( E + \Lambda \frac{DE}{Dt} \right) + \beta \mu_e \left\{ a_2 \frac{DE}{Dt} + a_3 \mathcal{D}[E^2] \right\},
$$

(2.7)

where

$$
\Lambda = \frac{(2\lambda + 3)(19\lambda + 16)}{40(\lambda + 1)} \beta, \quad a_1 = \frac{5\lambda + 2}{2(\lambda + 1)},
$$

$$
a_2 = -\frac{1}{40} \left( \frac{19\lambda + 16}{\lambda + 1} \right)^2, \quad a_3 = \frac{3(19\lambda + 16)(25\lambda^2 + 41\lambda + 4)}{140(\lambda + 1)^3}. \quad (2.8)
$$

We have found, though, that this simplified version is less robust than their full model (2.2) and (2.3), and therefore, only the results from (2.2) to (2.3) will be discussed in this paper.

2.3. New approach to constitutive modeling based on the generalized Oldroyd equation

We work with the five-parameter constitutive equation for the deviatoric stress tensor $\tau$

$$
\left( 1 + \lambda_1 \frac{D}{Dt} \right) \tau - \mu_1 (\tau \cdot E + E \cdot \tau) + \frac{2}{3} \mu_1 \text{tr} (\tau \cdot E) I
$$

$$
= 2\eta \left[ E + \lambda_2 \frac{DE}{Dt} - 2\mu_2 E^2 + \frac{2}{3} \mu_2 \text{tr} (E^2) I \right].
$$

(2.9)

Oldroyd [15] originally postulated a more general, eight-parameter model, which reduces to Eq. (2.9) if formulated for the deviatoric part of the stress [i.e., with $\text{tr}(\tau) = 0$]. In the classical Oldroyd’s approach, $\lambda_1$, $\mu_1$, $\lambda_2$, $\mu_2$, and $\eta$ are regarded as constant material parameters for each non-Newtonian fluid. Such a form of the constitutive Eq. (2.9), though, would impose limitations on the behavior of the rheological functions at finite flow intensities.
and could not match, for example, a prescribed dependence of the steady-shear viscosity and normal stress differences on the shear rate. Instead, we consider \( \lambda_1, \mu_1, \lambda_2, \mu_2, \) and \( \eta \) to be functions of one instantaneous flow invariant. The most obvious choice (referred to as the “I2-based” theory, in what follows) would be to use the second invariant of the rate-of-strain tensor, \( I_2(E) = E_{ij}E_{ij} \). This choice would be in line with constitutive modeling for a generalized Newtonian liquid (e.g., Astarita and Marucci [16]): \( \tau = 2\eta^* E \), where the viscosity \( \eta^* \) is a function of \( I_2(E) \) (although the deficiencies of such a constitutive model are well known [16]). The second, less obvious choice, also explored in the present work (and termed the “\( \tau : E \)-based” theory, in what follows), is to consider \( \lambda_i, \mu_i, \) and \( \eta \) as functions of the instantaneous energy dissipation rate \( \tau_{ij}E_{ij} = \text{tr}(\tau \cdot E) \) [which makes Eq. (2.9) implicit and nonlinear in \( \tau \)].

With both versions (obviously satisfying the objectivity principle), the essence of our method is to precisely match Eq. (2.9) to prescribed rheological behavior for two canonical flows—simple shear and PE—at arbitrary flow intensities. For simple-shear flow \( \boldsymbol{v} = (\dot{\gamma}, 0, 0) \), the tangential stress \( \tau_{12}^{sh} \) and normal stress differences \( \tau_{11}^{sh} - \tau_{22}^{sh} \), and \( \tau_{22}^{sh} - \tau_{33}^{sh} \) are assumed given as functions of the shear rate \( \dot{\gamma} \). Using Eq. (2.9) and the Jaumann derivatives (2.5) (with \( D/Dt = 0 \)), one obtains after some algebra

\[
\begin{align*}
\tau_{12}^{sh} &= \frac{\eta \dot{\gamma} \left[ 1 + \dot{\gamma}^2 \left( \lambda_1 \lambda_2 - \frac{1}{3} \mu_1 \mu_2 \right) \right]}{1 + \dot{\gamma}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)}, \quad (2.10) \\
\tau_{11}^{sh} - \tau_{22}^{sh} &= \frac{\eta \dot{\gamma}^2 \left[ 2(\lambda_1 - \lambda_2) + \frac{2}{3} \mu_1 \dot{\gamma} (\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + \dot{\gamma}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)}, \quad (2.11) \\
\tau_{22}^{sh} - \tau_{33}^{sh} &= \frac{\eta \dot{\gamma}^2 \left[ \mu_1 - \mu_2 + \lambda_2 - \lambda_1 + \frac{1}{3} \dot{\gamma}^2 (3\lambda_1 - \mu_1)(\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + \dot{\gamma}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)}. \quad (2.12)
\end{align*}
\]

For steady PE \( \boldsymbol{v} = (\dot{\Gamma} x_1, -\dot{\Gamma} x_2, 0) \), the rheological behavior is characterized by \( \tau_{11}^{pe} - \tau_{22}^{pe} \) and the cross-difference \( \tau_{11}^{pe} + \tau_{22}^{pe} - 2\tau_{33}^{pe} \) assumed to be prescribed functions of the deformation
rate $\dot{\Gamma}$. For this flow with $\mathcal{D}/\mathcal{D}t = 0$, Eq. (2.9) gives

$$
\tau_{pe}^{11} - \tau_{pe}^{22} = \frac{4\eta \dot{\Gamma} \left( 1 - \frac{4}{3} \mu_1 \mu_2 \dot{\Gamma}^2 \right)}{1 - \frac{4}{3} \mu_1^2 \dot{\Gamma}^2},
$$

(2.13)

$$
\tau_{pe}^{11} + \tau_{pe}^{22} - 2\tau_{pe}^{33} = \frac{8\eta \dot{\Gamma}^2 (\mu_1 - \mu_2)}{1 - \frac{4}{3} \mu_1^2 \dot{\Gamma}^2},
$$

(2.14)

In the $I_2$-based approach, Eqs. (2.10)–(2.12) and (2.13) to (2.14) are considered simultaneously at $\dot{\gamma} = 2 \dot{\Gamma}$. This constraint makes $I_2 = \dot{\gamma}^2/2 = 2\dot{\Gamma}^2$ and, hence, the material functions $\lambda_i, \mu_i$, and $\eta$ the same for both flows. So, five nonlinear equations (2.10)–(2.14) can be solved, in principle, for five unknowns $\lambda_1, \mu_1, \lambda_2, \mu_2$, and $\eta$ at arbitrary $\dot{\gamma}$ (or $\dot{\Gamma}$).

Mapping between $\dot{\gamma}$ and $\dot{\Gamma}$ is more complex in the $\tau : E$-based theory

$$
(\tau_{11}^{pe} - \tau_{22}^{pe}) \dot{\Gamma} = \tau_{12}^{sh} \dot{\gamma},
$$

(2.15)

which gives the same energy dissipation rate for both flows, and hence, the same material functions $\lambda_i, \mu_i$, and $\eta$. Equation (2.15) has to be solved numerically at each value of $\dot{\gamma}$ (or $\dot{\Gamma}$). In other respects, the method proceeds the same way as for the $I_2$-based approach. Namely, Eqs. (2.10)–(2.14) are solved simultaneously for every pair $\dot{\gamma}$ and $\dot{\Gamma}$ connected by (2.15).

In principle, this general approach (in either version) can be attempted for any non-Newtonian liquid with known viscometric and extensiometric functions in the left-hand sides of (2.10)–(2.14). Our choice of the steady shear and PE as the two base flows is not accidental. The existence of the periodic lattice that replicates itself in a cyclic manner has long been known for simple shear; this lattice is used in many long-time microstructural simulations with periodic boundary conditions to obtain steady-state viscometric functions $\tau_{12}^{sh}$, $\tau_{11}^{sh} - \tau_{22}^{sh}$, and $\tau_{22}^{sh} - \tau_{33}^{sh}$ at arbitrary shear rates (e.g., for emulsion rheology by Loewenberg and Hinch [9], and in large-scale simulations of Zinchenko and Davis [11] at high emulsion concentrations). Not obvious, Kraynik and Reinelt [14] showed the existence of a replicable periodic lattice for PE, which opens the way to calculating extensiometric functions $\tau_{11}^{pe} - \tau_{22}^{pe}$.
and $\tau_{11}^{pe} + \tau_{22}^{pe} - 2\tau_{33}^{pe}$ through computer simulations for many non-Newtonian liquids with well-defined microstructure. Periodic lattices of Kraynik-Reinelt [14] have already received much attention in molecular dynamics simulations.

In the present work, however, we apply the above general approach and test it for the case of dilute emulsions of deformable drops only, where exact results are easier to obtain. To simplify the notations, in what follows $\tau$ is used for the intrinsic single-drop contribution $\tau^d$ to the total stress Eq. (2.1), and Eq. (2.9) is applied to this intrinsic stress. The nondimensional viscometric and extensiometric functions are defined as

$$
\mu_{sh} = \frac{\tau_{12}^{sh}}{\mu_e \dot{\gamma}},
$$

$$
N_1^{sh} = \frac{\tau_{11}^{sh} - \tau_{22}^{sh}}{\mu_e \dot{\gamma}},
$$

$$
N_2^{sh} = \frac{\tau_{22}^{sh} - \tau_{33}^{sh}}{\mu_e \dot{\gamma}},
$$

and

$$
\mu_{pe} = \frac{\tau_{11}^{pe} - \tau_{22}^{pe}}{4\mu_e \dot{\Gamma}},
$$

$$
N_{pe} = \frac{\tau_{11}^{pe} + \tau_{22}^{pe} - 2\tau_{33}^{pe}}{\mu_e \dot{\Gamma}},
$$

respectively. The effective capillary number for any flow is defined as

$$
Ca = \frac{\mu_e a \left[ 2I_2(E) \right]^{1/2}}{\sigma}.
$$

The rheological functions (2.16)–(2.18) and (2.19) to (2.20), in addition to their dependence on the viscosity ratio $\lambda$, depend on $Ca$, which is $Ca_{sh} = \mu_e \dot{\gamma} a/\sigma$ for shear and $Ca_{pe} = 2\mu_e \dot{\Gamma} a/\sigma$ for PE, respectively. The Oldroyd coefficients $\lambda_i$ and $\mu_i$ are scaled with $\mu_e a/\sigma$, while $\eta$ is scaled with $\mu_e$. All the nondimensional Oldroyd coefficients depend on $Ca$ in the $I2$-based approach, and on $\zeta = a \sqrt{\mu_e (\tau : E)/\sigma}$ in the $\tau : E$-based theory. The
nondimensional forms of Eqs. (2.10)–(2.12) and (2.13) to (2.14) are

\[ \mu_{sh} = \frac{\eta \left[ 1 + C_{a_{sh}}^2 \left( \lambda_1 \lambda_2 - \frac{1}{3} \mu_1 \mu_2 \right) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \] (2.22)

\[ N_{1sh} = \frac{\eta C_{a_{sh}} \left[ 2(\lambda_1 - \lambda_2) + \frac{2}{3} \mu_1 C_{a_{sh}}^2 (\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \] (2.23)

\[ N_{2sh} = \frac{\eta C_{a_{sh}} \left[ \mu_1 - \mu_2 + \lambda_2 - \lambda_1 + \frac{1}{3} C_{a_{sh}}^2 (3\lambda_1 - \mu_1)(\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \] (2.24)

and

\[ \mu_{pe} = \frac{\eta \left( 1 - \frac{1}{3} \mu_1 \mu_2 C_{a_{pe}}^2 \right)}{1 - \frac{1}{3} \mu_1^2 C_{a_{pe}}^2} , \] (2.25)

\[ N_{pe} = \frac{4 \eta C_{a_{pe}} (\mu_1 - \mu_2)}{1 - \frac{1}{3} \mu_1^2 C_{a_{pe}}^2} , \] (2.26)

respectively. Mapping between \( C_{a_{sh}} \) and \( C_{a_{pe}} \) is simply \( C_{a_{sh}} = C_{a_{pe}} \) in the \( I_2 \) theory but is found implicitly in the \( \tau : E \) theory from

\[ C_{a_{sh}} \sqrt{\mu_{sh}} = C_{a_{pe}} \sqrt{\mu_{pe}} . \] (2.27)

An additional burden of numerically solving the mapping equation (2.27) is well offset by generally much better performance of the \( \tau : E \) theory vs the \( I_2 \) theory, as demonstrated in Sec. 2.6.

2.4. Boundary-integral method

We use the BI method for precise calculations of the rheological functions \( \mu_{sh}, N_{1sh}, N_{2sh}, \mu_{pe}, \) and \( N_{pe} \) at finite drop deformations necessary for determining the Oldroyd variable coefficients in the \( I_2 \) and \( \tau : E \) theories. By definition, both theories are designed to match all these five rheological functions. The BI method is also employed to test the resulting constitutive equation (2.9) for flows with arbitrary kinematics, different from simple shear.
or PE. The BI equation for the interfacial velocity $u(y)$ on the surface $S$ of a single drop freely suspended in a Stokes flow $u_\infty(y)$ is [17]

$$
u(y) = \frac{2}{(1+\lambda)} u_\infty(y) + \frac{2}{(1+\lambda)\mu_e} \int_S 2\sigma k(x) G(x - y) \cdot n(x) dS_x + \frac{2(\lambda - 1)}{\lambda + 1} \int_S [T(x - y) \cdot n(x)] \cdot u(x) dS_x ,$$  \hspace{1cm} (2.28)

where $k(x) = (k_1 + k_2)/2$ is the local mean surface curvature, and $n(x)$ is the outward unit normal vector on the drop surface. The free-space Green tensor $G$ and the corresponding stresslet $T$ are

$$G(r) = -\frac{1}{8\pi} \left[ \frac{I}{r} + \frac{rr}{r^3} \right],$$  \hspace{1cm} (2.29)

$$T(r) = \frac{3}{4\pi} \frac{rrr}{r^5}. \hspace{1cm} (2.30)$$

The integrands in (2.28) are regularized at $x = y$ by standard singularity subtractions (e.g., Zinchenko et al. [18]).

The surface of the drop is discretized by an unstructured mesh of triangles, and Eq. (2.28) is applied at each vertex, resulting in a large system of algebraic equations solved at each time step by minimal-residual iterations (like in Zinchenko and Davis [11]) when $\lambda \neq 1$; no iterations are required for matching viscosities $\lambda = 1$. To prevent mesh degradation when updating the drop shape, a form of passive mesh stabilization [19] is used at every time step; namely, a suitable tangential field is added to the interfacial velocity $u(y)$. More complex mesh tools [19] were not required in the present calculations. The intrinsic droplet contribution to the stress is calculated by Batchelor’s [20] method

$$\tau_{ij} = \frac{3}{4\pi a^3} \int_S [2\sigma kn_i x_j + (\mu_d - \mu_e)(u_i n_j + u_j n_i)] dS .$$  \hspace{1cm} (2.31)

In what follows, only the deviatoric part of this stress is considered. The five visco-metric/extensiometric quantities, defined by Eqs. (2.16)–(2.20), are computed for viscosity
ratios of $\lambda = 1$, 5, and 0.25, and a variety of capillary numbers. For accuracy, from 6000 (for moderate $Ca$) to 8640 (for small $Ca$) triangular elements on the drop surface were used. These results are shown in Figs. 2.1(a)–2.1(f) (solid lines), together with the predictions of the small-deformation theory (2.2) and (2.3) of Frankel and Acrivos [3] (short-dashed lines). It was also possible, for shear flow and $\lambda = 1$ only, to compare the exact BI results with those from the rigorous $O(e^3)$ theory of Vlahovska et al. [6]

$$\mu_{sh} = \frac{7}{4} - \frac{2107}{512} Ca^2, \quad N_{1}^{sh} = \frac{245}{32} Ca - \frac{249361}{442368} Ca^3,$$

$$N_{2}^{sh} = -\frac{35}{16} Ca - \frac{19440211}{14598144} Ca^3$$

(2.32)

[long-dashed lines in Fig. 2.1(a)]. The rigorous expansions (2.32) are seen to provide much better accuracy for $\mu_{sh}$ and $N_{1}^{sh}$ than FA but are less successful for $N_{2}^{sh}$. Although steady-state, single-drop BI rheological calculations were reported earlier for shear flow (at $\lambda = 1$ and 6.4, both in Kennedy et al. [21]; and in Zinchenko and Davis [11]), extensiometric calculations of this kind for PE are surprisingly absent in the literature, to the best of our knowledge. Unlike familiar shear thinning for the shear viscosity $\mu_{sh}$ [Figs. 2.1(a), 2.1(c), and 2.1(e)], the extensional effective viscosity $\mu_{pe}$ in Figs. 2.1(b), 2.1(d), and 2.1(f) shows significant “tension thickening” with increasing deformation rate. At each $\lambda$, our PE results in Fig. 2.1 are limited by the critical capillary number $Ca_{cr}$ for drop breakup; our values for $Ca_{cr}$ are in good agreement with the experiments of Grace [22]. For the shear flow at the same $\lambda$, the critical $Ca$ for breakup is significantly larger. For the reasons explained in Sec. 2.5, it was not possible to include the whole range of shear-flow results up to breakup in constitutive modeling; the relevant capillary numbers in Figs. 2.1(a), 2.1(c), and 2.1(e) are substantially subcritical.
Figure 2.1: Viscometric and extensiometric quantities for (a) and (b) \( \lambda = 1 \), (c) and (d) \( \lambda = 5 \), and (e) and (f) \( \lambda = 0.25 \). Simple shear: (a), (c), and (e). Planar extension: (b), (d), and (f). Solid lines: BI results. Short-dashed lines: Small-deformation FA theory. Long-dashed lines [in (a) only]: \( O(\epsilon^3) \) theory of Vlahovska et al. [6].
2.5. Generalized Oldroyd coefficients

Below, we discuss the nondimensional Oldroyd coefficients for the $\tau : E$ theory only, since this choice of the flow invariant is generally superior to $I_2$ in the present approach, as will be demonstrated in Sec. 2.6. At a given viscosity ratio and $Ca_{pe}$ from a table, Eq. (2.27) is first solved for $Ca_{sh}$ (Fig. 2.2) using local quadratic interpolation of tabulated values for the left-hand side. The value of $Ca_{pe}$ also sets the argument $\zeta$ of the Oldroyd coefficients. Five nonlinear equations (2.22)–(2.26) are then solved for the five unknown parameters $\lambda_1$, $\mu_1$, $\lambda_2$, $\mu_2$, and $\eta$ by Newton-Raphson iterations (using, again, quadratic interpolations from tables for the left-hand sides). The choice of the initial approximation requires some caution for the iterations to converge; for example, at $\lambda = 1$, it was usually sufficient to choose the Oldroyd coefficients initially between 0 and 2. Once a convergent solution is obtained, it is found to be independent of an initial approximation. Typically, the solution for $\lambda_1$, $\mu_1$, $\lambda_2$, $\mu_2$, and $\eta$ at the preceding $Ca_{pe}$ serves as an initial approximation for the next $Ca_{pe}$, and a few iterations suffice.

Figure 2.3 shows how the nondimensional material parameters in the Oldroyd equation vary with respect to the invariant $\zeta$ for viscosity ratios of $\lambda = 1$, 5, and 0.25. In the case of $\lambda = 1$ and 5, the upper limit on $\zeta$ is due to the critical capillary number for drop breakup in PE flow. For $\lambda = 0.25$, though, the left-hand side of Eq. (2.27) as a function of $Ca_{sh}$ reaches a maximum even before the critical $Ca_{pe}$ for breakup in PE is reached, so the mapping equation (2.27) has no solution for $\zeta$ approximately above 0.34. The parameter $\eta$ is related to the viscosity of the emulsion and increases with increasing capillary number. While simple-shear flow for an emulsion is shear thinning and PE is tension thickening, the tension-thickening component from including the PE flow dominates in determining the material parameter $\eta$. In the limit $\zeta \to 0$, the value of $\eta$ approaches Taylor’s [23] intrinsic viscosity $(2.5\lambda + 1)/(\lambda + 1)$ for an emulsion of nearly spherical drops.

The parameters $\lambda_1$ and $\lambda_2$ have the physical interpretation of the relaxation time and
Figure 2.2: Mapping between Ca\textsubscript{sh} and Ca\textsubscript{pe} in the \(\tau : E\) theory to solve Eqs. (2.22)–(2.26) for \(\lambda = 1\) (solid line), \(\lambda = 5\) (dashed line), and \(\lambda = 0.25\) (dashed-dotted line).

retardation time, respectively. A small shear stress will decay as \(e^{-t/\lambda_1}\) and a small rate of strain will decay as \(e^{-t/\lambda_2}\) [15]. In the spherical-drop limit \(\zeta \to 0\), the \(\lambda_1\) and \(\lambda_2\) parameters are easily provided by the FA theory (2.2)–(2.4)

\[
\lambda_1 = \frac{(2\lambda + 3)(19\lambda + 16)}{40(\lambda + 1)}, \quad \lambda_2 = \frac{1}{4} \frac{(19\lambda + 16)(\lambda - 1)}{(2 + 5\lambda)}. \tag{2.33}
\]

Our numerical results for \(\lambda_1\) and \(\lambda_2\) in Fig. 2.3 smoothly approach the limiting values (2.33), and with excellent accuracy, for all \(\lambda = 1, 5,\) and 0.25. Two other coefficients, \(\mu_1\) and \(\mu_2\), show sharp variation as \(\zeta \to 0\) (only \(\mu_1 - \mu_2\) is smooth). This behavior is not a numerical effect, but it is increasingly more difficult to calculate \(\mu_1\) and \(\mu_2\) accurately, as \(\zeta \to 0\), since determining these two coefficients from our fitting procedure becomes ill-conditioned in the spherical-drop limit. Fortunately, this loss of accuracy in \(\mu_1\) and \(\mu_2\) in the limit \(\zeta \to 0\) was inconsequential for the overall accuracy of our constitutive modeling, even at small Ca.
Figure 2.3: The Oldroyd parameters versus $\zeta$ for (a) $\lambda = 1$, (b) $\lambda = 5$, and (c) $\lambda = 0.25$. 
2.6. Validation of constitutive modeling

For a dilute emulsion of deformable drops, single-drop BI calculations based on Eqs. (2.28)–(2.31) can be used, in principle, to predict rheological response of the drop phase to any flow with arbitrary kinematics of a material element. However, such an exact model is still too complex and computationally intensive to be systematically used. Below, we test the accuracy of the much simpler generalized Oldroyd model (2.9) with our variable coefficients vs. exact BI results for several types of flow (both Lagrangian-steady and unsteady) different from simple shear or PE. Both the $I_2$-based and $\tau : E$-based theories are considered.

2.6.1 Planar mixed flows

Planar mixed flows are defined by the macroscopic velocity field $\mathbf{v} = (\dot{\Gamma} x_2, \dot{\Gamma} \chi x_1, 0)$, with constant $\dot{\Gamma} > 0$ and $\chi \in (-1, 1]$; according to Eq. (2.21), the capillary number is $Ca = \mu_e \dot{\Gamma} a (1 + \chi)/\sigma$. The $\chi$-parameter determines the fundamental type of flow, with $\chi = 0$ for simple shear and $\chi = 1$ for PE. The mixed flow is realized in a four-roll mill device [24]. In a BI simulation, the drop is brought to a steady state at various $\chi$ values and a range of capillary numbers, and the resulting intrinsic droplet contribution to the stress is compared to that predicted by the generalized Oldroyd equation and the FA equation; in the constitutive models (2.9) and FA, artificial time-relaxation is used to reach a steady state.

The results for the nondimensional deviatoric stress components $\nu_{ij} = \tau_{ij}/[\mu_e \dot{\Gamma} (1 + \chi)]$ are given in Figs. 2.4(a)–2.4(d) for various values of $\chi$ at $\lambda = 1$, 5, and 0.25; $\nu_{33}$ is not shown due to $\text{tr}(\nu) = 0$. For each Figs. 2.4(a)–2.4(d), the range of $Ca$ is restricted to keep the $\zeta$-parameter of Oldroyd functions in the $\tau : E$ theory within the tabulation range [Figs. 2.3(a)–2.3(c)]. For matching viscosities $\lambda = 1$ [Figs. 2.4(a) and 2.4(b)], the $\tau : E$ theory (circles) is in excellent agreement with the exact results (solid lines) in the whole range of $Ca$. The $I_2$ theory (dotted lines) is not nearly as accurate and is artificially limited to a smaller interval of $Ca < 0.24$ (by the breakup condition in PE). The drawback of
this choice of $I_2$ as the argument of Oldroyd's functions is particularly evident for a weak flow $\chi = -0.2$ [Fig. 2.4(b)], which does not break the drop for even much larger $Ca$ (if at all). The presence of $\nu_{12}$, a strongly decreasing function of $Ca$ [Fig. 2.4(b)] in the energy dissipation rate works to mitigate this artifact and greatly extends the range of validity of the $\tau : \mathbf{E}$-based theory vs the $I_2$ theory for the weak flow.

For higher viscosity ratio $\lambda = 5$ and $\chi = 0.5$ [Fig. 2.4(c)], the accuracy of the $\tau : \mathbf{E}$ theory is still very good and deteriorates only near the actual breakup conditions in this flow. This theory is still slightly better than the $I_2$ approach, as being more accurate and less restrictive in the capillary number. For small viscosity ratio $\lambda = 0.25$ and $\chi = 0.25$ [Fig. 2.4(d)], both $I_2$ and $\tau : \mathbf{E}$ theories are in very close agreement with the exact values in the range of $Ca$ shown. Note also a much better accuracy of the $\tau : \mathbf{E}$ theory compared to the small-deformation FA theory (dashed lines) for all substantial stress components in Figs. 2.4(a)-2.4(d) at finite drop deformations. So, overall, the $\tau : \mathbf{E}$ theory is a clear choice between the three constitutive models in the mixed-flow test.

2.6.2 Uniaxial extension and uniaxial compression

Another flow studied is uniaxial extension/compression, $\mathbf{v} = (-\dot{\Gamma}x_1, -\dot{\Gamma}x_2, 2\dot{\Gamma}x_3)$, with $\dot{\Gamma} > 0$ for uniaxial extension and $\dot{\Gamma} < 0$ for uniaxial compression. The capillary number (2.21) for this flow is $Ca = \sqrt{12\mu_e a|\dot{\Gamma}|}/\sigma$. The results for the nondimensional effective viscosity $\mu^* = \tau_{33}/(4\mu_e \dot{\Gamma})$ are presented in Figs. 2.5(a)-2.5(c) vs $Ca$ for $\dot{\Gamma} > 0$, and vs $Ca$ for $\dot{\Gamma} < 0$. With one exception (see below), the $\tau : \mathbf{E}$ theory (circles) is very close to the exact solution (solid lines) for uniaxial extension, practically up to breakup, for all viscosity ratios $\lambda = 1, 5, \text{and } 0.25$.

This theory is also accurate for uniaxial compression in a wide range of $Ca$, but the accuracy deteriorates as $|\dot{\Gamma}|$ grows, and the range of $Ca$ that the theory covers is artificially limited (although the drops do not break in compressional flow even at much larger magnitude of $Ca$). The reason for this loss of accuracy and a limited range of $Ca$ with the $\tau : \mathbf{E}$
Figure 2.4: The components of the nondimensional drop contribution to the stress, \( \nu_{ij} \), at (a) \( \lambda = 1 \) and \( \chi = 0.25 \), (b) \( \lambda = 1 \) and \( \chi = -0.2 \), (c) \( \lambda = 5 \) and \( \chi = 0.5 \), and (d) \( \lambda = 0.25 \) and \( \chi = 0.25 \), for mixed planar flow; BI (solid lines), \( \tau : E \) theory (circles), FA model (dashed lines), and \( I_2 \) theory (dotted lines).
theory is the absence of a pronounced tension-thinning in uniaxial compressional flow. Still, the $\tau : E$ theory is significantly more accurate and less restrictive in the capillary number than the $I_2$ theory. The small-deformation FA theory (dashed lines) is not nearly as accurate for finite deformations, both for compression and extension.

For $\lambda = 0.25$, the anomalous behavior of the $\tau : E$ theory at the very right end of the extension range [Fig. 2.5(c)] is a consequence of nonmonotonic behavior of the left-hand side of the mapping equation (2.27) vs $Ca_{sh}$. This behavior does not allow us to include the whole subcritical range of PE extensiometric data in constitutive modeling, leading to the above anomaly. This difficulty is only observed for small $\lambda$. It may be possible to overcome this drawback in future work, considering a mixed planar flow with a small $\chi > 0$ as a base flow (instead of simple shear $\chi = 0$) to avoid nonmonotonic behavior of $\tau : E$ in this flow.

Still, even in the present form, the $\tau : E$ theory is preferable over the $I_2$ theory and the small-deformation FA theory.

2.6.3 Flow in a rectangular cavity with a moving wall

The classical flow in a rectangular cavity with a moving wall provides an example of a time-periodic history of deformation of a material element containing a small emulsion drop. In the absence of drops, the macroscopic steady 2D flow in a square cavity $[0, L]^2$ is driven by the upper wall $x_2 = L$, $0 < x_1 < L$ moving with velocity $U$ along $x_1$, while the remaining three walls are at rest. The Reynolds number is $Re = \rho UL/\mu_c = 400$, where $\rho$ is the fluid density. This flow is computed in the standard stream function-vorticity formulation on a $400 \times 400$ finite-difference mesh; the streamlines are shown in Fig. 2.6(a). A microscopic drop, placed initially at $x_1 = 0.5$ and $x_2 = 0.93$, follows a macroscopic streamline [shown in bold in Fig. 2.6(a)], as a first approximation for dilute emulsions. The precise results for the drop rheological response along the trajectory were computed by the BI method linearizing the ambient flow velocity near the drop center to obtain $u_\infty(y)$ in Eq. (2.28). Integrating the generalized Oldroyd equation (2.9) (in the $\tau : E$ version) additionally requires $\nabla E$
Figure 2.5: Nondimensional effective viscosity $\mu^* = \tau_{33}/(4\mu_e\dot{\Gamma})$ for uniaxial extension and compression at (a) $\lambda = 1$, (b) $\lambda = 5$, and (c) $\lambda = 0.25$; BI (solid lines), $\tau: E$ theory (circles), FA model (dashed lines), and $I_2$ theory (dotted lines).
along the trajectory. All the necessary ambient-flow fields for these time integrations were interpolated from the finite-difference solution using local polynomial approximations for the stream function of the fourth order in $x_1$ and $x_2$. The intrinsic drop contribution $\tau$ to the stress quickly reaches a time-periodic regime after a few cycles. Nondimensional, deviatoric intrinsic stress components are defined as $\nu_{ij} = \tau_{ij}L/(\mu_eU)$. The degree of drop deformation along the trajectory is characterized by $Ca_{cav} = \mu_e aU/(\sigma L)$. For $\lambda = 1$ and $Ca_{cav} = 0.066$ [chosen to keep the argument $\zeta$ of the Oldroyd functions within the tabulation range, Fig. 2.3(a)], the results of the present $\tau : E$ theory (symbols) are shown in Figs. 2.6(b)–2.6(d) for one periodic cycle vs. the $\theta$ angle [Fig. 2.6(a)] of the drop position along the trajectory. Also shown are the exact BI results (solid lines) and the results by the small-deformation FA theory (dashed lines). For most of the trajectory, both the $\tau : E$ and FA results agree very well with the exact solution, although some modest discrepancies are observed in the areas with the largest stresses. It is not quite clear why the $\tau : E$ theory does not improve overall on the FA theory; the reason may be in modest drop deformation in this test. Note, however, that the $I_2$ theory would be limited to even smaller deformations ($Ca_{cav} < 0.044$) in this test.

### 2.6.4 Flow past a macroscopic sphere

This test is logically close to the one from Sec. 2.6.3. We now study the intrinsic rheological response $\tau$ from a microscopic drop freely suspended in a steady Stokes flow past a macroscopic sphere. Because the drop is much smaller than the sphere, it follows the streamline of the ambient flow shown in bold in Fig. 2.7(a), in the plane $x_2 = 0$. This classical axisymmetrical flow is described by the velocity field

$$v_i = U_\infty \left[ \delta_{i3} - \frac{3}{4} R \left( \frac{\delta_{i3}}{r} + \frac{x_i x_3}{r^3} \right) + \frac{1}{4} R^3 \left( \frac{3x_i x_3}{r^5} - \frac{\delta_{i3}}{r^3} \right) \right], \quad (2.34)$$
Figure 2.6: (a) The streamlines for cavity flow with a moving wall at $Re = 400$. The bold line denotes the path followed by the droplet in this test. Graphs (b)–(d) show the components of the droplet contribution to the stress, $\nu_{ij}$, at $Ca_{cav} = a\mu_e U/(\sigma L) = 0.066$ and $\lambda = 1$; BI (solid lines), $\tau : E$ theory (symbols), and FA model (dashed lines).
where \( R \) is the sphere radius, \( U_\infty \) is the flow velocity along \( x_3 \) far away from the sphere, and \( r = (x_1^2 + x_2^2 + x_3^2)^{1/2} \). The necessary components of the velocity gradient, and the gradient of the rate-of-strain tensor follow from Eq. (2.34):

\[
\frac{\partial v_i}{\partial x_j} = \frac{3RU_\infty}{4r^3} \left[ x_j \delta_{i3} - x_i \delta_{j3} - x_3 \delta_{ij} + \frac{3x_i x_j x_3}{r^2} \right] + \frac{3U_\infty R^3}{4r^5} \left[ x_i \delta_{j3} + x_j \delta_{i3} + x_3 \delta_{ij} - \frac{5x_i x_j x_3}{r^2} \right],
\]

(2.35)

\[
\frac{\partial E_{ij}}{\partial x_k} = \frac{9RU_\infty}{4r^5} \left[ x_k x_3 \delta_{ij} - \frac{r^2 \delta_{ij} \delta_{3k}}{3} + x_i x_3 \delta_{jk} + x_j x_3 \delta_{ik} + x_i x_j \delta_{k3} - \frac{5x_i x_j x_k x_3}{r^2} \right] + \frac{3R^3U_\infty}{4r^5} \left[ \delta_{j3} \delta_{ik} - \frac{5x_i x_k \delta_{j3}}{r^2} + \delta_{i3} \delta_{jk} - \frac{5x_j x_k \delta_{i3}}{r^2} + \delta_{k3} \delta_{ij} \right] + \frac{15R^3U_\infty}{4r^7} \left[ -x_k x_3 \delta_{ij} - x_i x_j \delta_{k3} - x_j x_3 \delta_{ik} - x_i x_3 \delta_{jk} + \frac{7x_i x_j x_k x_3}{r^2} \right].
\]

(2.36)

Expressions (2.34)–(2.36) are used in the plane \( x_2 = 0 \) to integrate the drop trajectory and linearize the ambient flow velocity near the drop in BI calculations, and also for time integration of the constitutive models (2.2), (2.3), and (2.9) along the trajectory. The trajectory starts from \( x_3 = -5.9986 \) and \( x_1 = 0.12955 \) [not shown in the graph of the streamlines, Fig. 2.7(a)]. Also, the initial condition is the drop spherical shape in BI simulation, and, accordingly, zero deviatoric stress in the constitutive models. Note that \( E_{22} \neq 0 \) along the trajectory, and this is not a planar-flow test for the constitutive models.

Nondimensional, deviatoric intrinsic stress is defined as \( \nu = \tau R/(\mu_e U_\infty) \). The degree of drop deformation along the trajectory is characterized by \( Ca_{sph} = \mu_e aU_\infty/\sigma R \). For \( \lambda = 1 \) and \( Ca_{sph} = 0.29 \), the results for different stress components \( \nu_{ij} \) along the trajectory vs. \( x_3 \) are shown in Figs. 2.7(b)–2.7(d). The small-deformation theory FA (dashed lines) is generally close to the exact solution (solid lines), but there are parts of the trajectory near the equator, with the largest stresses, where this theory gives large errors. The present \( \tau : E \) theory (symbols) eliminates this drawback almost entirely and is practically indistinguishable.
Figure 2.7: (a) The streamlines for Stokes flow past a sphere. The bold line denotes the path followed by the droplet. (b)–(d) Components of the drop contribution to the stress along the drop trajectory; solid lines: BI, circles: $\tau : E$ theory, dashed lines: FA model. Calculations performed at $Ca_{sph} = \mu_e aU_{\infty}/(\sigma R) = 0.29$ and $\lambda = 1$.

from the exact results for the whole trajectory. Note also that the $I_2$ theory would impose a tighter limitation ($Ca_{sph} < 0.228$) than the $\tau : E$ theory in this test.

2.7. Summary

An outstanding problem for any non-Newtonian liquid is in formulation of a constitutive equation valid in a broad range of kinematic conditions, not necessarily those encountered in rheological experiments (like shear flow). Knowing the constitutive equation would allow the solution of many problems of non-Newtonian hydrodynamics of technological interest. As
a step in this direction, we have explored a new general approach to constitutive modeling, with a particular application to a dilute emulsion of deformable drops (where exact results can be obtained by the BI method for comparison). We use a generalized traceless Oldroyd model, where all five material parameters are allowed to be functions of one instantaneous flow invariant. Two choices for this invariant are explored (1) second invariant of the rate-of-strain tensor ("$I_2$ theory") and (2) energy dissipation rate ("$\tau : E$ theory"). In either version, the idea of the approach is to find all five material parameters from simultaneously fitting the Oldroyd equation to theoretical viscometric and extensimetric data (the latter for planar-extensional flow, PE) at arbitrary flow intensities.

The Oldroyd functions were calculated for drop-to-medium viscosity ratios of $\lambda = 1, 5, \text{ and } 0.25$ in a wide range of capillary numbers, and the resulting constitutive models were compared with precise (although computationally intensive) BI results and the small-deformation theory of Frankel and Acrivos [3] for several flows (Lagrangian-steady and unsteady) different from simple shear and PE. The $\tau : E$ theory performs much better than the other two models ($I_2$ and FA) for planar mixed flows; in particular, it is not nearly as restrictive as $I_2$ on the flow intensity in the rheologically weak regime. The $\tau : E$ theory is also more accurate than the other two models for uniaxial extension/compression, although an anomalous behavior was found with this model at the very end of the extension interval near breakup for $\lambda = 0.25$; this difficulty only manifests itself for small viscosity ratios and has yet to be overcome. For an emulsion drop in a cavity flow with a moving wall (an example of Lagrangian time-periodic history of deformation), the drop rheological response is predicted with comparable accuracy by the $\tau : E$ and FA theories; both solutions are in good agreement with the exact BI results. For an emulsion drop in a Stokes flow past a macroscopic sphere, large intrinsic stress drop contributions near the sphere are not predicted well by FA; the $\tau : E$ theory fully eliminates this drawback. Overall, the small-deformation FA constitutive model is seen to be a versatile (although not always precise) approach for dilute emulsions at small-to-moderate drop deformations, but it is unclear, even in principle,
how this approach could be extended to large-strain flows of concentrated emulsions. In such flows, the instantaneous deformation of a drop would depend on the history of motion and deformation of all drops around it. Moreover, small-deformation expansions would be a problem of singular perturbations due to close interaction of slightly deformable drops. We see the main value of the present approach in that it opens the way for constitutive modeling of (highly) concentrated emulsions. One building block (rheological functions for simple shear) is already available from the large-scale, multidrop simulations of Zinchenko and Davis [11]. Reproducible lattices of Kraynik and Reinelt [14] in PE can be additionally used in periodic boundary conditions for long-time multidrop simulations of extensiometric functions; such simulations are underway in our research group. Still, it is unclear at present, even at small concentrations, how to formulate a constitutive model for an emulsion of drops experiencing breakup, so the range of capillary numbers for constitutive modeling is limited. This difficulty would not be encountered for many other non-Newtonian liquids with well-defined microstructure, and it is of interest to explore how the present general approach to constitutive modeling would work for those liquids. A dilute suspension of rodlike/disklike solid particles subject to Brownian rotations is an immediate candidate; much work has been reported on this system in the literature, but a closed-form constitutive model accurate in a broad range of kinematic conditions is still unavailable.

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2.9. References


Chapter 3: Application of a Generalized Oldroyd Model to a Suspension of Spheroids Subject to Brownian Rotations

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Synopsis

A new approach to constitutive modeling for non-Newtonian liquids is presented, with a particular application to a dilute suspension of spheroids (prolate and oblate) subject to Brownian rotations at finite Péclet numbers, but with a general framework that can be applied to other complex fluids, including concentrated suspensions and emulsions. A generalized traceless Oldroyd model is used for the particle contribution to the stress, with five material parameters as functions of one instantaneous flow invariant: the intrinsic energy dissipation rate. All five parameters are found from simultaneously fitting the model to numerical results for two base flows at arbitrary flow intensities: planar extensional flow and simple shear flow. Precise numerical solutions of the Fokker-Planck-Smoluchowski equation for the orientation distribution function are used to prepare the database rheological functions, and also to validate the resulting model in flows with arbitrary kinematics. The present work also verifies the accuracy of various closure models in the literature for dilute suspensions of spheroids in several test flows. Although these closure models give excellent results and are often more accurate than the present approach in the test cases, they are
relevant specifically to fiber suspensions, and it is not clear how to generalize the closure approach to other types of non-Newtonian, microstructurally complex liquids. In contrast, the present approach to constitutive modeling is more general and does not hinge on a particular microstructure; it can be applied to various systems with strong hydrodynamical interactions (highly-concentrated suspensions, emulsions, etc.).

3.1. Introduction

3.1.1 Background

Suspensions of small particulate matter in liquids are found both in nature and in industrial processes. The particulates in many cases are elongated and can be approximated as prolate spheroids; examples include rodlike bacteria, macromolecules, and fibers in suspension. Particles that can be approximated as oblate spheroids, such as red blood cells and clay platelets, are also of interest. The bulk stress and, consequently, the flow properties of a suspension of prolate or oblate particles are determined from the suspension microstructure. Fundamentally, in dilute systems, such bulk properties depend on the history of orientations of the particles; these orientations are influenced by hydrodynamic forces, Brownian rotations and (to a lesser extent) particle inertia. Once the history of the distribution of orientations is known, it is possible to calculate the bulk stress in a dilute suspension. In the present work, we construct and test a new constitutive model for dilute suspensions of rigid spheroids in a continuous-phase fluid. The approach is more general than previous work and may be applied to more complex microstructures, including concentrated suspensions and emulsions.

Jeffery [2] solved the Stokes problem for a small ellipsoidal particle immersed in a general linear flow. He derived expressions for the rotary motion of the ellipsoid and its contribution to the stress, and discussed simplifications for ellipsoids of revolution (spheroids). Later investigators built on this study by including Brownian rotations. For dilute suspensions of sin-
gle fibers, the precise rheological model is found by solving the Fokker-Planck-Smoluchowski (FPS) equation for the orientation distribution function, and averaging the particle stress over orientations. In addition to the indirect effect of Brownian motion through the orientation distribution function, there is also a direct Brownian contribution to the stress (which was overlooked in some early studies, prior to the work of Saitô [3]). Scheraga [4] numerically solved the FPS equation for prolate and oblate spheroids in simple shear in a wide range of parameters to compute the intrinsic viscosity; normal stress differences can be obtained from Scheraga et al. [5]. This line of research was considerably advanced by Leal and Hinch [6] and Hinch and Leal [7] to study the limiting case of weak (but finite) Brownian rotations in simple shear. For applications to non-Newtonian suspension flows in complex geometries, it is essential to have a constitutive model for the stress tensor valid for an arbitrary history of deformation of a material element, apart from simple shear. As a step in this direction, Hinch and Leal [8, 9] discussed the connections between general phenomenological models for non-Newtonian liquids and microstructural studies for dilute suspensions of fibers.

One major area of focus regarding suspensions of rigid spheroids is the development of closure approximations, i.e., approximating the fourth-moment orientation tensor as a function of the second-moment orientation tensor. The simplest and one of the most commonly-used closures is the quadratic closure [10], where the fourth moment is approximated as the tensor product of the second-moment orientation tensor on itself. In Hinch and Leal’s work of 1976 [9], they constructed two general interpolational closure approximations between the limits of strong and weak Brownian motion (assuming full particle orientation in the latter case). Their second, more elaborate interpolation was found to predict very accurate results for uniaxial/biaxial extension in the whole range of flow intensities, but not so accurate for simple shear (where flow-induced orientation does not take place, strictly speaking). Cintra and Tucker [11] formulated an orthotropic closure where the principal axes of the second and fourth moments are aligned. With this method, they proposed a polynomial function approximating the independent components of the fourth moment as functions of the eigen-
values of the second moment. Chaubal and Leal [12] developed a closure using the Bingham distribution and formulated a relation between the eigenvalues of the second moment to the independent components of the fourth moment (using a higher-order polynomial expression than in the similar method of Cintra and Tucker [11]). Kröger et al. [13] developed two more closure approximations termed the K-I and K-II closures. These closures predict the fourth moment of the orientation vector as a function of the eigenvectors and eigenvalues of the second-moment tensor. Szeri and Leal [14] have noted that some closure approximations can lead to non-physical results in extreme cases. In the present set of tests, though, we have found most of the above closures to work well, and we use them for comparisons with our modeling.

Although we focus herein on general rheology of dilute fiber suspensions in the presence of Brownian rotations (providing the material with fading memory), there are also studies to mention (mostly for high aspect ratio) where Brownian effects have been neglected and attempts have been made (although heuristically) to account for fiber-fiber interactions. For semi-dilute suspensions (with the average interfiber spacing smaller than the fiber length, but much larger than the fiber thickness), Dinh and Armstrong [15] and Phan-Thien and Graham [16] assumed that the fiber orientation dynamics is unaffected at all by interactions and follows Jeffrey’s equation for a single fiber. The fiber contribution to the stress, however, was modified to account for fiber interactions by using either Batchelor’s [17] cell model with order-of-magnitude estimations for the interfiber distance [15], or from fitting to experimental data on suspension shear viscosity [16]. The nondiffusive orientation dynamics could be handled by the method of characteristics, thus eliminating the need for closure approximations. These rheological models were applied to start-up shear and elongational flows [15] and falling-ball rheometry [16]. In these models, the stress does not reach a steady state even under stationary conditions, but undergoes periodic or even stochastic oscillations instead, due to the absence of fading memory.

In a markedly different approach [11, 18, 19], the fiber interaction effect is modeled simply
as hydrodynamical rotational diffusion in the FPS equation for a single fiber orientation. Unlike for Brownian rotations, the diffusion coefficient $D_R = C_I(2I_2)^{1/2}$ is postulated to depend on the flow intensity through the second invariant $I_2$ of the rate-of-strain tensor, with a phenomenological interaction coefficient $C_I$. These studies did not address the rheology, but only the fiber orientation. Eberle et al. [20] combined both approaches to formulate a rheological model, where nonzero solid volume fraction enters both the evolution equation for the orientation tensor $\langle pp \rangle$ (through hydrodynamic diffusion) and the equation for the macroscopic stress with adjustable parameters. The presence of the fourth moment $\langle pppp \rangle$ necessitated closure approximations. Fitting the model predictions to experiments on start-up of shear flow was not encouraging. Evidently, these heuristic approaches to include the nonzero solid volume fraction in suspension rheology oversimplify the problem. The work of Shaqfeh and Fredrickson [21] is a step towards more fundamental understanding of fiber-fiber interactions. Although apart from rheology, it is also interesting to mention direct numerical simulations of sedimentation of many interacting fibers, using the slender-body theory and particle-mesh Ewald algorithm [22]. Such algorithms, if extended to flowing Brownian suspensions of force- and torque-free fibers in a time-dependent periodic box, can potentially provide rheological functions for particular types of flow as building blocks for general rheology, in a manner proposed in the present paper.

3.1.2 Overview

In the present study, we consider creeping flows with single rodlike/disklike solid particles modeled as prolate/oblate spheroids and subject to Brownian rotations. The goal is to construct a general constitutive model for arbitrary (finite) aspect ratios and finite Péclet numbers, which would be reasonably accurate in a broad range of kinematic conditions, both steady and unsteady, and thus can be used to model a variety of complex flows. Although the existing closure approximations (most notably, the second closure of Hinch and Leal [9] and the Bingham closure approximation of Chaubal and Leal [12]) can be successfully used
for this purpose, this prior approach is specific for fiber suspensions, and it is difficult to see how it could be generalized to other non-Newtonian microstructurally complex fluids (e.g. highly-concentrated suspensions of compact particles, emulsions of deformable drops, solutions of flexible macromolecules with strong hydrodynamical interactions, etc.). As yet, fundamental approaches to constitutive modeling have been lacking for such systems. Thus, the main motivation behind the present study is to develop an alternative (and general) approach to constitutive modeling, not based on closure approximations, and validate its accuracy in the specific case of fiber suspensions through comprehensive testing in a broad range of kinematics. We adapt the constitutive modeling scheme recently suggested by Martin et al. [23] and tested therein for a dilute emulsion of deformable drops. In that work, a generalized traceless Oldroyd model was postulated for the dispersed-phase contribution to the stress, with five material parameters allowed to be functions of one instantaneous flow invariant. These five parameters were found from simultaneously fitting the model to two extensiometric (in steady planar extension, PE) and three viscometric (in steady simple shear) functions at arbitrary flow intensities. The model was validated in a broad range of kinematic conditions, with the intrinsic energy dissipation rate being the most successful choice for the flow invariant. The choice of PE and simple shear as the two database flows in our approach is intentional, keeping in mind potential applications to systems with strong hydrodynamical interactions. These are the flows that allow for reproducible lattices and hence, implementation of periodic boundary conditions in long-time simulations. Lattice reproducibility is obvious for simple shear (and has been heavily exploited before in simulations). For PE, such reproducibility was found by Kraynik and Reinelt [24]. They showed, however, the non-existence of reproducible lattices for other macroscopic flows (e.g. uniaxial/biaxial extension). The use of periodic boundaries allows reliable numerical simulation of the database rheology for many systems (concentrated suspensions, emulsions, etc.), thus making our constitutive modeling scheme quite general and suitable for systems with strong hydrodynamical interactions. Such constitutive modeling has been recently applied
to emulsions of deformable drops with up to 55% drop volume fraction [25].

The plan of the paper is as follows. In Section 3.2, the precise rheological formulation is presented for a dilute suspension of rodlike/disklike particles, and various prior closure approximations are discussed. Section 3.3 presents our alternative, general approach to constitutive modeling based on the Oldroyd equation with variable coefficients. In Sec. 3.4 and Appendix 3B, we outline the present algorithm to accurately solve the FPS equation for the orientation distribution function at arbitrary Péclet numbers. Although the solution expansion into a fast-converging series of spherical harmonics is not new, it has been applied to simple shear only [4], and the necessary details of the technique for an arbitrary flow kinematics have not been given in the literature. This FPS algorithm serves two purposes: (i) to obtain exact rheological functions for the two base flows (PE and simple shear) and (ii) to generate exact results for comparison with the constitutive model of Sec. 3.3 in flows with arbitrary kinematics. In Sec. 3.5, we discuss the generalized Oldroyd coefficients obtained by fitting the model to the base flows. In Sec. 3.6, the resulting constitutive model is validated against exact results in flows with various kinematics, both Lagrangian steady and unsteady, and compared to either the second closure model of Hinch and Leal [9] or the Bingham closure approximation of Chaubal and Leal [12]. Test examples include planar mixed flow, uniaxial/biaxial extension, time-dependent PE flow, and the flow past a macroscopic sphere at a moderate Reynolds number. Conclusions are formulated in Sections 3.7 (Discussion) and 3.8 (Summary). The present study is focused on finding the rheological response of the dispersed phase to flows with prescribed kinematics. Important future applications would include solving boundary-value problems with our constitutive model.
3.2. The exact rheological formulation and closure approximation models

The unit director $p$ of the particle axis is used to describe the instantaneous orientation of an axisymmetrical particle freely suspended in a flow with the rate-of-strain tensor $E = (\nabla v + \nabla v^T)/2$ and vorticity tensor $\Omega = (\nabla v - \nabla v^T)/2$, where $v$ is the local macroscopic flow velocity in the absence of the particle. For a spheroid with half-axes $a$ and $b$, and aspect ratio $R = b/a$ ($R > 1$ for prolate and $R < 1$ for oblate shapes), the dynamics of $p(t)$ in the absence of Brownian rotations is described by Jeffrey’s solution:

$$\dot{p} = \frac{dp}{dt} = \Omega \cdot p + G \left[ E \cdot p - (p \cdot E) \cdot p \right], \quad (3.1)$$

where $G = (R^2 - 1)/(R^2 + 1)$ is the shape factor. For Brownian particles, the orientation distribution function $N(p,t)$ must be determined instead. The evolution of $N(p,t)$ is governed by the FPS equation

$$\frac{DN}{Dt} + \nabla_s \cdot (N \dot{p} - D_R \nabla_s N) = 0 \quad (3.2)$$

along the trajectory of a material element, with $D/Dt$ being the material derivative, $\nabla_s$ the surface gradient operator on a unit sphere, and $D_R$ the rotational diffusion coefficient. The latter is connected in the usual way $D_R = kT/f_r$ to the Boltzmann temperature $kT$ and the rotational drag coefficient $f_r$.

The local macroscopic deviatoric stress for the suspension is

$$T = 2\mu E + \phi \tau, \quad (3.3)$$

where $\mu$ is the viscosity of the suspending fluid, and $\phi \ll 1$ is the particle volume fraction. For the assumption of a dilute suspension to remain valid, the volume fraction should be set to $\phi \ll (D_s/L)^2$ for prolate spheroids, where $D_s$ is the diameter and $L$ is the length of
the prolate spheroids [26]. To within an isotropic part I.T., the intrinsic stress \( \mathbf{\tau} \), locally averaged over orientations with the weight function \( N(p,t) \), can be expressed as

\[
\mathbf{\tau} = \text{I.T.} + \left( \frac{3}{2} k_1 - 2 k_2 + \frac{k_3}{2} \right) \langle pppp \rangle : \mathbf{E}
\]

\[
+ (k_2 - k_3) [\langle pp \rangle \cdot \mathbf{E} + \mathbf{E} \cdot \langle pp \rangle] + k_3 \mathbf{E} + k_b \langle pp \rangle ,
\]

(3.4)

where

\[
k_1 = \frac{4\mu (R^2 - 1)}{3a^2 b (R^2 \gamma - \alpha)},
\]

\[
k_2 = \frac{4\mu (R^2 - 1)}{a^2 b (\alpha - \gamma)(R^2 + 1)},
\]

\[
k_3 = \frac{4\mu (R^2 - 1)}{a^2 b [2a^2 \gamma'(1 - R^2) - 3\alpha + R^2 (2\alpha + \gamma)]},
\]

\[
k_b = \frac{12\mu (R^2 - 1) D_R}{a^2 b (\alpha + R^2 \gamma)}.\]

(3.5)

The angular brackets in Eq. (3.4) are for orientational averaging, and the integrals \( \alpha, \gamma, \) and \( \gamma' \) (first defined by Jeffrey [2]) take the forms

\[
\alpha = \frac{1}{(b^2 - a^2)^{3/2}} \left[ \frac{\pi}{2} - R \sqrt{1 - R^2} - \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) \right],
\]

\[
\gamma = \frac{1}{(b^2 - a^2)^{3/2}} \left[ \frac{\pi}{2} + \frac{2\sqrt{1 - R^2}}{R} \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) - \frac{\pi}{2} \right],
\]

\[
\gamma' = \frac{3}{4(a^2 - b^2)^{5/2}} \left\{ \frac{\pi}{2} - \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) - R \sqrt{1 - R^2} - \frac{2}{3} R (1 - R^2)^{3/2} \right\}
\]

(3.6)

for prolate, and

\[
\alpha = \frac{1}{(a^2 - b^2)^{3/2}} \left[ \frac{\pi}{2} - R \sqrt{1 - R^2} - \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) \right],
\]

\[
\gamma = \frac{2}{(a^2 - b^2)^{3/2}} \left[ \sqrt{1 - R^2} + \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) - \frac{\pi}{2} \right],
\]

\[
\gamma' = \frac{3}{4(a^2 - b^2)^{5/2}} \left\{ \frac{\pi}{2} - \tan^{-1} \left( \frac{R}{\sqrt{1 - R^2}} \right) - R \sqrt{1 - R^2} - \frac{2}{3} R (1 - R^2)^{3/2} \right\}
\]

(3.7)
for oblate particles. Except for the last term (direct Brownian contribution to the stress derived by Saitô [3]), the general expression (3.4) may be obtained from Jeffrey’s [2] solution, but we list the detailed forms (3.4)-(3.7) herein for the sake of completeness. Equation (3.4) is equivalent to the one used by Hinch and Leal [9]. However, it is convenient in the context of the present work to make $\tau$ deviatoric ($\tau : I = 0$) by a suitable choice of the isotropic part $I$. 

In principle, integrating the FPS equation (3.2) along the material trajectory and using (3.4) allows one to compute $\tau(t)$ for an arbitrary history of deformation $\{E(t'), \Omega(t')\}(t' \leq t)$ of a material element. However, such a model (exact, as long as hydrodynamical interactions can be neglected) is unattractively complex and computationally inefficient for systematic use in non-Newtonian hydrodynamics, because of the need to solve the partial differential equation (3.2) along each trajectory. For simplified modeling, Hinch and Leal [9] first derived the moment equation from the FPS equation (3.2):

$$
\frac{D\langle pp \rangle}{Dt} = \Omega \cdot \langle pp \rangle + \langle pp \rangle \cdot \Omega^T + G[E \cdot \langle pp \rangle + \langle pp \rangle \cdot E - 2\langle pppp \rangle : E] + 6D_R \left( \frac{1}{3}I - \langle pp \rangle \right).
$$

However, this equation, as well as (3.4), contains an unknown fourth moment $\langle pppp \rangle$. Many closure approximations have been proposed to form a relationship between $\langle pppp \rangle$ and $\langle pp \rangle$. A few closure approximations are reviewed here.

### 3.2.1 Closures of Hinch and Leal

Hinch and Leal [9] built two interpolations between the limits of strong and weak Brownian motion to express $\langle pppp \rangle : E$ in terms of $\langle pp \rangle$. Their simplest interpolation is of the form

$$
\langle pppp \rangle : E = \frac{1}{5} \left( 6\langle pp \rangle \cdot E \cdot \langle pp \rangle - \langle pp \rangle \langle pp \rangle : E - 2I\langle pp \rangle^2 : E + 2I\langle pp \rangle : E \right).
$$

The more elaborate, second interpolation scheme, which is a higher-order approximation
and provides a better fit between the weak-flow and the strong-flow limits, is given as

\[
\langle pppp \rangle : E = \langle pp \rangle \langle pp \rangle : E + 2[\langle pp \rangle \cdot E \cdot \langle pp \rangle - \langle pp \rangle ^2 : E / (I : \langle pp \rangle ^2)] \\
+ \alpha_o \left[ \frac{52}{313} E - \frac{8}{21} \left( E \cdot \langle pp \rangle + \langle pp \rangle \cdot E - \frac{2}{3} I \langle pp \rangle : E \right) \right].
\]

(3.10)

Here, \( \alpha_o \) is a scalar that approaches zero in the strong-flow limit and unity in the weak-flow limit. A suitable expression for \( \alpha_o \), as suggested by Hinch and Leal \[9\], is

\[
\alpha_o = \exp\left[ 2(1 - 3\langle pp \rangle ^2 : I) / (1 - \langle pp \rangle ^2 : I) \right].
\]

(3.11)

With any of these interpolations, Eq. (3.8) becomes a closed system for the evolution of \( \langle pp \rangle \), and the intrinsic stress can be found from Eq. (3.4) and the known \( \langle pp \rangle \). Two remarks are in order, though. Both versions, (3.9) and (3.10), are based on the assumption of full particle orientation in the strong flow limit (i.e., in the absence of Brownian diffusion). Some exclusive flows (simple shear, most notably) do not meet this requirement, so such flows are not modeled exactly even in this limit. Second, Eqs. (3.4) and (3.8) are substantially based on the particular microstructure of a dilute suspension of rods/disks; there appears to be no justifiable way to generalize these equations for suspensions with strong hydrodynamical interactions or other microstructurally complex liquids. Since Hinch and Leal \[9\] found the interpolation (3.10) to be generally superior to (3.9), only their model based on (3.10) is compared, in what follows, to our constitutive model.

3.2.2 Orthotropic closure

The orthotropic closure approximation was originally postulated by Cintra and Tucker \[11\], where the principal axes of the fourth moment \( \langle pppp \rangle \) are matched with those of the second moment \( \langle pp \rangle \). The three eigenvalues \( \lambda_1^e, \lambda_2^e, \) and \( \lambda_3^e \) of \( \langle pp \rangle \) are calculated and defined so that \( \lambda_1^e \geq \lambda_2^e \geq \lambda_3^e \), where \( \sum \lambda_i^e = 1 \). The independent components of the fourth moment
\langle pппp \rangle are then calculated as functions of the two independent eigenvalues \( \lambda_1^e \) and \( \lambda_2^e \) by taking advantage of the symmetric properties of the fourth moment when it is rotated into its principal axes, as described by Cintra and Tucker [11]. They show that the fourth moment can be reduced in these axes to three independent components \( \langle pппp \rangle_{1111} \), \( \langle pппp \rangle_{2222} \), and \( \langle pппp \rangle_{3333} \). These three components are approximated as functions of the two eigenvalues \( \lambda_1^e \) and \( \lambda_2^e \):

\[
\langle pппp \rangle_{iii} = C_1^i + C_2^i \lambda_1^e + C_3^i (\lambda_1^e)^2 + C_4^i \lambda_2^e + C_5^i (\lambda_2^e)^2 + C_6^i \lambda_1^e \lambda_2^e
\]  

(3.12)

(no summation in \( i \)). In this way, all the components of \( \langle pппp \rangle \) can be obtained as functions of \( \lambda_1^e \) and \( \lambda_2^e \) once the coefficients are known. Cintra and Tucker [11] calculated the second and fourth moments in a large number of flows, both steady and transient, and tabulated the coefficients in Eq. (3.12) found by least-square fitting. For the present purposes of using Eqs. (3.4) and (3.8), \( \langle pппp \rangle : E \) is evaluated in the special coordinate system (aligned with the principal axes of \( \langle pp \rangle \)) before being rotated back to the original coordinate system.

3.2.3 Bingham closure

Using the same diagonalizing coordinate system for \( \langle pp \rangle \) and \( \langle pппp \rangle \) as in Cintra and Tucker [11], and postulating a two-parameter Bingham distribution for \( N(p) \), Chaubal and Leal [12] showed how to relate the second and forth moment components in these particular coordinates. Using then a large number of eigenvalue pairs \( (\lambda_1^e, \lambda_2^e) \) in the physically allowable region and least-square fitting, Chaubal and Leal [12] arrived at the high-order polynomial approximation

\[
\langle pппp \rangle_{iii} = C_1^i + C_2^i \lambda_1^e + C_3^i (\lambda_1^e)^2 + C_4^i (\lambda_1^e)^3 + C_5^i \lambda_2^e + C_6^i (\lambda_2^e)^2 + C_7^i (\lambda_2^e)^3
\]

\[
+ C_8^i \lambda_1^e \lambda_2^e + C_9^i (\lambda_1^e)^2 \lambda_2^e + C_{10}^i (\lambda_1^e)^2 \lambda_2^e
\]

(3.13)
The coefficients in Eq. (3.13) are available from their work. The relation (3.13) replaces (3.12); in other respects, the calculation of \( \langle pppp \rangle : E \) follows the same path as for the orthotropic closure. In the test cases of the present paper, the Bingham closure was found to perform similarly to the orthotropic closure. Neither model was found to outperform HL in our tests, except for one case (Fig. 3.10 below), where the Bingham closure is markedly more accurate than the HL model.

### 3.2.4 K-I and K-II closures

Two more closures that we tested are the K-I and K-II approximations proposed by Kröger et al. [13]. In these closures, the principal values of \( \langle pppp \rangle \) are approximated solely from the principal values of \( \langle pp \rangle \) (to prevent an overdetermined system from arising). Both closures give \( \langle pppp \rangle : E \) as

\[
\langle pppp \rangle : E = D_1 E + D_2 E : nn + D_3 E : mm + D_4 (nn \cdot E + E \cdot nn) \\
+ D_5 (mm \cdot E + E \cdot mm) + D_6 (m \cdot E \cdot n) (nm + mn) .
\] (3.14)

Here, \( n \) and \( m \) are the eigenvectors of the second-moment tensor, corresponding to \( \lambda_1 \) and \( \lambda_2 \), respectively. For completeness, the coefficients in the right-hand side of Eq. (3.14) are given in Appendix 3A.

The K-I and K-II closure approximations are accurate in many cases, although the other closure approximations outlined above perform better than the K-I and K-II closures in most test cases considered in this work. Thus, these two closure approximations are not discussed further in this paper. The one advantage, though, of the K-I and K-II closures is that they are parameter-free (similar to the two Hinch and Leal [9] closures), and do not require the numerical determination of coefficients, as the orthotropic and Bingham closures do.
3.3. Approach to constitutive modeling based on the generalized Oldroyd equation

An alternative, and quite general, approach to constitutive modeling is to postulate the Oldroyd equation for the intrinsic stress:

\[
\left(1 + \lambda_1 \frac{D}{Dt}\right) \tau = \mu_1 (\tau \cdot E + E \cdot \tau) + \frac{2}{3} \mu_1 (\tau : E) I \\
= 2\eta \left[ E + \lambda_2 \frac{D E}{Dt} - 2\mu_2 E^2 + \frac{2}{3} \mu_2 (E : E) I \right],
\]

(3.15)

where \(\lambda_1, \lambda_2, \mu_1, \mu_2\) and \(\eta\) are material parameters of the fluid. The Jaumann or corotational derivative \(\frac{D}{Dt}\) can be calculated in fixed Cartesian axes for any tensor \(A\) as

\[
\left(\frac{DA}{Dt}\right)_{ij} = \left(\frac{DA}{Dt}\right)_{ij} + \Omega_{ki} A_{kj} + A_{ik} \Omega_{kj}.
\]

(3.16)

As discussed by Zinchenko and Davis [25], Eq. (3.15) can be derived from a very general multiparameter phenomenological model of Hand [27], if his coefficients \(\beta_i\) for \(i \geq 3\), \(\alpha_j\) for \(j \geq 6\) and \(\alpha_3\) are all set to zero. With these restrictions, the structural tensor \(a\) in Hand’s model is linearly connected to \(E\) and \(\tau\), and Hand’s evolution equation for \(a\) results in (3.15) (see Sec. 3.7 for more detail). Oldroyd [28] originally postulated an eight-parameter model (with constant coefficients) for non-Newtonian liquids, which reduces to (3.15) if formulated for a deviatoric tensor \(\tau\). The assumption of constant coefficients in Oldroyd’s theory, though, is too restrictive, since it does not allow us to fit the model (3.15) to the rheological functions for chosen base flows at arbitrary flow intensities. Instead, following the general approach of Martin et al. [23], we allow \(\lambda_1, \lambda_2, \mu_1, \mu_2\) and \(\eta\) to be functions of one instantaneous flow invariant (still satisfying the objectivity principle). For dilute emulsions of deformable drops, two choices were explored [23] for this invariant: (i) the second invariant \(I_2(E) = E : E\) of the rate-of-strain tensor (“\(I_2\)” theory) and (ii) the
intrinsic energy dissipation rate $\tau : E$. The second choice was found to be universally better in Martin et al. [23] and, on these grounds, it was also adopted as default in the present work on suspensions. Limited comparison between the two options suggests (as discussed in Sec. 3.6) that the “$I_2$” theory gives a significantly less accurate rheological model for a suspension of prolate particles (of most interest in the present study). For oblate solid shapes, however, the choice of $I_2(E)$ as the invariant would be advantageous, but only marginally. The present choice of $\tau : E$ as the argument of the Oldroyd coefficients makes the model (3.15) only quasi-linear and implicit in $\tau$ without significant complications, though. In comparison, Hand’s model allows the material functions to depend on many more flow invariants. Obviously, in its most general form, Hand’s model would be too flexible and difficult to use.

To calculate the five coefficients in Eq. (3.15), two base flows are chosen that have a total of five independent rheological functions. In Martin et al. [23], these coefficients were found by matching Eq. (3.15) to the rheological behavior in two steady canonical flows: simple shear $\mathbf{v} = (\dot{\gamma}x_2, 0, 0)$ and planar extension (PE) $\mathbf{v} = (\dot{\Gamma}x_1, -\dot{\Gamma}x_2, 0)$ (with $\dot{\gamma}, \dot{\Gamma} > 0$, without a loss of generality). A similar approach is followed in the present work. The three independent, nondimensional viscometric functions for simple shear are

$$
\mu_{sh} = \frac{\tau_{12}^{sh}}{\mu \dot{\gamma}}, \quad N_{1}^{sh} = \frac{\tau_{11}^{sh} - \tau_{22}^{sh}}{\mu \dot{\gamma}}, \quad N_{2}^{sh} = \frac{\tau_{22}^{sh} - \tau_{33}^{sh}}{\mu \dot{\gamma}},
$$

(3.17)

where the index $sh$ relates to simple shear quantities, $\mu_{sh}$ is the intrinsic shear viscosity, and $N_{1}^{sh}$ and $N_{2}^{sh}$ are the first and second normal stress differences, respectively. In turn, there are two independent, nondimensional rheological functions for PE, namely the effective PE viscosity $\mu_{pe}$ and cross-difference $N_{pe}$ defined as

$$
\mu_{pe} = \frac{\tau_{11}^{pe} - \tau_{22}^{pe}}{4\mu \dot{\Gamma}}, \quad N_{pe} = \frac{\tau_{11}^{pe} + \tau_{22}^{pe} - 2\tau_{33}^{pe}}{\mu \dot{\Gamma}},
$$

(3.18)
where the index \( pe \) relates to PE quantities. In general, the Péclet number is defined as

\[
P_e = \frac{[2I_2(E)]^{1/2}}{D_R},
\]

which gives \( P_{e_{sh}} = \dot{\gamma}/D_R \) for simple shear and \( P_{e_{pe}} = 2\dot{\Gamma}/D_R \) for PE flows.

The Oldroyd coefficients \( \lambda_i \) and \( \mu_i \) are scaled with \( 1/D_R \), while \( \eta \) is scaled with \( \mu \). The nondimensional argument of all these functions is \( \zeta = \sqrt{\tau : E/(D_R\sqrt{\mu})} \). Applying the model (3.15) to simple shear, using (3.16) and the definitions (3.17), three nondimensional equations are obtained:

\[
\mu_{sh} = \frac{\eta \left[ 1 + P_{e_{sh}}^2 \left( \lambda_1 \lambda_2 - \frac{1}{3} \mu_1 \mu_2 \right) \right]}{1 + P_{e_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)},
\]

\[
N_{1sh} = \frac{\eta P_{e_{sh}} \left[ 2(\lambda_1 - \lambda_2) + \frac{2}{3} \mu_1 P_{e_{sh}}^2 (\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + P_{e_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)},
\]

\[
N_{2sh} = \frac{\eta P_{e_{sh}} \left[ \mu_1 - \mu_2 + \lambda_2 - \lambda_1 + \frac{1}{3} P_{e_{sh}}^2 (3\lambda_1 - \mu_1) (\mu_1 \lambda_2 - \mu_2 \lambda_1) \right]}{1 + P_{e_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)}.
\]

For any given aspect ratio, the left-hand sides of (3.20)-(3.22) are assumed to be known functions of \( P_{e_{sh}} \). The nondimensional Oldroyd coefficients \( \lambda_i, \mu_i \) and \( \eta \) in the right-hand sides also depend on \( P_{e_{sh}} \) through \( \zeta = P_{e_{sh}}\sqrt{\mu_{sh}} \).

Similarly, applying the model (3.15) to PE, using (3.16) and the definitions (3.18), two more nondimensional equations follow:

\[
\mu_{pe} = \frac{\eta \left( 1 - \frac{1}{3} \mu_1 \mu_2 P_{e_{pe}}^2 \right)}{1 - \frac{1}{3} \mu_1^2 P_{e_{pe}}^2},
\]

\[
N_{pe} = \frac{4\eta P_{e_{pe}}(\mu_1 - \mu_2)}{1 - \frac{1}{3} \mu_1^2 P_{e_{pe}}^2}.
\]

Here, again, for any given aspect ratio, the left-hand sides of (3.23) and (3.24) are assumed to be known functions of \( P_{e_{pe}} \), while the Oldroyd coefficients in the right-hand sides depend on \( P_{e_{pe}} \) through \( \zeta = P_{e_{pe}}\sqrt{\mu_{pe}} \).
To use (3.20)-(3.22) and (3.23)-(3.24) simultaneously, the argument $\zeta$ must be the same for both flows, which gives the mapping between $Pe_{sh}$ and $Pe_{pe}$:

$$Pe_{sh}\sqrt{\mu_{sh}} = Pe_{pe}\sqrt{\mu_{pe}} = \zeta .$$

(3.25)

With the Péclet numbers $Pe_{sh}$ and $Pe_{pe}$ connected by (3.25), the system (3.20)-(3.24) may be regarded as five nonlinear equations for five unknowns $\lambda_1$, $\mu_1$, $\lambda_2$, $\mu_2$ and $\eta$, and solved by iterations for these coefficients.

3.4. Solution of the Fokker-Planck-Smoluchowski equation

As follows from the preceding section, determining the variable Oldroyd coefficients requires database rheological functions (3.17) and (3.18) at arbitrary flow intensities. These data may be obtained through accurate, fast-convergent numerical solutions of the FPS equation (3.2) and stress relation (3.4). Numerical solutions of Eq. (3.2) are also used to generate exact results for flows with arbitrary kinematics $\{E(t), \Omega(t)\}$, to be compared with predictions of the constitutive model (3.15) and selected closure models from Sec. 3.2.

With $p = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, we follow the standard practice of expanding the solution into spherical harmonics:

$$N(p, t) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \{A_n^m(t)Y_{n,m}(\theta, \varphi)\} \quad , \quad A_n^{-m} = (-1)^m \overline{A_n^m} ,$$

(3.26)

where $A_n^m(t)$ are time-dependent complex coefficients and the overbar refers to the complex conjugate. Due to symmetry $N(-p, t) = N(p, t)$, only even values of $n$ contribute to (3.26).

The normalized harmonics $Y_n^m$ are defined as

$$Y_n^m = \left[ \frac{(2n + 1)(n - m)!}{4\pi(n + m)!} \right]^{1/2} P_n^m(\cos \theta)e^{im\varphi} ,$$

(3.27)
where $P^m_n$ is the associated Legendre function

$$P^m_n(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_n(x) ,$$

and $P_n(x)$ is the standard Legendre polynomial of degree $n$. Substituting (3.26) into the FPS equation (3.2) and using the dynamics (3.1) and recurrent relations for spherical harmonics yield a sparse system of equations relating $dA^m_n/dt$ to several neighboring coefficients $A^m_{n'}$; some details are given in the Appendix 3B. To advance $A^m_n(t)$ from this system, the diffusive term is handled implicitly for numerical stability at small Péclet numbers. Such time integration is only first-order accurate, but the time steps were sufficiently small so that neither of the results in Sections 3.6.3 and 3.6.4 were affected, within graphical accuracy, when the time steps were reduced five-fold. Once the coefficients $A^m_n$ are known, an attractive way to calculate the stress (3.4) is through Gaussian quadratures of sufficient order, thus avoiding any further approximations and cumbersome algebra. The algorithm was verified by (i) comparing our viscometric functions with those of Scheraga [4] in a broad range of aspect ratios and Péclet numbers and (ii) comparing with a much simpler (but much less efficient) finite-difference solution of Eq. (3.2) in a flow with general kinematics.

3.5. Database rheological functions and generalized Oldroyd coefficients

Figure 3.1 gives examples of the nondimensional database rheological functions (3.17) and (3.18) vs. $Pe$ for prolate and oblate spheroids with aspect ratio $R = 5$ (a,b), 20 (c,d), and 0.1 (e,f). For all geometries, the effective shear viscosity $\mu_{sh}$ exhibits thinning effects being a decreasing function of $Pe$ [Figs. 3.1(a,c,e)]. The PE effective viscosity $\mu_{pe}$ shows tension-thickening for prolate particles [Figs. 3.1(b) and 3.1(d)] but tension-thinning for oblate particles [Fig. 3.1(f)]. Of course, both $\mu_{sh}$ and $\mu_{pe}$ approach the same value in the
limit of slow flows.

This limiting viscosity is easily predicted analytically. In the slow flow limit \( Pe \to 0 \), the suspension must obey the second-order fluid model (from Hinch and Leal \[9\], with some typos corrected):

\[
\tau = \left( \frac{8}{15} A + \frac{8}{3} B + 2C + \frac{2GF}{15} \right) E - \frac{GF \mathcal{D}E}{45 \mathcal{D}t}
+ 2G \left( \frac{8}{7} A + 4B + \frac{GF}{7} \right) \left[ E^2 - \frac{1}{3} (E : E) I \right],
\]

(3.29)

where

\[
A = \frac{3}{8} k_1 - \frac{1}{2} k_2 + \frac{1}{2} k_3, \quad B = \frac{1}{4} (k_2 - k_3), \quad C = \frac{1}{2} k_3, \quad F = \frac{1}{2} k_b,
\]

(3.30)

and \( k_1, k_2, k_3, \) and \( k_b \) are defined in Eq. (3.5). From (3.29), the zero deformation rate viscosity is

\[
\mu_{sh} = \mu_{pe} = \eta_o = \frac{4}{15} A + \frac{4}{3} B + C + \frac{GF}{15} \quad (Pe = 0),
\]

(3.31)

in full agreement with the numerical values from Fig. 3.1. It is useful to note that Eq. (3.31) also gives the limiting value of the nondimensional \( \eta \)-parameter for the Oldroyd equation at \( \zeta = 0 \), which justifies the notation \( \eta_o \) for the quantities in Eq. (3.31).

The database rheological functions in Fig. 3.1 have been also extended to other aspect ratios \( R = 10 \) and \( R = 15 \) (not shown) to cover the whole range \( 5 \leq R \leq 20 \) of prolate shapes. To calculate the nondimensional Oldroyd coefficients from the database rheological functions as described in Sec. 3.3, the given aspect ratio \( R \) and \( Pe_{pe} \) are selected from a table and Eq. (3.25) is solved to determine \( Pe_{sh} \) using local quadratic interpolation of tabulated values for the left-hand side. Figure 3.2 shows the example mapping between \( Pe_{pe} \) and \( Pe_{sh} \) for prolate spheroids with \( R = 5 \) (dashed line) and \( R = 20 \) (dotted line), and oblate spheroids with \( R = 0.1 \) (dash-dot line). The value of \( Pe_{pe} \) also sets the argument \( \zeta \) of the Oldroyd coefficients. Five nonlinear equations (3.20)-(3.24) are then solved for the five unknown parameters \( \lambda_1, \mu_1, \lambda_2, \mu_2 \) and \( \eta \). Again, quadratic interpolations of the tabulated values
Figure 3.1: The five database rheological functions as calculated from the FPS equation; (a) and (b): prolate spheroids with $R = 5$; (c) and (d): prolate spheroids with $R = 20$; (e) and (f): oblate spheroids with $R = 0.1$. 
are used for the left-hand sides of (3.20)-(3.22). To eliminate difficulties with the choice of an initial approximation to the Oldroyd coefficients, many steepest descent iterations are first performed to localize the solution, followed by just a few Newton-Raphson iterations. Importantly, the converged solution was found to be always independent of an initial guess.

Figures 3.3(a-d) show the nondimensional Oldroyd coefficients \( \lambda_i \) and \( \mu_i \) versus the invariant \( \zeta \) for prolate spheroids with \( R = 5, 10, 15 \) and \( 20 \), respectively. These four coefficients depend strongly on \( \zeta \), but are relatively mild functions of the aspect ratio. In contrast, the remaining parameter \( \eta \) varies relatively slightly with \( \zeta \), but depends very strongly on the particle geometry and can attain high values for high aspect ratios. So, to facilitate the description of \( \eta \) in the whole range of aspect ratios from 5 to 20, we scale this parameter with its limiting value \( \eta_0(R) \) at \( \zeta = 0 \) given analytically by (3.31); the results for \( \eta/\eta_0 \) are presented in Fig. 3.3(e). In a similar way, Fig. 3.4 gives (a) \( \lambda_i \) and \( \mu_i \) and (b) \( \eta/\eta_0 \) for oblate spheroids \( R = 0.1 \). The values of \( \eta_0 \) are 5.806, 13.634, 24.627, 38.530 and 8.043 for \( R = 5, 10, 15, 20 \) and \( 0.1 \), respectively. In contrast to \( \eta \), the second-order fluid approximation (3.29) is insufficient to establish the limiting behavior of the other Oldroyd coefficients as \( \zeta \to 0 \).
Figure 3.3: Non-dimensional Oldroyd coefficients vs $\zeta = \sqrt{\tau} : E((D_R^2 \sqrt{\mu})$ for a suspension of prolate spheroids. (a-d) values of $\lambda_i$ and $\mu_i$ for $R= 5, 10, 15$ and $20$, respectively; (d) values of $\eta/\eta_o$ for $R = 5$ (solid line), $10$ (dotted line), $15$ (dot-dash line) and $20$ (dashed line), where the values of $\eta_o(R)$ are given analytically by Eq. (3.31).
Figure 3.4: Non-dimensional Oldroyd coefficients vs $\zeta = \sqrt{\tau / (D_R \sqrt{\mu})}$ for a suspension of oblate spheroids with $R = 0.1$. (a) values of $\lambda_i$ and $\mu_i$ (b) values of $\eta / \eta_o$, where $\eta_o$ is given analytically by Eq. (3.31).

3.6. Validation of the generalized Oldroyd model

For a dilute suspension of rigid spheroids, the generalized Oldroyd model (3.15) with variable coefficients from Figs. 3.3 and 3.4 can predict the rheological response of a material element to any flow with arbitrary kinematics. In most relevant applications to non-Newtonian flow, the initial state of a material element is far in the past to not affect the results at later times of interest, which makes an initial condition for $\tau$ in Eq. (3.15) unimportant (it was set to zero). In Sec. 3.7 it is further explained why our constitutive modeling scheme does not contain any microstructural tensors, but only the macroscopic stress. Several flows, both Lagrangian steady and unsteady, are chosen below to compare these model predictions with the exact results based on the solution of the FPS equation, and with the predictions of selected closure approximations. The isotropic distribution function $N$ and isotropic orientation tensor $\langle pp \rangle$ were the initial conditions for FPS and closure models, respectively. For steady problems in all modes of calculation, time relaxation is used to reach the steady state; in all but one of the examples, the range of the effective Péclet numbers (3.19) is limited by $Pe < 30$. It is shown that our modeling is most accurate for small and moderate Péclet numbers (see later
3.6.1 Planar mixed flow

Planar mixed (PM) flow is one of the kinematic conditions chosen to validate the accuracy of the generalized Oldroyd model (3.15). This flow is defined by \( \mathbf{v} = (\dot{\gamma}_{pm} x_2, \dot{\gamma}_{pm} x_1, 0) \), where \( \chi \) is the flow parameter (equal to zero for simple shear; \( \chi = 1 \) gives the flow equivalent to PE [29, 30, 31]). For testing purposes, we choose \( \chi = 0.5 \). The nondimensional intrinsic stress components \( \nu_{ij} = \tau_{ij} / [\mu \dot{\gamma}_{pm} (1 + \chi)] \) are given in Figs. 3.5(a-c) for prolate spheroids with (a) \( R = 5 \) and (b) \( R = 20 \), and (c) oblate spheroids \( R = 0.1 \); the intrinsic stress component \( \nu_{12} \) is interpreted as the effective PM flow viscosity. For prolate spheroids (both \( R = 5 \) and \( R = 20 \)), the present model (3.15) (dashed lines) shows good agreement with the exact solution (solid lines), especially for \( \nu_{11} \); there are greater discrepancies at higher Péclet numbers for \( \nu_{12} \) and \( \nu_{33} \). The present model (3.15) slightly improves in accuracy when the aspect ratio is increased from \( R = 5 \) to 20 for the stress components \( \nu_{12} \) and \( \nu_{33} \). The HL model (circles) shows excellent agreement and is indistinguishable from the exact FPS solution in the whole range of Péclet numbers for prolate spheroids. For the oblate spheroid case in Fig. 3.5(c), the present model is also close to the exact solution, with slight discrepancies in \( \nu_{11} \) as the Péclet number increases; the HL model is even more accurate. The deviations of the present model from the exact results at increasing \( Pe \) may be due to the sharply aligned orientations in the base flow when Brownian motion is weak, causing the model to become less accurate for other flows with different orientation distributions. For all three PM stress components, the second-order theory (3.29) gives straight lines tangent to the lines in Figs. 3.5(a-c) at \( Pe = 0 \), and hence the second-order theory is limited to very small Péclet numbers.

Although the whole present work is based on using the intrinsic energy dissipation rate \( \mathbf{\tau} : \mathbf{E} \) as the argument of the Oldroyd coefficients, it is useful to note that the alternative, “\( I_2 \)” version compares much less favorably with the exact solution for the PM flow than the
Figure 3.5: The components of the nondimensional particle contribution to the stress, $\nu_{ij} = \tau_{ij} / [\mu \dot{\gamma} (1 + \chi)]$, for PM flow at $\chi = 0.5$; (a) prolate spheroids with $R = 5$, (b) prolate spheroids with $R = 20$, and (c) oblate spheroids with $R = 0.1$. Exact results (solid lines), present model (dashed lines), and HL model (circles).

$\tau : E$ version does in the case of prolate spheroids, Fig. 3.5(a,b), especially at the highest aspect ratio of $R = 20$. For oblate spheroids $R = 0.1$, however, the two versions give almost identical predictions.

### 3.6.2 Uniaxial extension and uniaxial compression

A further test to validate the generalized Oldroyd model (3.15) involves predicting the rheological response of a material element of a suspension of rigid spheroids subject to uniaxial extension/compression, $\mathbf{v} = (-\dot{\Gamma} x_1, -\dot{\Gamma} x_2, 2\dot{\Gamma} x_3)$, with $\dot{\Gamma} > 0$ for uniaxial extension and $\dot{\Gamma} < 0$ for uniaxial compression. The Péclet number (3.19) for this flow is $Pe = 2\sqrt{3}|\dot{\Gamma}|/D$.

The results for the nondimensional effective viscosity $\mu^\ast = \tau_{33}/(4\mu\dot{\Gamma})$ are shown in Fig. 3.6 vs. $Pe$ for $\dot{\Gamma} > 0$, and vs. $-Pe$ for $\dot{\Gamma} < 0$. For prolate spheroids with $R = 5$ in Fig. 3.6(a), the present model (3.15) (dashed line) shows good agreement with the exact FPS results (solid line) over the whole range of Péclet numbers considered, with an error of 1% for uniaxial extension at $Pe = 30$ and an error of 4% for uniaxial compression at $Pe = -30$; the HL model (circles) matches the exact results even more accurately. Figure 3.6(b) shows the effective viscosity for prolate spheroids with $R = 20$. The present model (dashed line) gives
Figure 3.6: Non-dimensional effective viscosity $\mu^* = \tau_{33}/(4\mu\dot{\Gamma})$ for uniaxial extension and compression; (a) prolate spheroids with $R = 5$, (b) prolate spheroids with $R = 20$, and (c) oblate spheroids with $R = 0.1$. Exact results (solid lines), present model (dashed lines), and HL model (circles).

good results, although less accurate for this higher aspect ratio than for $R = 5$, while the HL model (circles) again yields accurate results. Figure 3.6(c) shows the effective viscosity for oblate spheroids with $R = 0.1$. The present model (3.15) (dashed line) has larger discrepancies at the lower and upper limits, with an error of 8% for both uniaxial extension and compression at $Pe = \pm 30$. In contrast, the HL model (circles) remains in excellent agreement with the exact results in the whole range of Péclet numbers. The remarkable accuracy of the HL model for steady uniaxial extension/compression with both geometries (prolate/oblate spheroids) may be partially due to the successful choice of the exponential interpolating function (3.11) for $\alpha_0$.

As for PM flow (Section 3.6.1), the choice of $\tau : E$ instead of $I_2(E)$, as the argument of the Oldroyd coefficients, greatly improves the accuracy of the present constitutive modeling for suspensions of prolate spheroids, especially at the highest aspect ratio of $R = 20$. For oblate spheroids $R = 0.1$, however, switching to $I_2(E)$ greatly improves the accuracy of our modeling scheme for the extensional part (compared to the results shown in Fig. 3.6(c) by the dashed line), but is no better for the compressional part. There is a fundamental difference between dilute emulsions of deformable drops (for which $\tau : E$ was found in Martin et al.)
[23] to be a universally better invariant) and suspensions of rigid spheroids considered here. Namely, deformable drops adjust their shape to the type and intensity of the flow, while solid particles do not; in particular, oblate particles remain oblate in uniaxial extension—thus the $I_2(E)$ invariant is sometimes preferable for suspensions. For more complex microstructures (e.g., with flexible macromolecules capable of adjusting their shape to the flow), $\tau : E$ is expected to be a universally better choice in our scheme of constitutive modeling.

A major distinction between the principles of constitutive modeling in the present work and those in Hinch and Leal [8, 9] is that the HL model exactly matches both the weak-flow and strong-flow limits for arbitrary flows (assuming full particle orientation in the strong-flow limit), and seeks to interpolate such predictions to flows with finite intensity; the modeling principles in Hinch and Leal [9] are substantially based on the particular microstructure of a dilute suspension of noninteracting rodlike/disklike particles. In contrast, the present modeling relies on the exact results (when available) for two base flows at arbitrary (finite) intensities, and seeks to extend these results to flows with arbitrary history of deformation of a material element through a generalized Oldroyd equation. Since both base flows (PE and simple shear) allow for periodic boundaries implementation, such database rheological functions can be obtained from first principles by numerical simulations for a number of microstructurally complex materials with strong hydrodynamical interactions between the inclusions. The case of highly-concentrated emulsions of deformable drops is the first example [25] of such constitutive modeling.

Obviously, flows with time-dependent kinematics would provide more relevant testing of the rheological models, closer to real nonNewtonian hydrodynamics in complex geometries. Two such examples are considered in the following subsections.

3.6.3 Time-dependent PE flow

The next test performed for the generalized Oldroyd model is an oscillating PE flow, as defined in Zinchenko and Davis [25], with the velocity gradient $\text{diag}(\dot{\Gamma}, -\dot{\Gamma}, 0)$ and the de-
Figure 3.7: Non-dimensional viscosity function $\mu^\omega_{pe} = (\tau^{pe}_{11} - \tau^{pe}_{22})/(4\mu\langle\dot{\Gamma}\rangle)$ for time-dependent PE flow with prolate spheroids, $Pe = \overline{Pe}(\varphi(t))$ and $\overline{Pe} = 5$: (a) $R = 5$ (b) $R = 20$. Exact results (solid lines), present model (dashed lines), and HL model (circles).

The formation rate $\dot{\Gamma}(t) = \varphi(t)\langle\dot{\Gamma}\rangle$, where $\langle\dot{\Gamma}\rangle > 0$ is constant. The prefactor is defined as $\varphi(t) = 0.6614/(1 + 0.75 \sin 2\pi \omega t)$ with $\omega = \langle\dot{\Gamma}\rangle$; this form provides strong, non-harmonic seven-fold oscillations in the deformation rate. The numerical constant of 0.6614 is conveniently chosen to make the average of $\varphi(t)$ equal to one [25]. The Péclet number $\overline{Pe} = 2\langle\dot{\Gamma}\rangle/D$, based on the average deformation rate $\langle\dot{\Gamma}\rangle$, is set to $\overline{Pe} = 5$.

Two nondimensional, time-dependent rheological functions for this flow are

$$
\mu^\omega_{pe}(t) = \frac{\tau^{pe}_{11} - \tau^{pe}_{22}}{4\mu\langle\dot{\Gamma}\rangle}, \quad N^\omega_{pe}(t) = \frac{\tau^{pe}_{11} + \tau^{pe}_{22} - 2\tau^{pe}_{33}}{\mu\langle\dot{\Gamma}\rangle}.
$$

The second quantity, $N^\omega_{pe}(t)$, makes a small contribution to the deviatoric stress in this test, so we limit the analysis to the viscosity function $\mu^\omega_{pe}(t)$.

Figure 3.7(a,b) shows $\mu^\omega_{pe}(t)$ for suspensions of prolate spheroids with aspect ratio (a) $R = 5$ and (b) $R = 20$. Zero deviatoric stress $\tau$ is chosen as the initial condition for the present modeling based on the Oldroyd equation (3.15). With this (artificial) initial condition, slightly negative values of the Oldroyd functions argument $\zeta$ occurred (only briefly near startup), which was remedied by taking the absolute value of $\zeta$. The exact solution
The models quickly attain periodic regimes. Except for the short transient stage of little interest, the present modeling (dashed lines) is close to the exact solution. The error is slightly greater for $R = 20$ than for $R = 5$, but it is mostly localized in narrow regions near maxima/minima. Applying the database results for steady PE to this strongly-oscillating flow in a quasisteady manner is insufficient to predict the stresses and leads to large deviations from the exact solution. In contrast, combining the steady-state results for PE with those for simple shear through the generalized Oldroyd equation (3.15) dramatically improves the prediction for the time-dependent PE flow.

The HL closure model (dotted lines) gives again an excellent approximation in this test. It is able to capture the isotropic initial state for the FPS equation (3.2) by a suitable choice of the microstructural tensor $\langle pp \rangle$, thus extending the accuracy to small times.

### 3.6.4 Flow past a macroscopic sphere at moderate Reynolds number

The rheological response from microscopic solid particles (prolate or oblate) freely suspended in a stationary flow past a macroscopic sphere at a moderate Reynolds number is now studied. As the first approximation for small particle volume fraction, the suspended particles follow the streamlines of a pure liquid. We calculate these streamlines and the kinematics of a material element along a trajectory from the small Reynolds number expansion of the nondimensional stream function for flow around a unit sphere [32, 33]:

$$
\psi(r, \theta) = \frac{1}{4} (r - 1)^2 \sin^2 \theta \left\{ \left( 1 + \frac{3}{8} Re \right) \left( 2 + \frac{1}{r} \right) - \frac{3}{8} Re \left( 2 + \frac{1}{r} + \frac{1}{r^2} \right) \cos \theta \right\}. \tag{3.33}
$$

In this equation, $r$ and $\theta$ are spherical coordinates related to the Cartesian coordinates by $x_1 = r \sin \theta \cos \varphi$, $x_2 = r \sin \theta \sin \varphi$, $x_3 = r \cos \theta$ (Fig. 3.8), the Reynolds number is defined as $Re = U_\infty \rho R_o / \mu$, where $U_\infty$ is the far-field fluid velocity along the axis of symmetry $x_3$, $R_o$ is the physical sphere radius, and $\rho$ is the fluid density. In the limit of $Re \to 0$, the stream function for Stokes flow past the sphere is recovered. As the Reynolds number increases
above $Re \cong 8$, an eddy begins to form in the wake behind the sphere. The eddy grows larger until $Re \cong 60$, when the flow can no longer be assumed stationary \[33\]. Strictly speaking, the form (3.33) is valid at small $Re$ only, but it describes the flow reasonably accurately, and qualitatively correctly, for Reynolds numbers even near 60 \[33\]. It is sufficient in the present context that the same kinematics (3.33) is used to generate rheological results for both the present (3.15) and closure approximation models, and for the exact FPS solutions along the trajectories. The HL and Bingham closure approximations are chosen for comparisons in this test, as they are most successful compared to the other closures described in Sec. 3.2. Although the flow field is stationary in space, the kinematics of a material element along a trajectory is, of course, Lagrangian-unsteady.

The Reynolds number is set to 50, and the test is carried out in the $x_2 = 0$ plane due to axial symmetry, without a loss of generality. Note that this is not a planar-flow test, since $E_{22} \neq 0$ along the trajectories. The relative importance of the flow strength and Brownian rotations of the suspended particles is characterized by $Pe_{sph} = U_\infty/(R_o D_R)$. One open and one closed trajectory are chosen for the analysis. The open trajectory [Fig. 3.8(a)] begins far from the sphere at $x_3 = -20$ and $x_1 = 0.15$, and the FPS equation and the models [the present (3.15), HL, and Bingham] are integrated along the trajectory. The initial conditions are uniform $N(p,t)$ for the FPS equation, isotropic second moment $\langle pp \rangle$ for the HL and Bingham models, and zero intrinsic stress $\tau$ for the generalized Oldroyd equation (3.15). For a trajectory starting far upstream, though, the effect of the initial conditions is negligible. The nondimensional intrinsic deviatoric stress is defined as $\nu_{ij}^s = \tau_{ij} R_o/(U_\infty \mu)$. Figure 3.8(b) shows the local value of the Péclet number (3.19) along this trajectory. Figures 3.8(c)-3.8(e) show the three independent components, $\nu_{11}^s$, $\nu_{13}^s$, and $\nu_{33}^s$ vs. $x_3$ along the open trajectory, for a suspension of prolate spheroids with $R = 5$ and $Pe_{sph} = 3.8$. Both the present and HL models are practically indistinguishable from the exact solution on the upstream part $x_3 < -2$. For $\nu_{11}^s$ in Fig. 3.8(c), the present model (3.15) deviates slightly from the exact solution only in the small vicinity of the equator $x_3 = 0$, while the HL model gives good
agreement over the entire trajectory. The HL model likewise gives accurate predictions of the intrinsic stress components $\nu_{13}^s$ and $\nu_{33}^s$ over the open trajectory. While the present model gives accurate agreement for $\nu_{33}^s$ in Fig. 3.8(e), it gives a significant discrepancy for $\nu_{13}^s$ in the vicinity of the equator $x_3 = 0$ in Fig. 3.8(d); this deviation is most likely due to the large values of the local Péclet number along this part of the streamline [shown in Fig. 3.8(b)].

Figure 3.9(a) shows the streamline in the eddy zone, chosen as a closed trajectory for rheological testing. This streamline passes through the point $x_1 = 0.1, x_3 = 1.8$; angle $\alpha$ measures the rotation of the trajectory vector around the center $x_1 = 0.3685, x_3 = 1.7349$. Along this path, the history of deformation of a material element is time periodic, and the suspension rheological response also attains a periodic regime after a few cycles. Figure 3.9(b) shows the local value of the Péclet number (3.19) along the closed trajectory. For prolate spheroids with $R = 5$, this periodic regime is shown vs. $\alpha$ in Figs. 3.9(c)-3.9(e) for all three components $\nu_{11}^s, \nu_{13}^s, \nu_{33}^s$. Since the values of the local Péclet number in this case are moderate, as seen from in Fig. 3.9(b), the present model (3.15) can be expected to be accurate over the closed trajectory. Indeed, Figs. 3.9(c-e) show the present rheological model (3.15) (dashed lines) to yield very accurate results for all three intrinsic stress components for the whole period, even more accurate than from the HL model (circles). Note that the chosen $Pe_{sph} = 3.8$ is far outside the range of validity of the second-order theory (3.29) for both the open and closed trajectories in Figs. 3.8 and 3.9. Since the value of the local Péclet number remains substantially lower in the eddy zone than on the open trajectory, only the more interesting results along the open trajectory are considered for aspect ratios other than $R = 5$.

To determine the effect of $Pe_{sph}$ on the performance of the models, an additional test was conducted for the flow past a sphere with $Pe_{sph} = 0.5$ for prolate spheroids with $R = 5$. Figure 3.10 shows the three intrinsic stress components for the open trajectory. The present model (3.15) is much better behaved at this lower $Pe_{sph}$ compared to the case $Pe_{sph} = 3.8$. Although this model (3.15) (dashed lines in Fig. 3.10) still gives some discrepancies near
Figure 3.8: Intrinsic stress on the open trajectory for flow around a sphere at $Re = 50$ and $Pe_{sph} = 3.8$ for a suspension of prolate spheroids with $R = 5$. The streamline is shown in (a) and the local Péclet number along the streamline is shown in (b). The nondimensional stress components $\nu^s_{ij} = \tau_{ij} R_o / (U_\infty \mu)$ are shown in (c)-(e). Exact results (solid lines), present model (dashed lines), and HL model (circles).
the equator $x_3 = 0$ for the component $\nu_{11}^s$ [compare Fig. 3.10(a) to Fig. 3.8(c)], there is a remarkable accuracy improvement for the stress components $\nu_{13}^s$ and $\nu_{33}^s$ in Figs. 3.10(b,c) when compared to the higher $Pe_{sph}$ case [see Figs. 3.8(d,e)]. This improvement is obviously due to smaller local Péclet numbers over the trajectory, which is another evidence that our general constitutive modeling scheme is very accurate at finite (although not extreme) flow intensities. The HL model (circles) accurately covers the whole trajectory, including near the equator $x_3 = 0$. Even at this low value of $Pe_{sph}$, the second-order theory (3.29) (not shown) is still inadequate to fully model the stress components on this trajectory.

Using the same macroscopic trajectories as in Figs. 3.8(a), the rheological testing for prolate spheroids ($R = 20$) and oblate spheroids ($R = 0.1$) is presented in Fig. 3.11 and includes the Bingham model (which is found to be more accurate than HL model in these cases). Two different values of $Pe_{sph}$ are chosen, to again assess the relative importance of the local Péclet number along the trajectory. In Figs. 3.11(a,b), the rheological components $\nu_{11}^s$, $\nu_{13}^s$, and $\nu_{33}^s$ are shown for prolate spheroids with $R = 20$ and $Pe_{sph} = 3.5$. The present model (3.15) (dashed lines) gives accurate results overall, with some discrepancies near the equator $x_3 = 0$ when compared to the exact solution (solid lines). The Bingham model (circles) has less discrepancy, but is still not ideal near $x_3 = 0$. Figure 3.11(c) presents the components $\nu_{11}^s$ and $\nu_{33}^s$ at $Pe_{sph} = 0.5$ for $R = 20$. Although the present model still shows some deviations for the component $\nu_{11}^s$, there is a noticeable improvement for the component $\nu_{33}^s$.

Figures 3.11(d,e) contain the results for oblate spheroids ($R = 0.1$) along the open trajectory at $Pe_{sph} = 3.5$. The present model (3.15) (dashed lines) shows noticeable deviations around the equator $x_3 = 0$ for $\nu_{11}^s$ and $\nu_{13}^s$ from the exact solution (solid lines), but provides accurate results for $\nu_{33}^s$ over the whole trajectory. The Bingham closure (circles) is more accurate than the present model (3.15) in predicting all three intrinsic stress components, with modest discrepancies for $\nu_{11}^s$ and $\nu_{13}^s$. The present model predictions for $\nu_{13}^s$ and $\nu_{33}^s$ considerably improve when $Pe_{sph}$ is reduced to 0.5 in Fig. 3.11(f). The local Péclet number
Figure 3.9: Intrinsic stress on the closed trajectory in the eddy zone for flow past a sphere at $Re = 50$ and $Pe_{sph} = 3.8$ for a suspension of prolate spheroids with $R = 5$. The closed streamline is shown in (a) and the local Péclet number $Pe$ along the streamline is shown in (b). The nondimensional stress components $\nu_{ij}^s = \tau_{ij} R_o / (U_\infty \mu)$ are shown in (c)-(e). Exact results (solid lines), present method (dashed lines, which are indistinguishable from the solid lines), and HL model (circles).
Figure 3.10: Intrinsic stress for flow in the vicinity of a macroscopic sphere on the open trajectory at $Re = 50$ for a suspension of prolate spheroids with $R = 5$ and $Pe_{sph} = 0.5$, with the nondimensional stress components defined as $\nu_{ij} = \tau_{ij} R_o / (U_\infty \mu)$. Exact results (solid lines), present model (dashed lines), and HL model (circles).

(3.19) is still not small in this case reaching approximately 13 near the equator.

3.7. Discussion

The formulation of a constitutive equation for a non-Newtonian fluid is essential to modeling flows in a broad range of kinematics and solving boundary-value problems of non-Newtonian hydrodynamics in complex geometries. In the present work, we have chosen a classical complex fluid—a dilute suspension of solid spheroids (prolate or oblate) subject to Brownian rotations—as a test case to explore the capabilities of a new general approach to constitutive modeling. This approach [23] postulates a traceless Oldroyd equation with five variable coefficients for the deviatoric stress. These five parameters are assumed to be functions of one instantaneous flow invariant (chosen as the intrinsic energy dissipation rate), and they are found by simultaneously fitting the Oldroyd model to a total of five rheological functions from two base flows at arbitrary flow intensities. The base flows are steady simple shear and steady planar extension (PE). In Martin et al. [23] this method was validated against the exact results for a dilute emulsion of non-Brownian deformable drops in a broad class of kinematic conditions.
Figure 3.11: Intrinsic nondimensional stress components $\nu_{ij}^s = \tau_{ij} R_0 / (U_\infty \mu)$ along the open trajectory for suspension flow past a macroscopic sphere at $Re = 50$; (a)-(b): prolate spheroids with $R = 20$ and $Pe_{sph} = 3.5$; (d)-(e): oblate spheroids with $R = 0.1$ and $Pe_{sph} = 3.5$. Also shown is the $Pe_{sph} = 0.5$ case for (c) prolate spheroids with $R = 20$ and (f) oblate spheroids with $R = 0.1$. Exact results (solid lines), present model (dashed lines), and Bingham closure model (circles).
For the present case of a dilute suspension of spheroids, the five necessary database rheological functions (two for PE and three for simple shear) are precisely evaluated at arbitrary Péclet numbers (and various aspect ratios) through the solution of the Fokker-Planck-Smoluchowski (FPS) equation by expanding the orientation distribution function into spherical harmonics. Precise numerical solutions of the FPS equation are also used to verify the accuracy of our (much simpler) constitutive model for the intrinsic stress for rodlike and disklike particle suspensions in various flows with prescribed kinematics. Examples include planar mixed (PM) flow (with \( \chi = 0.5 \)), uniaxial extension/compression, time-dependent PE flow with strong non-harmonic oscillations in the deformation rate, and flow past a macroscopic sphere at a moderate Reynolds number. The second constitutive model of Hinch and Leal [9] (HL) and Bingham closure [12] are also included for comparison, representative of the best closure approximations available in the literature for suspensions of rods/disks. Prolate spheroids with aspect ratio \( R = 5, 10, 15 \) and \( 20 \), and oblate spheroids with \( R = 0.1 \), have been considered. In the steady flow tests mentioned above, the present modeling scheme is sufficiently accurate as long as the Péclet number is \( \leq O(10) \) (except for the uniaxial extension case with oblate particles \( R = 0.1 \), where this modeling is less successful). The present approach also accurately describes the long-time periodic rheological response in the time-dependent PE flow test. For flow past a sphere (an example of Lagrangian-unsteady kinematics, closer to real non-Newtonian hydrodynamics in complex geometries), accuracy is lost for some intrinsic stress components, but only in small areas near the equator where the local Péclet number reaches 50 or higher. All other parts of the studied trajectories with smaller \( Pe \) (including the whole closed trajectory in the eddy zone) are described very accurately. The fidelity of the proposed constitutive modeling quickly improves with a decrease in the flow intensity.

We also demonstrated that the HL and Bingham closures perform remarkably well (with only very small deviations from the exact solution in the sphere test) and to have a higher range of validity in the Péclet number than the present modeling scheme. These closure mod-
els (as any other closures discussed in Sec. 3.2) are specific, though, for a dilute suspension of rodlike/disklike particles described by a single director \( \mathbf{p} \). The expressions for the fourth moment \( \langle pppp \rangle \) in terms of the second moment \( \langle pp \rangle \) can only be useful due to the moment evolution equation (8) [and the specific stress equation (4)]. In turn, the moment equation (8) follows from the rotational dynamics (1) and the Fokker-Plank-Smoluchowski equation (2) for a single director \( \mathbf{p} \). When there are no microstructural equations like (1)-(2) as a starting point, it is not clear how to proceed with closure models. In particular, this shortcoming is the case for other more complex non-Newtonian fluids (e.g., highly-concentrated Brownian suspensions with compact particle shapes, highly concentrated emulsions of non-Brownian deformable drops, solutions of flexible macromolecules with strong hydrodynamical interactions).

In contrast, the present approach to theoretical constitutive modeling is general. Our choice of simple shear and planar extension, as the two base flows, is intentional. These two flows are not only fundamentally different, but they both allow for reproducible lattices and, hence, implementation of periodic boundary conditions—one of the prerequisites for successful long-time simulations with many particles, drops, etc., and strong hydrodynamical interactions. So, with advanced numerical tools, the five database rheological functions can be obtained from first-principle simulations, to incorporate them as building blocks into a general rheology framework through the generalized Oldroyd equation. The paper of Zinchenko and Davis [25] gives the first example of such constitutive modeling for highly-concentrated emulsions of deformable drops, with up to 55% drop volume fractions.

It is also noteworthy that our general scheme of constitutive modeling does not include any microstructural tensors, but only the deviatoric macroscopic stress \( \mathbf{\tau} \). For fiber suspensions with axisymmetrical particles, the ensemble average \( \langle pp \rangle - (1/3) I \) is the only natural definition of the microstructural deviatoric second-rank tensor \( \mathbf{A} \). For other systems, though, with many more degrees of freedom (e.g., concentrated emulsions of deformable drops or solutions of flexible macromolecules with strong interactions), there is uncertainty even in how
to define $A$. Unlike for dilute fiber suspensions [Eq. (3.4) supplemented with some closure approximation for $\langle \text{pppp} \rangle : E$], one cannot expect, in general, to have an \textit{a priori} relationship between $\tau$ and $A$. To proceed, a constitutive law from Hand’s [27] phenomenological theory can be postulated, however:

$$\tau = \text{I.T.} + \beta_1 A + \beta_2 E + \beta_5 (A \cdot E + E \cdot A) + \ldots$$  \hspace{1cm} (3.34)

(omitting cubic and higher-order terms), with some material parameters $\beta_1$, $\beta_2$ and $\beta_5$. The microstructural tensor evolution can be also assumed from Hand’s theory:

$$\frac{DA}{Dt} = \text{I.T.} + \alpha_1 A + \alpha_2 E + \alpha_3 A^2 + \alpha_4 E^2 + \alpha_5 (A \cdot E + E \cdot A) + \ldots$$  \hspace{1cm} (3.35)

(omitting cubic and higher-order terms), with additional material parameters $\alpha_i$. Stipulating $\beta_5 = \alpha_3 = 0$, the microstructural tensor $A$ can be excluded from (3.34) and (3.35), thus removing the uncertainty and yielding (for constant $\alpha_i$ and $\beta_j$) the Oldroyd Eq. (3.15). This connection to Hand’s theory at least rationalizes the choice of Eq. (3.15) as the starting point of our constitutive modeling (when the material parameters depend on a flow invariant, there are subtle differences between the two theories deemed not very significant and not discussed here). The Oldroyd Eq. (3.15) requires an artificial initial condition for $\tau$, which cannot adequately represent an initial material microstructure and may be a source of significant errors at small times (Fig. 3.7 for time-dependent PE is an example). However, in many (if not most) applications of constitutive modeling to non-Newtonian hydrodynamics, the initial conditions for a material element are far in the past and do not affect the stress at later stages of interest owing to fading memory. Examples include open trajectories originating at infinity, and closed trajectories in the eddy zone for a steady flow past a sphere (Sec. 3.6.4). Although excluding microstructural variables from constitutive modeling is usually considered undesirable [8], it is currently difficult to see an alternative to the proposed scheme, if one wants to keep it general and potentially applicable to a broad class of microstructurally
complex liquids. The main motivation behind the present study was to test how this constitutive modeling scheme performs for a particular case of dilute fiber suspensions, where exact results and specialized closure methods provide excellent benchmarks for comparison. Note also that if extensiometric functions for steady PE flow become available experimentally, they could be used in our scheme (together with experimental viscometric functions from steady simple shear) as building blocks for general rheology, instead of simulation results. Extracting information about the microstructural tensor $A$ from experiments would be very difficult for any system more complex than fiber suspensions, providing another argument in favor of the Oldroyd Eq. (3.15), which does not require such information.

One final remark may be useful. When Brownian motion is the relaxation mechanism providing fading memory, a microstructurally complex fluid is expected to behave like a Rivlin-Ericksen fluid in the limit of slow flows, described by the hierarchy of Rivlin-Ericksen models (second-order fluid, fourth-order fluid, etc., e.g. Astarita and Marrucci [34]). However, it would be a formidable task to theoretically calculate the parameters of such models (except for dilute systems with non-interacting inclusions), and we are not aware of any such calculations. Our constitutive modeling scheme, which becomes asymptotically correct and very accurate for arbitrary kinematics in the limit of slow flows, gives a viable alternative to describe a material near this limit, even for concentrated systems with strong hydrodynamical interactions. Such modeling is also expected to have a much broader range of validity in the flow intensities than (hypothetical) Rivlin-Ericksen expansions.

3.8. Summary

A new general scheme of constitutive modeling of non-Newtonian liquids has been developed and tested for a dilute suspension of Brownian rodlike/disklike particles. Oldroyd’s equation for the deviatoric stress is employed to predict the rheological response of a material element in these suspensions, with five variable parameters dependent on one instantaneous
flow invariant. These parameters are found by fitting the Oldroyd equation to the rheological functions in two steady database flows (simple shear and planar extension) at arbitrary deformation rates. The resulting model is then compared with exact results for other flows, both Lagrangian-steady and unsteady with various flow kinematics (planar mixed flow, uniaxial extension/compression, time-dependent planar extension, steady flow past a sphere at a moderate Reynolds numbers). The model is more accurate for prolate than for oblate particles and is particularly accurate for small to moderately large flow intensities (although it loses accuracy for rheologically strong flows). An alternative, well-established approach to the rheology of dilute fiber suspensions based on closure approximations (most notably, the second closure of Hinch and Leal [9]) is shown to give versatile and usually very accurate modeling in a wider range of flow intensities than does the present approach. However, the benefit of the present constitutive modeling scheme is in its general applicability, since it can be applied, apart from fiber suspensions, to many other microstructurally complex liquids, e.g., highly-concentrated Brownian suspensions with compact particles, highly-concentrated emulsions of deformable drops, and solutions of flexible macromolecules with strong hydrodynamical interactions. The resulting generalized Oldroyd equation then has practical utility in solving boundary-value problems for non-Newtonian flows in complex geometries.
3.9. Appendices

3.9.1 Appendix 3A: Details of K-I and K-II closures

The coefficients for the K-I and K-II closures from Eq. (3.14) are defined as [13]:

\[ D_1 = \frac{2}{15} - \frac{4S_2}{21} + \frac{2S_4}{35} - \frac{2B_2}{7} + \frac{B_4}{28} + \frac{M_4}{21}, \]

\[ D_2 = \frac{1}{7} \left( \frac{S_2}{3} + \frac{4S_4}{9} + \frac{B_2}{2} - \frac{B_4}{2} + \frac{8M_4}{9} \right) I + \left( S_4 - \frac{3B_4}{8} + \frac{M_4}{2} \right) n_{[2]} + \frac{M_4}{6} m_{[2]}, \]

\[ D_3 = \frac{1}{7} \left( \frac{B_2}{3} + \frac{4B_4}{9} \right) I + \frac{M_4}{6} n_{[2]} + B_4 m_{[2]}, \]

\[ D_4 = \frac{2}{7} \left( \frac{S_2}{2} - \frac{S_4}{2} + \frac{B_2}{2} - \frac{3B_4}{8} - \frac{2M_4}{3} \right), \]

\[ D_5 = \frac{2}{7} \left( \frac{B_2}{2} - \frac{B_4}{2} - \frac{M_4}{6} \right), \quad D_6 = \frac{M_4}{3}, \quad (3A.1) \]

where \( n_{[2]} = nn - I/3, \quad m_{[2]} = mm - I/3, \quad S_2 = (3\lambda_1^e - 1)/2, \) and \( B_2 = \lambda_2^e - \lambda_3^e. \) For K-I,

\[ S_4 = \left( \frac{S_2^2}{8} + \frac{1}{8} B_2^2 \right) \zeta_k, \quad B_4 = B_2^2 \zeta_k, \quad M_4 = (2S_2B_2 + B_2^2) \zeta_k, \quad (3A.2) \]

where

\[ \zeta_k = \frac{1 - (1 - S_2)\nu_k}{S_2}, \quad \nu_k \approx \frac{3}{5}, \]

with \( \zeta_k \approx \nu_k \) when \( S_2 = 0. \) For K-II, relations (3A.2) are replaced by

\[ S_4 = \left( \frac{S_2^2}{8} + \frac{1}{8} B_2^2 \right) \zeta_k, \quad B_4 = B_2^2, \quad M_4 = 2S_2B_2 + B_2^2. \quad (3A.3) \]
3.9.2 Appendix 3B: Solution of the FPS equation

The solution method of the Fokker-Planck-Smoluchowski equation, Eq. (3.2), is as follows. This equation is rewritten as

$$\frac{DN}{Dt} + N \nabla_s \cdot \dot{p} + \dot{p} \cdot \nabla_s N - D_R \nabla_s^2 N = 0 . \quad (3B.1)$$

The orientation distribution function $N(p, t)$ is then expanded in a series of spherical harmonics, as defined in Eqs. (3.26)-(3.28), giving

$$\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ Y^m_n \frac{dA^m_n}{dt} + A^m_n Y_n^m \nabla_s \cdot \dot{p} + A^m_n \dot{p} \cdot \nabla_s Y_n^m - D_R A^m_n \nabla_s^2 Y_n^m \right\} = 0 . \quad (3B.2)$$

Using the relations

$$\nabla_s \cdot \dot{p} = -3G(p \cdot E \cdot p) \quad \text{and} \quad \nabla_s^2 Y_n^m = -n(n+1)Y_n^m , \quad (3B.3) \quad (3B.4)$$

the equation (3B.2) becomes

$$\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ Y^m_n \frac{dA^m_n}{dt} - 3G(p \cdot E \cdot p)A^m_n Y_n^m + A^m_n \dot{p} \cdot \nabla_s Y_n^m + n(n+1)D_R A^m_n Y_n^m \right\} = 0 . \quad (3B.5)$$

We can expand the term $\dot{p} \cdot \nabla_s Y_n^m$ as

$$\dot{p} \cdot \nabla_s Y_n^m = \left\{ \Omega \cdot p + G[E \cdot p - (p \cdot E \cdot p)p] \right\} \cdot \nabla_s Y_n^m , \quad (3B.6)$$

and the last term in this expression simplifies to

$$-G(p \cdot E \cdot p)p \cdot \nabla_s Y_n^m = -nG(p \cdot E \cdot p)Y_n^m . \quad (3B.7)$$
Substituting these expansions into the Fokker-Planck-Smoluchowski equation results in

\[
\sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ Y_n^m \frac{dA_n^m}{dt} - (3 + n) G(\mathbf{p} \cdot \mathbf{E}) A_n^m Y_n^m + A_n^m (\mathbf{q} \cdot \mathbf{p}) \cdot \nabla_s Y_n^m \\
+ A_n^m G(\mathbf{E} \cdot \mathbf{p}) \cdot \nabla_s Y_n^m + D_R n (n + 1) A_n^m Y_n^m \right\} = 0.
\]

(3B.8)

Using (3B.8) and appropriate recurrent relations between spherical harmonics, \(dA_n^m/dt\) is evaluated in terms of the neighboring coefficients \(A_{n'}^m\) to advance \(A_n^m\) to the next time step.

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### 3.11. References


Chapter 4: The Rheology of Dilute Emulsions in the Presence of Surfactants

4.1. Introduction

Emulsions have a wide range of applications, and arise both in industrial settings and in the environment. An emulsion consists of two immiscible fluids: the droplet phase and the continuous phase. In many emulsions, the surfaces of the dispersed phase liquid are often contaminated with artificial or natural surfactants. When surfactants are introduced to the surface of the drops, they affect the behavior of the drops and the overall rheology of the bulk mixture. The surfactants lower the interfacial tension of the drops, and the drops then deform more readily. They may also give rise to gradients in interfacial tension and, hence, in tangential stresses. The interfacial tension is related to the surfactant concentration on the surface through an equation of state; many studies have used a linear relationship between the interfacial tension and the surfactant concentration [1, 2], while some studies have explored nonlinear equations of state [3, 4, 5]. The linear equation of state is valid for low surfactant concentrations, while a nonlinear relationship is more suitable for higher surfactant concentrations.

Stone and Leal [2] studied the deformation and breakup of drops in the presence of surfactants in a uniaxial extensional flow with equal viscosities in the drop and continuous phases. They derived an analytical, small-deformation theory for a drop covered with surfactant and extended this work by numerically calculating large deformations of a drop covered with
surfactant. When the surfactant distribution is dominated by diffusion on the surface of the drop, the surfactant concentration is nearly uniform along the surface of the drop, but becomes diluted by the increase in surface area as the drop deforms. This dilution leads to a higher interfacial tension on the drop, and causes the drop to achieve greater deformations before breakup when compared to a drop with constant interfacial tension. When the surfactant motion on the drop interface is convection-dominated, the surfactant is advected to the back end of the drop, causing this region to have a lower interfacial tension. This mechanism increases the deformation at the ends of the drop, and causes the drop to break up at lower shear rates. Large gradients in the surfactant concentration also lead to Marangoni stresses on the surface of the drop. In areas with high interfacial tension gradients, large Marangoni stresses retard surface velocity and thus limit the convection of surfactants across the drop’s surface.

Li and Pozrikidis [1] conducted further studies on drop deformations in shear flow and planar mixed flows in the presence of surfactants with equal viscosities of the dispersed and continuous phases. In their study, drops covered with surfactant deformed to a greater extent than drops without surfactant. This increased deformation was caused by the increased concentration of surfactant at the tips of the drop, thus decreasing the interfacial tension in those regions, leading to greater deformation. They also studied the rheology in shear flow of a drop covered with surfactant.

Pawar and Stebe [4] investigated a drop covered with surfactant using both linear and nonlinear equations of state for the relationship between the interfacial tension and the surfactant concentration. While the linear equation of state is valid at low concentrations, the nonlinear equation of state used by Pawar and Stebe (the Frumkin equation) incorporates surface saturation and interactions between surfactant molecules as the surfactant concentration increases. They found that nonlinear equations of state greatly affect the deformations and concentration gradients on the drop. Bazhlekov et al. [5] used the nonlinear Langmuir equation of state, also known as the Szyszkowski equation, simulating a drop in shear flow.
covered with surfactants at various viscosity ratios between the drop and continuous phases. Milliken et al. [3] also explored a variety of viscosity ratios, and found that surfactants have the greatest effect on drop deformation when the drop-to-continuous-phase viscosity ratio is less than unity.

Although much work has been dedicated to studying the deformation of drops covered in surfactant, previous studies have only lightly touched on the resulting rheology of the bulk mixture when surfactants are present, and there are few works on constitutive equations for emulsions in the presence of surfactants that are valid in arbitrary kinematics. In this study we evaluate the rheology of dilute emulsions in the presence of surfactants and apply the generalized Oldroyd model to describe such rheology, developed in the previous work of Martin et al. [6]. The generalized Oldroyd equation requires that five rheological functions are obtained from two base flows: simple shear and planar extension. To solve for the rheology for these two base flows, and also to test the resulting constitutive model, the boundary-integral method is used to solve for the drop deformation. In this approach, the surfactant evolution on the surface of the drop is calculated from the convection-diffusion equation. The physical system and equations are set forth in Sec. 4.2, as is the solution method. In Sec. 4.3, we define the equations of state that relate the local surfactant concentration to the local interfacial tension. The generalized Oldroyd model is described in Sec. 4.4, as are the base flows and values of the Oldroyd parameters. In Sec. 4.5, we validate the generalized Oldroyd model in planar mixed flow and flow between two eccentric spheres. Concluding remarks are given in Sec. 4.6.

4.2. Problem statement and equations

The goal of this work is to develop a constitutive model valid for dilute emulsions in the presence of surfactants. To develop this model, the rheology of the system is determined using the exact solutions from the boundary-integral and convection-diffusion equations,
outlined in subsections 4.2.1 and 4.2.2, respectively.

4.2.1 Boundary-integral equation

Consider an immiscible fluid drop of viscosity $\mu$ in a continuous-phase fluid of viscosity $\mu_e$ subject to an arbitrary flow field. The surface of the drop is covered with a surfactant that is insoluble in both the dispersed and continuous phases. The analysis is restricted to small Reynolds numbers, so that inertial effects are negligible. The nondimensional surfactant concentration is defined as $\Gamma = \Gamma^*/\Gamma_{eq}$, where $\Gamma^*$ is the dimensional surfactant concentration and $\Gamma_{eq}$ is the uniform surfactant concentration of an undeformed drop in the absence of flow. The evolution of the drop is calculated from the boundary-integral (BI) equation [7]:

$$
\mathbf{u}(y) = \frac{2}{1 + \lambda} \mathbf{u}_\infty(y) + \frac{2}{(1 + \lambda)\mu_e} \int_S \Delta f(x) \cdot \mathbf{G}(r) dS_x \\
+ \frac{2(\lambda - 1)}{(\lambda + 1)} \int_S [\mathbf{T}(r) \cdot \mathbf{n}(x)] \cdot \mathbf{u}(x) dS_x ,
$$

(4.1)

where $\mathbf{u}(y)$ is the velocity of the drop’s surface, $\mathbf{u}_\infty(y)$ is the velocity of the continuous-phase fluid far from the drop, $\lambda = \mu/\mu_e$ is the viscosity ratio, and $r = x - y$. The vector $\Delta f(x)$ is the stress jump across the interface and is defined as

$$
\Delta f(x) = 2\sigma(x)k(x)n(x) - \nabla_s \sigma(x) ,
$$

(4.2)

where $\mathbf{n}(x)$ is the normal vector pointing outward from the drop’s surface and $k(x)$ is the local mean surface curvature. The interfacial tension is scaled by the equilibrium interfacial tension $\sigma_{eq}$, giving $\sigma = \sigma^*/\sigma_{eq}$, where $\sigma^*$ is the dimensional interfacial tension. The BI equation also contains the Green’s function $\mathbf{G}(r)$ and the corresponding stresslet $\mathbf{T}(r)$,
given by

\[ G(r) = -\frac{1}{8\pi} \left[ \frac{I}{r} + \frac{rr}{r^3} \right] \] and

\[ T(r) = \frac{3}{4\pi} \frac{rrr}{r^5}. \]

Solutions of the BI equation (4.1) are well documented for clean drops [7, 8], as are methods to deal with the singularities in Eq. (4.1) as \( x \to y \). When the drops are in the presence of surfactants, solutions of the BI equation become more complex due to variable interfacial tension. In addition to the Laplace pressure jump across the interface of the drop, which acts normally to the surface, tangential Marangoni stresses are present. These stresses increase the difficulty in removing the singularity in the first integral of Eq. (4.1). To deal with this singularity, we expand the function \( \Delta f(x) \) to:

\[ \Delta f(x) = f_n(x)n(x) + f_t(x), \quad (4.3) \]

where \( f_n(x) = 2\sigma(x)k(x) \) and \( f_t(x) = -\nabla_x \sigma(x) \) are the normal and tangential components of \( \Delta f(x) \), respectively. Substituting Eq. (4.3) into Eq. (4.1) results in

\[ u(y) = \frac{2}{(1 + \lambda)} u_\infty(y) + \frac{2}{(1 + \lambda)\mu_e} \int_S \left[ f_n(x)n(x) + f_t(x) \right] \cdot G(r) dS_x \]

\[ + \frac{2(\lambda - 1)}{(\lambda + 1)} \int_S [T(r) \cdot n(x)] \cdot u(x)dS_x. \quad (4.4) \]

The singularity in the first integral of Eq. (4.4) is removed by a method developed by Klaseboer et al. [9], with further details given in the Appendix. After the singularity from
the first integral is removed, Eq. (4.4) becomes

\[
\begin{align*}
    u(y) &= \frac{2}{1 + \lambda} U_\infty(y) + \frac{2}{1 + \lambda} \mu e \int_S \mathbf{F} \cdot \mathbf{G}(r) dS_x \\
    &\quad + \frac{2}{1 + \lambda} \mu e \int_S \{ r \cdot \mathbf{n}(y) \} \mathbf{f}_t(y) \cdot \{ T(r) \cdot \mathbf{n}(x) \} dS_x \\
    &\quad + \frac{2(\lambda - 1)}{(\lambda + 1)} \int_S \{ T(r) \cdot \mathbf{n}(x) \} \cdot \mathbf{u}(x) dS_x ,
\end{align*}
\]

(4.5)

where

\[
\mathbf{F} = \mathbf{f}_t(x) - \mathbf{f}_t(y) [ \mathbf{n}(x) \cdot \mathbf{n}(y) ] - \mathbf{n}(y) [ \mathbf{f}_t(y) \cdot \mathbf{n}(x) ] + \mathbf{n}(x) [ f_n(x) - f_n(y) ] .
\]

The singularity in the second integral of Eq. (4.5) is removed by a standard singularity subtraction method as outlined in Zinchenko et al. [8]. Equation (4.5) requires that we know the local interfacial tension at every point, which depends on the surfactant distribution. The surfactant distribution is governed by the convection-diffusion equation, which is described in the next subsection.

### 4.2.2 Convection-diffusion equation

When the drop is subjected to a flow, it induces a surface velocity on the drop, which causes the drop to deform and the surfactant to redistribute on the drop’s surface. The surfactant distribution on the surface of the drop is governed by the convection-diffusion equation, which, for an insoluble surfactant and laminar flow, is given in nondimensional form as

\[
\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot ( \Gamma \mathbf{u}_s ) + 2 \Gamma k ( \mathbf{u} \cdot \mathbf{n} ) - \frac{1}{\Lambda} \nabla_s^2 \Gamma = 0 ,
\]

(4.6)

where \( \nabla_s = ( \mathbf{I} - \mathbf{nn} ) \cdot \nabla \) is the surface gradient operator, \( \mathbf{u} \) is the velocity of the surface of the drop, and \( \mathbf{u}_s \) is the tangential velocity on the surface of the drop. The dimensionless parameter \( \Lambda = Pe/Ca \) is a measure of the relative importance of diffusion to convection.
on the surface of the drop, where $Pe$ is the Péclet number and $Ca$ is the effective capillary number:

$$Pe = \frac{a_d^2 [2I_2(E)]}{D_s}, \quad (4.7)$$

$$Ca = \frac{a_d \mu e [2I_2(E)]^{1/2}}{\sigma_{eq}}, \quad (4.8)$$

In Eqs. (4.7) and (4.8), $D_s$ is the surface diffusivity, $a_d$ is the undeformed drop radius, $E = (\nabla u + \nabla u^T)/2$ is the rate-of-strain tensor, where $\nabla u$ is the velocity gradient, and $I_2(E)$ is the second invariant of the rate-of-strain tensor. The parameter $\Lambda$ is only dependent on the material properties of the system, and is independent of the flow rate. Thus, the effects of the capillary number can be studied independently of the other parameters.

To numerically implement the convection-diffusion equation (4.6), we use the alternate form [1],

$$\frac{\partial \Gamma}{\partial t} = w \cdot \nabla_s \Gamma - \Gamma \nabla \cdot u_s - 2k\Gamma (u \cdot n) + \frac{1}{\Lambda} \nabla_s^2 \Gamma, \quad (4.9)$$

where $w = v - u$. The velocity $v$ is the velocity of the mesh nodes, and is chosen in order to preserve the quality of the mesh, calculated so that $v \cdot n = u \cdot n$, following the procedure of Zinchenko et al. [8]. To solve Eq. (4.9), a local surface parameterization is used, consisting of covariant basis vectors:

$$e_i = \frac{\partial r_s}{\partial \xi_i}, \quad i = 1, 2,$$

where $\xi_1$ and $\xi_2$ are local surface coordinates and $r_s = r_s(\xi_1, \xi_2)$. Applying differential geometry, the terms $\nabla_s \cdot u_s$, $\nabla_s \Gamma$, and $\nabla_s^2 \Gamma$ from Eq. (4.9) can be evaluated with the
\[ \nabla_s \cdot \mathbf{u}_s = \frac{\partial u_x}{\partial \xi_1} + \frac{\partial u_y}{\partial \xi_2} - 2k (\mathbf{u} \cdot \mathbf{n}) , \]  
(4.10)  
\[ \nabla_s \Gamma = \begin{pmatrix} \frac{\partial \Gamma}{\partial \xi_1}, & \frac{\partial \Gamma}{\partial \xi_2}, & 0 \end{pmatrix} , \]  
(4.11)  
\[ \nabla_s^2 \Gamma = \frac{\partial^2 \Gamma}{\partial \xi_1^2} + \frac{\partial^2 \Gamma}{\partial \xi_2^2} , \]  
(4.12)  

The derivatives are calculated locally by approximating the values for \( u_x, u_y, \) and \( \Gamma \) using a quadratic polynomial. For example, \( \Gamma \) is approximated by the equation  
\[ \Gamma = \Gamma_o + \alpha \xi_1 + \beta \xi_2 + \gamma \xi_1^2 + \delta \xi_1 \xi_2 + \epsilon \xi_2^2 , \]  
where \( \Gamma_o \) is the surfactant concentration at the central node. The coefficients \( \alpha, \beta, \gamma, \delta, \) and \( \epsilon \) are determined by minimizing the function  
\[ F_1(\xi_1, \xi_2) = \sum_{j=1}^{N} \left[ \alpha \xi_1 + \beta \xi_2 + \gamma \xi_1^2 + \delta \xi_1 \xi_2 + \epsilon \xi_2^2 - (\Gamma - \Gamma_o) \right]^2 , \]  
where \( j \) is summed over the number of neighboring nodes \( N \). Substituting Eq. (4.10) into Eq. (4.9) gives  
\[ \frac{\partial \Gamma}{\partial t} = \mathbf{w} \cdot \nabla_s \Gamma - \Gamma \left( \frac{\partial u_x}{\partial \xi_1} + \frac{\partial u_y}{\partial \xi_2} \right) + \frac{1}{\Lambda} \nabla_s^2 \Gamma , \]  
(4.13)  
which can be used in conjunction with Eqs. (4.11) and (4.12) to solve for the evolution of the surfactant on the drop’s surface.

The nondimensional form of the BI equation (4.5) is solved in conjunction with the convection-diffusion equation (4.13) by discretizing the drop’s surface into triangular elements. An arbitrary far-field flow \( \mathbf{u}_\infty \) is applied to an initially spherical drop covered in surfactant, where \( \Gamma \) is initially set to unity at every point on the drop’s surface. The mesh nodes and surfactant distribution are updated at each time step. The total amount surfactant on the surface of the drop is conserved throughout the simulation by normalizing the
surfactant concentration $\Gamma_i$ at each node through the equation

$$\Gamma_i^{\text{new}} = \Gamma_i \frac{m^o_s}{\int_S \Gamma(x) dS_x},$$  \hspace{1cm} (4.14)

at every time step, where $m^o_s$ is the total initial amount of surfactant on the drop.

4.3. Surface equations of state

The interfacial tension $\sigma$ is related to the surfactant concentration $\Gamma$ through a surface equation of state. The three equations of state discussed herein are the linear, Langmuir (or Szyszkowski), and the Frumkin equations. The linear equation of state is:

$$\sigma = \frac{\sigma^*}{\sigma_{eq}} = \frac{1 - \beta \Gamma}{1 - \beta},$$  \hspace{1cm} (4.15)

where $\beta$ is the elasticity parameter

$$\beta = \frac{R_g T \Gamma_{eq}}{\sigma_o},$$  \hspace{1cm} (4.16)

$\sigma_o$ is the interfacial tension of the clean interface, $R_g$ is the ideal gas constant, and $T$ is the absolute temperature. The elasticity parameter $\beta$ is a measure of the sensitivity of the interfacial tension to changes in $\Gamma$, where a large value of $\beta$ indicates a high sensitivity of the interfacial tension to the surfactant concentration.

While the linear equation of state is adequate for low surfactant concentrations, a non-linear equation of state is a more robust model at higher concentrations. One of these models is the Langmuir, or Szyszkowski, equation of state:

$$\sigma = \frac{\sigma^*}{\sigma_{eq}} = \frac{1 + E_l \ln (1 - x_s \Gamma)}{1 + E_l \ln (1 - x_s)}.$$  \hspace{1cm} (4.17)

The parameter $E_l$ is similar to the elasticity parameter $\beta$, in that it measures the sensitivity
of the interface to changes in surfactant concentration. It is defined as

$$E_l = \frac{R_g T \Gamma_\infty}{\sigma_o},$$

where $\Gamma_\infty$ is the maximum surfactant concentration; this upper packing limit of the surfactant on the interface of the drop arises because each surfactant molecule occupies a finite area. The parameter $x_s$ is the initial fractional coverage of surfactant on the interface and is defined as $x_s = \Gamma_{eq}/\Gamma_\infty$. Bazhlekov et al. [5] noted that the Langmuir equation can yield negative interfacial tensions [which is also a drawback of the linear equation of state (4.15)]. Pawar and Stebe [4] state that the increased Marangoni stresses predicted by the nonlinear equations of state help prevent $\sigma$ from becoming negative, although in our work we have found that regions of high surfactant concentration are formed, which results in the Langmuir equation of state predicting negative interfacial tension (see Figure 4.1).

The final equation of state discussed is the Frumkin equation of state [4]:

$$\sigma = \frac{\sigma^*}{\sigma_{eq}} = \frac{1 + E_l \left[ \ln (1 - x_s \Gamma) - K (x_s \Gamma)^2/2 \right]}{1 + E_l \left[ \ln (1 - x_s) - K x_s^2/2 \right]},$$

(4.18)

where $K = (\nu_a - \nu_d) \Gamma_\infty/(R_g T)$ is the interaction parameter, and $\nu_a$ and $\nu_d$ are the coefficients for the energy barriers for adsorption and desorption, respectively. When $K = 0$, Eq. (4.18) reduces to the Langmuir equation of state (4.17). Further analysis of the Frumkin equation is performed by Pawar and Stebe [4].

In order to compare the linear, Langmuir, and Frumkin equations of state, we calculate the steady-state stresses in planar mixed (PM) flow vs. the capillary number. Planar mixed flow is defined by the velocity $\mathbf{u} = (\dot{\gamma}_{pm} x_2, \dot{\gamma}_{pm} \chi x_1, 0)$, where $\chi$ is the flow parameter ($\chi = 0$ for simple shear; $\chi = 1$ gives PE flow [10, 11, 12]). Figure 4.2 shows the BI calculations from the linear (dashed lines), Langmuir (solid lines), and Frumkin (dash-dot lines) equations of state. The linear equation of state is calculated at $\beta = E_l x_s = R_g T \Gamma_{eq}/\sigma_o = 0.15$, so that it is comparable to the parameters from the nonlinear equations of state. The linear
Figure 4.1: The Langmuir equation of state predicts negative values of $\sigma$ at elevated values of $\Gamma$. The parameters for the Langmuir equation in this plot are set at $E_l = 0.5$ and $x_s = 0.3$.

and Frumkin equations are shown to be more limited in their range of possible capillary numbers than the Langmuir equation of state. At higher capillary numbers, the equations of state can predict negative interfacial tensions when the local surfactant concentration is elevated. When the equations of state predicted negative interfacial tension, the simulations were stopped and not continued to higher capillary numbers. The linear equation of state has a greater range than the Frumkin equation (when $K = -3$), but both are confined to lower capillary numbers than the Langmuir equation of state.

Common values $E_l$ are given by Eggleton et al. [13] and reproduced in Table 4.1, where realistic values of $E_l$ are less than unity, and $x_s$ can range from extremely dilute ($x_s = 0.01$) to the critical micelle concentration $x_s^{max}$. In this work, we use the values $E_l = 0.5$ and $x_s = 0.3$ in most cases for consistency.
Figure 4.2: The three independent stress components of planar mixed flow defined as \( \nu_{ij} = \frac{\tau_{ij}}{[\mu_{c}\gamma_{pm}(1 + \chi)]} \) with a viscosity ratio of \( \lambda = 0.25 \). The stress components are calculated using the BI equation with (i) the Langmuir equation of state with \( E_l = 0.5, x_s = 0.3, \) and \( \Lambda = 5000 \) (solid lines), (ii) with the Frumkin equation of state (dash-dot lines) with the same parameters as the Langmuir equation and \( K = -3 \), and (iii) with the linear equation of state with \( \beta = 0.15 \) (dashed lines).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( E_l^{min} )</th>
<th>( E_l^{max} )</th>
<th>( x_s^{max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{12}E_8 ) (a/w)</td>
<td>0.07</td>
<td>0.15</td>
<td>0.999</td>
</tr>
<tr>
<td>( C_{12}E_6 ) (a/w)</td>
<td>0.08</td>
<td>0.19</td>
<td>0.998</td>
</tr>
<tr>
<td>TritonX 100 (a/w)</td>
<td>0.10</td>
<td>0.24</td>
<td>0.997</td>
</tr>
<tr>
<td>TritonX 100 (o/w)</td>
<td>0.08</td>
<td>0.53</td>
<td>&gt; 0.999</td>
</tr>
</tbody>
</table>

Table 4.1: Table of common parameters for the equations of state for three different surfactants. The table is from Eggleton et al. [13], where (a/w) denotes air/water interfaces and (o/w) denotes oil/water interfaces.
4.4. The generalized Oldroyd model and base flows

The total Cauchy stress tensor $\Sigma$ for a suspension is defined as

$$\Sigma = 2\mu_e E + \phi \tau, \quad (4.19)$$

where $\tau$ is the particle contribution to the stress (or the intrinsic stress). In the current modeling of emulsions in the presence of surfactants, we consider the dilute regime where the drop volume fraction is $\phi \ll 1$. For the constitutive modeling of dilute emulsions in the presence of surfactants, we use the Oldroyd equation for the intrinsic stress $\tau$:

$$\left(1 + \lambda_1 \frac{D}{Dt}\right) \tau - \mu_1 (\tau \cdot E + E \cdot \tau) + \frac{2}{3} \mu_1 \text{tr} (\tau \cdot E) I = 2\eta \left[ E + \lambda_2 \frac{DE}{Dt} - 2\mu_2 E^2 + \frac{2}{3} \mu_2 \text{tr} (E^2) I \right], \quad (4.20)$$

where $\lambda_1, \lambda_2, \mu_1, \mu_2$, and $\eta$ are material parameters of the fluid. The Jaumann or corotational derivative $D/Dt$ can be calculated in fixed Cartesian axes for any tensor $A$ as

$$\left(\frac{D}{Dt} A\right)_{ij} = \left(\frac{D}{Dt} A\right)_{ij} + \Omega_{ki} A_{kj} + A_{ik} \Omega_{kj}. \quad (4.21)$$

Oldroyd (1958) originally postulated a more general, eight-parameter model (with constant coefficients) for non-Newtonian liquids, which reduces to (4.20) if formulated for a deviatoric tensor $\tau$. Following the general approach of Martin et al. [6], we allow $\lambda_1, \lambda_2, \mu_1, \mu_2$, and $\eta$ to be functions of one instantaneous flow invariant. For dilute emulsions of clean deformable drops, two choices were explored for this invariant in the work of Martin et al. [6]: (i) the second invariant $I_2 = E : E$ of the rate-of-strain tensor ("$I_2$ theory") and (ii) the intrinsic energy dissipation rate $\tau : E$ ("$\tau : E$ theory"). The second choice is adopted in the present study, since it was found to produce a more accurate model in past studies (as for emulsions with clean drops [6]).
To determine the five coefficients in Eq. (4.20), two base flows are chosen that yield a total of five independent rheological functions. In Martin et al. (2014), these coefficients were found by matching Eq. (4.20) to the rheological behavior in two canonical flows: simple shear \( \mathbf{v} = (\dot{\gamma} x_2, 0, 0) \) and planar extension (PE) \( \mathbf{v} = (\dot{\Gamma} x_1, -\dot{\Gamma} x_2, 0) \) (with \( \dot{\gamma}, \dot{\Gamma} > 0 \), without a loss of generality). A similar approach is followed in the present work. The three independent, nondimensional viscometric functions are defined as:

\[
\begin{align*}
\mu_{sh} &= \frac{\tau_{12}}{\mu_e \dot{\gamma}}, & N_{1sh} &= \frac{\tau_{11} - \tau_{22}}{\mu_e \dot{\gamma}}, & N_{2sh} &= \frac{\tau_{22} - \tau_{33}}{\mu_e \dot{\gamma}},
\end{align*}
\]

where \( \mu_{sh} \) is the shear viscosity and \( N_{1sh} \) and \( N_{2sh} \) are the first and second normal stress differences, respectively. The index \( sh \) relates to shear quantities. In turn, there are two independent, nondimensional rheological functions for PE, namely the effective PE viscosity \( \mu_{pe} \) and cross-difference \( N_{pe} \) defined as

\[
\begin{align*}
\mu_{pe} &= \frac{\tau_{11}^{pe} - \tau_{22}^{pe}}{4 \mu_e \dot{\Gamma}}, & N_{pe} &= \frac{\tau_{11}^{pe} + \tau_{22}^{pe} - 2 \tau_{33}^{pe}}{\mu_e \dot{\Gamma}},
\end{align*}
\]

where the index \( pe \) relates to PE quantities. The rheological functions (4.22) and (4.23) depend on the viscosity ratio and the capillary number, as well as the chosen parameters of \( \beta, \Lambda, E_l, x_s, \) and \( K \), depending on the selected equation of state. The Oldroyd coefficients \( \lambda_i \) and \( \mu_i \) are scaled with \( \mu_e a / \sigma_{eq} \), while \( \eta \) is scaled with \( \mu_e \). The nondimensional Oldroyd coefficients all depend on \( \zeta = a \sqrt{\mu_e (\mathbf{\tau} : \mathbf{E}) / \sigma_{eq}} \) in the \( \mathbf{\tau} : \mathbf{E} \)-based theory. The nondimensional forms
of Eqs. (4.22) and (4.23) are

\[ \mu_{sh} = \frac{\eta \left[ 1 + C_{a_{sh}}^2 \left( \lambda_1 \lambda_2 - \frac{1}{3} \mu_1 \mu_2 \right) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \]  

(4.24)

\[ N_{1_{sh}} = \frac{\eta C_{a_{sh}} \left[ 2 \left( \lambda_1 - \lambda_2 \right) + \frac{2}{3} \mu_1 C_{a_{sh}}^2 \left( \mu_1 \lambda_2 - \mu_2 \lambda_1 \right) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \]  

(4.25)

\[ N_{2_{sh}} = \frac{\eta C_{a_{sh}} \left[ \mu_1 - \mu_2 + \lambda_2 - \lambda_1 + \frac{1}{3} C_{a_{sh}}^2 \left( 3 \lambda_1 - \mu_1 \right) \left( \mu_1 \lambda_2 - \mu_2 \lambda_1 \right) \right]}{1 + C_{a_{sh}}^2 \left( \lambda_1^2 - \frac{1}{3} \mu_1^2 \right)} , \]  

(4.26)

\[ \mu_{pe} = \frac{\eta \left( 1 - \frac{1}{3} \mu_1 \mu_2 C_{a_{pe}}^2 \right)}{1 - \frac{1}{3} \mu_1^2 C_{a_{pe}}^2} , \]  

(4.27)

\[ N_{pe} = \frac{4 \eta C_{a_{pe}} \left( \mu_1 - \mu_2 \right)}{1 - \frac{1}{3} \mu_1^2 C_{a_{pe}}^2} . \]  

(4.28)

The mapping between \( C_{a_{sh}} \) and \( C_{a_{pe}} \) in the \( \tau : E \) theory is found implicitly from \( C_{a_{sh}} \sqrt{\mu_{sh}} = C_{a_{pe}} \sqrt{\mu_{pe}} \), and this mapping is used to match the Oldroyd coefficients to database rheological values from simple shear and planar extension at various values of \( \zeta \).

To determine the parameters of the Oldroyd equation, values are tabulated for the two base flows. Since surfactants have the most noticeable effects on drop deformation and rheology at lower viscosity ratios [3], we set the viscosity ratio to \( \lambda = 0.25 \). In Fig. 4.3 we show the shear viscosity for the Langmuir equation of state (solid line) versus the capillary number with parameters \( E_l = 0.5, x_s = 0.3 \), and \( \Lambda = 5000 \). The shear viscosity for a clean drop is also shown (dashed line). When surfactant is added, the shear viscosity increases in magnitude, and also has a more limited range of possible capillary numbers when compared to a clean drop. In the simulations, the maximum capillary number declines with increased surfactant concentration due to numerical limitations, wherein negative values of the interfacial tension are predicted in regions of high surfactant concentration. The maximum capillary number achievable in the simulations declines with the addition of surfactant In Fig. 4.4(a), we show the other two viscometric functions \( N_{1_{sh}} \) and \( N_{2_{sh}} \), and show the two extensiometric functions \( \mu_{pe} \) and \( N_{pe} \) in Fig. 4.4(b). In these figures the Langmuir equation of state is used (solid lines), with the same parameter values as in Fig. 4.3. The rheological functions for clean
Figure 4.3: The shear viscosity $\mu_{sh}$ calculated using the Langmuir equation of state with $E = 0.5$, $x_s = 0.3$, and $\Lambda = 5000$ (solid line), compared with $\mu_{sh}$ for a clean drop with $\sigma = \sigma_{eq}$ (dashed line).

drops (dashed lines) are also shown. The two normal stress differences in Fig. 4.4(a) increase in magnitude when surfactants are added, since the surfactants increase the deformation of the drops at a given capillary number. The values of $\mu_{pe}$ and $N_{pe}$ in Fig. 4.4(b) also increase when surfactant is added (solid lines). The value of $\Lambda$ for this case is large and keeps the surfactant motion in the convection-dominated regime. There is no significant effect to the rheology of the emulsion when $\Lambda$ is further increased above 5000.

It is also interesting to see how the rheology is affected by changes in $x_s$ and $E_l$. Figure 4.5 shows how the shear viscometric functions vary with the parameters $x_s$ and $E_l$. In Fig. 4.5(a), the shear viscosity increases with increasing $x_s$, as a greater surfactant coverage leads to greater deformations. The stress differences $N_{1sh}$ and $N_{2sh}$ initially increase in magnitude with increasing $x_s$, but begin to decline in magnitude when $x_s > 0.3$. The viscometric functions show the same trend in Fig. 4.5 with increasing $E_l$. The increase in the viscometric values is again due to increased deformation caused by an increase in $E_l$. The decline in magnitude of the normal stress differences when $E_l > 0.4$ is unclear, but will be investigated in future work.
Figure 4.4: The two base flows for the generalized Oldroyd model with a viscosity ratio of $\lambda = 0.25$ obtained using the Langmuir equation of state with $E_l = 0.5$, $x_s = 0.3$, and $\Lambda = 5000$ (solid lines) compared with the results for a clean drop (dashed lines) with $\sigma = \sigma_{eq}$; (a) shows the two viscometric functions $N_1^{sh}$ and $N_2^{sh}$ from simple shear and (b) shows the two extensiometric functions from planar extension.

Figure 4.5: The three viscometric quantities at a viscosity ratio of $\lambda = 0.25$ using the Langmuir equation of state at $\Lambda = 5000$. Figure (a) varies the initial surface coverage $x_s$ with $E_l = 0.5$ and (b) varies the elasticity parameter $E_l$ with $x_s = 0.3$. 
Figure 4.6: The Oldroyd coefficients vs. $\zeta$ calculated from the base flows in Fig. 4.4, which were calculated using the Langmuir equation of state with $E_l = 0.5$, $x_s = 0.3$, $\Lambda = 5000$, and $\lambda = 0.25$ (solid lines). The Oldroyd coefficients for a clean drop (dashed lines) are also given for comparison. The $c$ superscript on the $\lambda_1$ and $\eta$ parameters indicates the parameters for a clean drop.

Once the rheological functions of the two base flows are calculated, the five unknown parameters $\lambda_1$, $\mu_1$, $\lambda_2$, $\mu_2$, and $\eta$ are determined by solving the five nonlinear equations (4.24)–(4.28). To eliminate difficulties with the choice of an initial approximation to the Oldroyd coefficients, many steepest descent iterations are first performed to localize the solution, followed by just a few Newton-Raphson iterations. The nondimensional Oldroyd coefficients (based on calculation using the Langmuir equation of state) are shown in Fig. 4.6 for the same parameters as in the above example with $E_l = 0.5$, $x_s = 0.3$, $\lambda = 0.25$, and $\Lambda = 5000$ (solid lines). The Oldroyd coefficients for a clean drop at a viscosity ratio of $\lambda = 0.25$ are also given for comparison (dashed lines). All the coefficients increase in magnitude when surfactant is added to the drop. While all the parameters contribute to different terms in the generalized Oldroyd equation (i.e., all remain nonzero over the entire range of $\zeta$, besides the parameter $\mu_1$ for a clean drop at one value of $\zeta$), the parameters $\lambda_1$ (the relaxation time) and $\eta$ (the effective viscosity) have a greater magnitude than the other coefficients, and thus have a greater significance in determining the stress. The parameter $\eta$ is shown
to increase slightly with increasing $\zeta$, indicating a slight tension-thickening characteristic of the model. The Oldroyd parameters for a drop in the presence of surfactants also have a slightly more limited range in $\zeta$, when compared to the parameters calculated for a clean drop. This is due to a numerical limitation, in which the simulation is stopped when a negative interfacial tension is calculated; the more limited range is not due to the difference in the critical capillary numbers.

4.5. Validation of the generalized Oldroyd model

In this section, the generalized Oldroyd model is validated for dilute emulsions in the presence of surfactants. The intrinsic stress is calculated in two types of flow using the generalized Oldroyd model, and the results are compared to exact calculations from the BI equation. Planar mixed flow is analyzed in subsection 4.5.1, and flow between two eccentric spheres is analyzed in subsection 4.5.2.

4.5.1 Planar mixed flow

The coefficients shown in Fig. 4.6 were used to predict the rheological functions in planar mixed (PM) flow. This flow provides a test to validate the generalized Oldroyd model by predicting the rheology and comparing the results to calculations from the BI Eq. (4.1). In Fig. 4.7, the stress parameters $\nu_{ij} = \frac{\tau_{ij}}{\mu_e \dot{\gamma}_{pm}(1 + \chi)}$ are shown for $\chi = 0.5$, with $\lambda = 0.25$, $E_l = 0.5$, $x_s = 0.3$, and $\Lambda = 5000$, using the Langmuir equation of state. Results are shown only for the Langmuir equation of state, since this equation is more stable over a larger range of the flow invariant $\zeta$ than the other equations of state (see Fig. 4.2). The present method (circles) agrees very well with the BI equation (solid lines), indicating that the generalized Oldroyd equation provides an accurate prediction of the stress for PM flows. The BI calculations are exact, but computationally expensive. Although the generalized Oldroyd model only approximates the stress, it is much more efficient than the BI equation.
and can still be applied to complex flow situations.

The limited range of the two base flows also limits the range of the generalized Oldroyd equation. The range of the base flows is limited by the critical capillary number, above which the drop does not reach a steady shape, but deforms continuously. When surfactants are present, the range can be more limited to lower capillary numbers when the equation of state predicts negative values of the interfacial tensions. This upper limit restricts the range of $\zeta$. However, in PM flow, the generalized Oldroyd model does extend nearly the whole range of $\zeta$ when using the Langmuir equation of state, where the model predicts accurately up to $Ca = 0.18$, close to the critical capillary number of $Ca_{cr} = 0.20$.

### 4.5.2 Flow between two eccentric spheres

To further validate the generalized Oldroyd equation, a Lagrangian-unsteady flow field is evaluated in a fluid contained between two eccentric spheres. The flow between the eccentric spheres is induced by the rotation of the smaller sphere inside the stationary larger sphere.
Figure 4.8: Model of two eccentric spheres, with the larger sphere of radius $b$ and the smaller sphere of radius $a$. A fluid between the spheres has an induced velocity caused by the rotation $\mathbf{\Omega} = (0, \Omega, 0)$ about the $x_2$ axis in the coordinate system centered at $O_2$.

The two spheres are shown in Fig. 4.8, where the smaller sphere has a radius of $a$ with its center at $O_2$ and the larger sphere has a radius of $b$ with its center at $O_1$. The smaller sphere rotates at an angular velocity $\Omega$ about the $x_2$ axis centered at $O_2$.

The velocity everywhere in the flow field is evaluated by using Lamb’s general series; positive-order solid harmonics are used to evaluate the velocity for the larger sphere and negative-order solid harmonics are used to evaluate the velocity for the smaller sphere. For the velocity $\mathbf{v}_1$ centered at $O_1$ of the larger sphere, Lamb’s regular series is given as [14]:

$$\mathbf{v}_1 = \sum_{n=1}^{\infty} \left[ \nabla \times \left( R_1 \chi_n^{(1)} \right) + \nabla \Phi_n^{(1)} + \frac{(n + 3) R_1^2 \nabla p_n^{(1)}}{2(n + 1)(2n + 3)} - \frac{n R_1 p_n^{(1)}}{(n + 1)(2n + 3)} \right], \quad (4.29)$$
where the solid spherical harmonics $p_n$, $\Phi_n$, and $\chi_n$ are defined as:

$$
p_n^{(1)} = \sum_{n=1}^{\infty} A_n^{(1)} \left( \frac{R_1}{b} \right)^n P_n^1(\cos \theta_1) \cos \varphi ,
$$

$$
\Phi_n^{(1)} = \sum_{n=1}^{\infty} B_n^{(1)} \left( \frac{R_1}{b} \right)^n P_n^1(\cos \theta_1) \cos \varphi ,
$$

$$
\chi_n^{(1)} = \sum_{n=1}^{\infty} C_n^{(1)} \left( \frac{R_1}{b} \right)^n P_n^1(\cos \theta_1) \sin \varphi .
$$

In Eqs. (4.30), $P_n^1$ are the associated Legendre polynomials with $m = 1$, and $A_n^{(1)}$, $B_n^{(1)}$, and $C_n^{(1)}$ are the coefficients associated with the positive-order solid harmonics. For the velocity $v_2$ centered at $O_2$ of the smaller sphere, Lamb’s singular series is used with negative-order solid harmonics:

$$
v_2 = \sum_{\nu=1}^{\infty} \left[ \nabla \times \left( R_2 \chi_{-(\nu+1)}^{(2)} \right) + \nabla \Phi_{-(\nu+1)}^{(2)} - \frac{(\nu - 2) R_2^2 \nabla p_{-(\nu+1)}^{(2)}}{2\nu(2\nu - 1)} + \frac{(\nu + 1) R_2^2 p_{-(\nu+1)}^{(2)}}{\nu(2\nu - 1)} \right].
$$

The solid spherical harmonics of order $-(\nu + 1)$ are given as:

$$
p_{-(\nu+1)}^{(2)} = \sum_{\nu=1}^{\infty} A_{-(\nu+1)}^{(2)} \left( \frac{a}{R_2} \right)^{\nu+1} P_{\nu}^1(\cos \theta_2) \cos \varphi ,
$$

$$
\Phi_{-(\nu+1)}^{(2)} = \sum_{\nu=1}^{\infty} B_{-(\nu+1)}^{(2)} \left( \frac{a}{R_2} \right)^{\nu+1} P_{\nu}^1(\cos \theta_2) \cos \varphi ,
$$

$$
\chi_{-(\nu+1)}^{(2)} = \sum_{\nu=1}^{\infty} C_{-(\nu+1)}^{(2)} \left( \frac{a}{R_2} \right)^{\nu+1} P_{\nu}^1(\cos \theta_2) \sin \varphi ,
$$

where $A_{-(\nu+1)}^{(2)}$, $B_{-(\nu+1)}^{(2)}$, and $C_{-(\nu+1)}^{(2)}$ are the associated coefficients. No-slip boundary conditions are applied on the larger sphere, while the inner sphere rotates with angular velocity $\Omega$ about the $x_2$ axis centered at $O_2$. In solving for the flow field, the negative-order solid harmonics are re-expanded from point $O_2$ to point $O_1$ to satisfy the no-slip condition on the stationary larger sphere, and the positive-order solid harmonics are re-expanded from point $O_1$ to point $O_2$ to satisfy the no-slip boundary conditions on the smaller sphere which rotates.
at an angular velocity of $\Omega = (0, \Omega, 0)$. A method similar to that presented by Zinchenko and Davis [15] is employed to calculate the re-expansions between the two origins. The first re-expansion from point $O_2$ to point $O_1$ is carried out with the formula

$$R_2^{-(\nu+1)} P_{\nu}^1(\cos \theta_2) = \sum_{n=\nu}^{\infty} \frac{(-1)^{(n+\nu)} d^{(n-\nu)} (n-1)!}{(n-\nu)! (\nu-1)!} R_1^{-(\nu+1)} P_{n}^1(\cos \theta_1) ,$$  \hfill (4.33)

where $d$ is the distance between the two origins $O_1$ and $O_2$. The second re-expansion from point $O_1$ to point $O_2$ is carried out with the formula

$$R_1^\nu P_{\nu}^1(\cos \theta_1) = \sum_{\nu=1}^{n} \frac{(-1)^{(n+\nu)} d^{(n-\nu)} (n+1)!}{(n-\nu)! (\nu+1)!} R_2^\nu P_{\nu}^1(\cos \theta_2) .$$  \hfill (4.34)

After applying the boundary conditions, a large system of linear of equations results for the coefficients of the solid harmonics ($A_{n}^{(1)}$, $B_{n}^{(1)}$, $C_{n}^{(1)}$, $A_{-(\nu+1)}^{(2)}$, $B_{-(\nu+1)}^{(2)}$, and $C_{-(\nu+1)}^{(2)}$). The number of linear equations to be solved depends on the maximum value of $n$ in Lamb’s series, set at $N_{max} = 300$ in this work. The number of coefficients is equal to $6 \times N_{max}$, and are solved by standard Gaussian elimination. Once the coefficients are calculated, the velocity profile is evaluated as a sum of contributions of Eqs. (4.29) and (4.31). The solution is validated by comparison to results from O’Neill and Majumdar [16].

The streamlines are determined using a second-order Runge-Kutta scheme. The streamlines in the $x_2 = 0$ plane (at origin $O_1$) are shown in Fig. 4.9(a) for $a/b = 0.6$ and minimum distance between the spheres $\epsilon = 0.1$. In this plane, $\varphi = 0$ at every point along the streamlines. A drop (with $a_d \ll b$) is initially placed at the point $x_o = (0, 0, 0.9604)$ (shown as a point in Fig. 4.9) and the intrinsic stress is calculated as the drop is advected along the streamline with $Ca_{ecc} = \Omega \mu_e a_d / \sigma = 0.18$. The drop is small in comparison to the sphere radius of the large sphere, so that the drop follows the streamline and is uniformly subject to the local velocity gradient. Figures 4.9(b)–(d) show the stress components $\nu_{ij} = \tau_{ij} / (\mu_e \Omega)$ vs. the distance along the streamline $s/b$. The generalized Oldroyd method (dashed lines) is used to predict the intrinsic stress, and the stress components are compared to the exact
Figure 4.9: Streamlines between two eccentric spheres, with $a/b = 0.6$. The minimum distance between the spheres is $\epsilon = 0.1$. The small sphere rotates around the $x_2$ axis centered at $O_2$ at angular velocity $\Omega$. The streamlines shown in (a) are in the $x_2 = 0$ plane. The intrinsic stress components for a drop starting at $x_0 = (0, 0, 0.9604)$ are shown in (b)–(d) vs. the distance traveled along the streamline $s/b$, with $\nu_{ij} = \tau_{ij}/\mu_s \Omega$. The exact results (solid lines) and the generalized Oldroyd model (dashed lines) are shown. The calculations use the Langmuir equation of state with $E_l = 0.5$, $x_s = 0.3$, $\Lambda = 5000$, and $\lambda = 0.25$. The results for clean drops are also shown (dotted lines).
BI results (solid lines). The BI results for a clean drop are also shown (dotted lines). The generalized Oldroyd method is accurate along the streamline when the effective capillary number is low. In regions of higher effective capillary numbers (closer to the smaller sphere where the velocity gradients are larger), the stresses predicted by the generalized Oldroyd equation are less accurate when compared to the exact BI equation.

It is also of interest to validate the generalized Oldroyd equation on a streamline where \( \varphi \neq 0 \), as shown in Fig. 4.10. A drop is placed in one of these streamlines at \( x_o = (0.5, 0.4, 0.7) \) (shown in Fig. 4.10) and the intrinsic stress is calculated along this streamline. Figure 4.11 shows four components of the stress vs. the distance traveled along the streamline \( s/b \), showing the results from both the BI equation (solid lines) and the generalized Oldroyd equation (dashed lines). The BI results for a clean drop are also shown (dotted lines). The stress components \( \nu_{11}, \nu_{13}, \) and \( \nu_{33} \), shown in Figs. 4.11(a), (c), and (d), respectively, are accurately predicted by the generalized Oldroyd equation, except in regions where the effective capillary number is high (closer to the small sphere). The loss of accuracy
Figure 4.11: Stress components shown between two eccentric spheres along one of the streamlines shown in Fig. 4.10. The stress components shown are (a) $\nu_{11}$, (b) $\nu_{12}$, (c) $\nu_{13}$, and (d) $\nu_{33}$. A drop is placed at the point $x_0 = (0.5, 0.4, 0.7)$ and the stress components $\nu_{ij} = \tau_{ij}/\mu_e\Omega$ are calculated vs. the distance traveled along the streamline $s/b$. The calculations use the Langmuir equation of state with $E_l = 0.5$, $x_s = 0.3$, $\Lambda = 5000$, and $\lambda = 0.25$. The stress components for a clean drop are also shown (dotted lines).
of the Oldroyd equation in this region could be a contribution of two different factors: the presence of higher velocity gradients near the small sphere and the higher rate of change of the velocity gradient as the drop approaches and moves away from the small sphere. It would be valuable to run additional tests to distinguish which of these two causes produces the greatest effect on the accuracy of the generalized Oldroyd model. The stress component $\nu_{12}$ shown in Fig. 4.11(b) is smaller in magnitude than the other three components, and the generalized Oldroyd equation is more accurate in predicting $\nu_{12}$ over the entire streamline. Overall, the generalized Oldroyd model is shown to accurately predict the stress components in this Lagrangian-unsteady case, especially at lower values of the capillary number.

4.6. Concluding Remarks

In this work, simulations to determine the rheology of dilute emulsions in the presence of surfactants were performed in shear, planar extensional, and planar mixed flows, as well as the Lagrangian-unsteady case of flow between eccentric spheres. The physical problem is pertinent because of the widespread use of surfactants in industry, and the frequency of natural surfactants found in the environment. A rheological constitutive equation was developed for dilute emulsions in the presence of surfactants, based on the generalized Oldroyd equation, which can be used to predict the stress in flows with arbitrary kinematics. The parameters for this model were tabulated from the rheological functions of simple shear and planar extension (the two base flows), following the procedure in Martin et al. [6]. To determine the rheological functions of the base flows, the boundary-integral (BI) equation was used to calculate the evolution of the drop shape with non-uniform interfacial tension. The convection-diffusion equation was then used to calculate the distribution of surfactant on the drop’s surface. A method developed by Klaseboer et al. [9] was applied to remove the singularity in the BI equation that appears when surfactants are added to the drop’s surface. To validate the generalized Oldroyd equation, rheological predictions were carried
out for planar mixed flow and flow between eccentric spheres. The present method is found
to be an accurate model for the case of dilute emulsions in the presence of surfactants when
applied to planar mixed flows. For eccentric spheres, the model deviates in regions of large
velocity gradients, but is shown to be very accurate in regions of low capillary numbers.

One disadvantage of the equations of state is that they predict negative interfacial tension
when the local surfactant concentration is high; future work can explore methods to mitigate
this effect. Extending the range of the equations of state will also extend the range of the
generalized Oldroyd model. The Langmuir equation is shown to be valid for a greater range
of capillary numbers than the linear or Frumkin equations of state.

4.7. Appendix 4A

The singularity in the first integral of Eq. (4.1) presents a difficult task, since $\Delta \mathbf{f}(\mathbf{x})$ in
Eq. (4.2) contains both normal and tangential components. To remove this singularity, we
expand the first integral on the right-hand side of Eq. (4.1) as

$$\int_S \{[f_n(\mathbf{x})\mathbf{n}(\mathbf{x}) + f_t(\mathbf{x})] \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x = \int_S \{f_n(\mathbf{x})\mathbf{n}(\mathbf{x}) \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x$$

$$+ \int_S \{f_t(\mathbf{x}) \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x. \quad (4A.1)$$

This operation separates the normal and tangential components of $\Delta \mathbf{f}(\mathbf{x})$ into two integrals
(with each one still containing a singularity). The singularity can be removed from the first
integral on the right-hand side of Eq. (4A.1) by subtracting $f_n(\mathbf{y})$ from $f_n(\mathbf{x})$ and adding
$f_n(\mathbf{y})$ back in a separate integral:

$$\int_S \{f_n(\mathbf{x})\mathbf{n}(\mathbf{x}) \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x = \int_S \{[f_n(\mathbf{x}) - f_n(\mathbf{y})] \mathbf{n}(\mathbf{x}) \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x$$

$$+ \int_S \{f_n(\mathbf{y})\mathbf{n}(\mathbf{x}) \cdot \mathbf{G}(\mathbf{r}) \} \, dS_x. \quad (4A.2)$$
In Eq. (4A.2), there is no longer any singularity in the first integral on the right-hand side as \( x \rightarrow y \), and the second integral on the right-hand side is equal to zero. The singularity from the second integral on the right side of Eq. (4A.1) can be removed by using the relationship derived from the method of Klaseboer et al. [9]:

\[
\int_S f_i(x) \cdot G(r) dS_x = \int_S [f_i(x) - \Sigma_n(x, y)] \cdot G(r) dS_x + \int_S w_1(x, y) \cdot [T(r) \cdot n(x)] dS_x ,
\]

(4A.3)

where

\[
\Sigma_n(x, y) = f_i(y) [n(x) \cdot n(y)] + n(y) [f_i(y) \cdot n(x)] \quad \text{and} \quad (4A.4)
\]

\[
w_1(x, y) = f_i(y) [r \cdot n(y)] . \quad (4A.5)
\]

Combining the results of Eqs. (4A.2)-(4A.5), Eq. (4A.1) is written as:

\[
\int_S \{[f_n(x)n(x) + f_i(x)] \cdot G(r)\} dS_x = \int_S F \cdot G(r) dS_x + \int_S [r \cdot n(y)] f_i(y) \cdot [T(r) \cdot n(x)] dS_x , \quad (4A.6)
\]

where

\[
F = f_i(x) - f_i(y) [n(x) \cdot n(y)] - n(y) [f_i(y) \cdot n(x)] + n(x) [f_n(x) - f_n(y)] . \quad (4A.7)
\]

In this way, the singularity in the first integral of Eq. (4.1) is removed.

4.8. References


Chapter 5: Concluding Remarks

In this dissertation, a generalized Oldroyd constitutive model has been developed and applied to dilute suspensions. The three types of suspensions considered in this work are (i) dilute emulsions of deformable drops, (ii) dilute suspensions of rigid spheroids subject to Brownian rotations, (iii) and dilute emulsions in the presence of surfactants. The development of the generalized Oldroyd model consisted of solving the equations of motion for the suspensions, and using the simulation results to determine the five rheological functions of the base flows: simple shear and planar extension (PE). These five rheological functions were used to calculate the five parameters of the generalized Oldroyd equation. The validation of the generalized Oldroyd equation consisted of predicting the deviatoric intrinsic stress in a variety of different flows from the model and comparing them to exact results from the simulations. The simulations are based on the solution of the equations of motion on the micro-scale, i.e., they take into account the microstructure of the droplets and rigid particles (where, in the limit of low Reynolds number, they result in the exact solutions for these cases). These simulations, though, are computationally expensive, whereas constitutive models, such as the generalized Oldroyd equation, require less computational effort to predict the stresses. The present work demonstrates the wide applicability of the generalized Oldroyd model in many kinematic conditions. A summary of the key findings from each of the three preceding chapters in this dissertation is given in Secs. 5.1–5.3. In Sec. 5.4, conclusions are made concerning the applicability, impact, and possible areas for extension of the generalized Oldroyd model. Recommendations for future work are outlined in Sec. 5.5, and final remarks are presented in Sec. 5.6.
5.1. Summary of Chapter 2

In Chapter 2, the generalized Oldroyd equation was introduced as a general constitutive model for non-Newtonian fluids. As a starting point for the development of the constitutive model, the equation developed by Oldroyd [1] was used [Eq. (2.9)]. When the Oldroyd equation is written for the deviatoric intrinsic stress, there are five unknown material parameters. In the development of this model, these five material parameters are allowed to be functions of a flow invariant. It is necessary that the material parameters are functions of a flow invariant, since flow invariants remain unchanged upon any rotation of the coordinate system. The two invariants of the flow that were chosen in this work are the second invariant of the rate-of-strain tensor (the “I₂ theory”) and the energy dissipation rate (the “τ : E theory”).

To solve for the five parameters from the generalized Oldroyd equation, five rheological functions are needed. In this work, the rheological functions were found from simple shear and PE. There are three rheological functions from simple shear flow: \( \mu_{sh}, N_{1}^{sh}, \) and \( N_{2}^{sh} \); two additional rheological functions come from PE flow: \( \mu_{pe} \) and \( N_{pe} \). These provide the five functions needed to determine the Oldroyd parameters as functions of either \( \tau : E \) (for the “\( \tau : E \) theory”) or \( I_2(E) \) (for the “I₂ theory”). The “\( \tau : E \) theory” was used more extensively in this work, since it was found to be more accurate than the “I₂ theory” in a number of cases.

In Chapter 2, the rheological functions for the base flows were determined for a dilute emulsion of deformable drops using the boundary-integral (BI) Eq. (2.28). In the dilute limit, this was accomplished by placing a single drop in either simple shear or PE flow and allowing the drop to reach a steady shape, where it no longer deforms. The intrinsic stress of the fluid was then calculated using Batchelor’s method [2]. Once the rheological functions were tabulated for the base flows, the parameters for the generalized Oldroyd equation were calculated by matching the rheological values of simple shear and PE at equal values of the flow invariant \( \tau : E \). The Oldroyd parameters were determined for three viscosity ratios:
A comment concerning the above procedure is briefly mentioned here. The parameters of the generalized Oldroyd equation were calculated based on steady-state values of the stress (in simple shear or PE). It would also be possible to incorporate the transient values of the stress (before the drops reach a steady state) into the calculation of the Oldroyd parameters. In this way, additional data from the simulations could be transferred to the Oldroyd parameters, which may provide a way to capture additional memory or elastic effects into the resulting constitutive equation. This could prove an interesting study for future investigations.

After the generalized Oldroyd parameters were calculated (from the steady state values), the model was validated on several different flows, different than the two base flows of simple shear and PE. These flows include planar mixed (PM) flow, uniaxial extension/compression, flow in a rectangular cavity with a moving wall, and Stokes flow around a macroscopic sphere. For PM flow and uniaxial extension/compression, a single drop was brought to a steady shape and the intrinsic stress was calculated using the BI equation. The exact intrinsic stress calculated from the BI equation was then compared to the predictions from the generalized Oldroyd model (2.9) and the small-deformation model of Frankel and Acrivos [3]. The generalized Oldroyd equation was found to be accurate in predicting the intrinsic stress for both steady PM and uniaxial extensional/compressional flows. The Frankel and Acrivos (FA) model is accurate in these cases also, though it becomes less accurate at higher capillary numbers for which the deformation is larger.

In Chapter 2, the test cases of flow in a rectangular cavity with a moving wall and Stokes flow around a macroscopic sphere were used as two examples of Lagrangian-unsteady flows. A single drop was placed along a streamline and the intrinsic stress (the extra stress due to the presence of the drop) was calculated along one of the streamlines. For the flow in a cavity with a moving wall, both the generalized Oldroyd equation and the FA model predict the stress accurately, with both having minor deviations from the exact BI results in regions
of large velocity gradients. For Stokes flow around a macroscopic sphere, the generalized Oldroyd equation accurately predicts the intrinsic stress, when compared to the exact results from the BI equation. The FA model also is accurate in this case in regions far from the sphere. Near the equator of the sphere, the FA model shows slight discrepancies in predicting the intrinsic stress when compared to the BI solution. The work in Chapter 2 demonstrates that the parameters of the generalized Oldroyd equation could be readily evaluated from the two base flows of simple shear and PE. It was also shown to be an accurate model for predicting the intrinsic stress in a variety of arbitrary flows, both Lagrangian-steady and unsteady. Chapter 2 was originally published in the *Journal of Rheology*, with co-authors Alexander Zinchenko and Robert Davis [4].

### 5.2. Summary of Chapter 3

For Chapter 3, the generalized Oldroyd equation was developed for another suspension, different from a dilute emulsion of deformable drops. The suspension studied in Chapter 3 consisted of rigid spheroids subject to Brownian rotations. To apply the generalized Oldroyd model to this suspension, the stress of the system was calculated by solving the Fokker-Planck-Smoluchowski (FPS) Eq. (3.2) along with Jeffery’s solution (3.1) for Stokes flow around an ellipsoid. The FPS equation was solved using spherical harmonics, and the intrinsic stress for the system was then calculated. Additionally, two closure approximations (constitutive models for rigid spheroids) were also examined. The Hinch and Leal (HL) [5] and Bingham [6] closure models were used to predict the intrinsic stresses and compared to the solutions of the FPS equation and the generalized Oldroyd model.

Similar to the approach in Chapter 2, the generalized Oldroyd model was applied to this system by determining the rheological functions of the two base flows, simple shear and PE, at various Péclet numbers and aspect ratios (both prolate and oblate ellipsoids). The parameters for the generalized Oldroyd equation were determined and validated in a
number of arbitrary kinematic conditions. The test cases included PM flow, uniaxial extension/compression, time-dependent PE flow, and flow around a macroscopic sphere at a moderate Reynolds number. For the steady-state PM flow, the generalized Oldroyd equation predicts the intrinsic stress accurately, with some deviations at higher Péclét numbers. The HL model is very accurate for all the intrinsic stress components. Both the generalized Oldroyd model and the HL model are accurate for prolate spheroids in uniaxial extension/compression, but the Oldroyd model is less accurate for oblate spheroids while the HL model remains accurate for oblate spheroids (see Fig. 3.6).

The two cases in Chapter 3 of Langrangian-unsteady dynamics are time-dependent PE flow and flow around a macroscopic sphere at a moderate Reynolds number. For the case of time-dependent PE flow, the generalized Oldroyd model is accurate, with some discrepancies at the maxima/minima of the stress components. The HL model is again very accurate in this case, with close agreement to the FPS solution. The flow around a macroscopic sphere presents a case where both an open and closed trajectory are present, with the closed trajectory being in the eddy zone in the wake of the sphere. The generalized Oldroyd equation is accurate in predicting the stress components for the flow around a sphere, with more discrepancies close to the equator of the sphere when compared to the solution of the FPS equation. Accuracy of the generalized Oldroyd equation was shown to improve at lower values of the Péclét number over the sphere [with $Pe_{sph} = U_\infty/(R_oD_R)$, see Chapter 3 for details]. The generalized Oldroyd equation is also very accurate in the closed trajectory in the eddy zone of the sphere, since the value of effective Péclét number remained low in this region. The HL and Bingham closure approximations were shown to be very accurate at predicting the intrinsic stresses over the sphere. Overall, Chapter 3 demonstrates the generalized Oldroyd model could be applied to a suspension much different from dilute emulsions of deformable drops. Chapter 3 was originally published in the *Journal of Rheology*, with co-authors Alexander Zinchenko and Robert Davis [7].
5.3. Summary of Chapter 4

Chapter 4 revisits dilute emulsions, and considers the case when surfactants are present on the surface of the drops. The addition of surfactants to the emulsion lowers the interfacial tension of the drops. Because the surfactant concentration can vary along the surface of the drop, the local interfacial tension varies likewise. To solve the rheological functions for the base flows, the BI Eq. (4.1) was employed, as in Chapter 2. The variable interfacial tension makes the singularity in the first integral of the BI Eq. (4.1) more difficult to evaluate as $x \to y$. This singularity was regularized by a method of Klaseboer et al. [8].

A relationship between the surfactant concentration and the interfacial tension, known as a surface equation of state, is also necessary to solve the BI equation when surfactants are present. Three surface equations of state were evaluated: the linear, Langmuir, and Frumkin equations of state. Using the Langmuir of state, the rheological functions for simple shear and PE were determined, along with the material parameters of the generalized Oldroyd equation. To validate the generalized Oldroyd model, the rheology of a dilute emulsion in the presence of surfactants was determined in PM flow using the Langmuir equation of state, and shown to yield accurate results. The linear and Frumkin equations of state were also used to determine the intrinsic stress components in PM flow, and were shown to have a more limited range in capillary numbers than the Langmuir equation of state. The generalized Oldroyd equation was also validated with the Lagrangian-unsteady case of flow between eccentric spheres, where the inner sphere rotates at a constant rate. The velocity profile for this solution was calculated using spherical harmonics. The generalized Oldroyd constitutive model was shown to yield accurate predictions for the intrinsic stresses in this case. The work outlined in Chapter 4 is currently being prepared for publication.
5.4. General conclusions and recommendations concerning the generalized Oldroyd model

The generalized Oldroyd model was shown to be valid for a wide range of fluid systems and a variety of kinematics. For a given complex fluid, the application of the generalized Oldroyd equation requires the evaluation of the stresses of two base flows. In this work, the two base flows chosen were simple shear and planar extensional flow. It is also possible to use planar mixed flow as a base flow in place of simple shear, since it provides three independent rheological functions that can replace the rheological functions $\mu_{sh}, N_{1}^{sh}$, and $N_{2}^{sh}$ from simple shear. The five Oldroyd parameters, $\mu_1$, $\lambda_1$, $\mu_2$, $\lambda_2$, and $\eta$, are functions of an invariant of the flow, either the second invariant of the rate-of-strain tensor $I_2(E)$ or the energy dissipation rate $\tau : E$.

Although the generalized Oldroyd equation can be applied to a wide range of complex fluids, the stress for the base flows must be calculated in every condition of interest. The rheological functions can be obtained from either simulations or experiments. The approach in this work has relied on simulations, where the rheological properties of a complex fluid can be readily calculated for a variety of different microstructural conditions. For example, for the case of dilute emulsions of deformable drops in Chapter 2, a large range of viscosity ratios can be investigated with little extra effort once the framework for the simulation is in place. Likewise, in Chapter 3, many different aspect ratios of rigid spheroids could be considered in the simulations. It would be a more time-intensive task to set up experiments to determine the rheology for a range of properties of the fluid. If the properties do not vary much in the complex fluid (i.e., the aspect ratio of the rigid rods remains the same), experimental data could be reliably used to evaluate the parameters for the generalized Oldroyd equation for a specific condition.

The range of applicability of the generalized Oldroyd equation is, in some cases, limited to the lower range of the flow invariants. For example, for dilute emulsions, simple shear flow
and PE flow reach critical capillary numbers, where the drops do not reach steady shapes and continue to deform. This limitation sets an upper bound when evaluating the generalized Oldroyd coefficients. For example, in Chapter 2, the upper limit of $\zeta = a \sqrt{\mu_e (\tau : \mathbf{E})}/\sigma$ is approximately 0.368 for the viscosity ratio of $\lambda = 1$. This restriction limited the range of applicability of the generalized Oldroyd equation to some of the test flows that were investigated.

It was shown in Chapter 3 that in some cases the generalized Oldroyd equation does not perform as well as models derived for a specific microstructure of a suspension (in this case, for suspensions of rigid spheroids). The closure approximations described in Chapter 3 are very accurate for many different aspect ratios, and are shown to be useful for predicting the stress for a wide range of kinematic conditions. However, the drawback of these closure approximations is that they can be applied only to specific types of complex fluids (suspensions of rigid spheroids), and it would be difficult to extend them to apply to concentrated systems with strong hydrodynamical interactions. The generalized Oldroyd model, on the other hand, can be applied to a variety of non-Newtonian fluids. It can also be extended to concentrated suspensions (as was done by Zinchenko and Davis [9]).

5.5. Areas of future research

The generalized Oldroyd equation is shown to be a useful constitutive tool for predicting the stress in a variety of complex fluids. This dissertation focused on the derivation of the generalized Oldroyd model and its application to three types of suspensions: dilute emulsions of deformable drops, dilute suspensions of rigid spheroids subject to Brownian rotations, and dilute emulsions in the presence of surfactants. These suspensions were subject to a range of kinematic conditions (both Lagrangian-steady and unsteady) and the generalized Oldroyd equation was utilized to predict the particle contribution to the stress. In the future, the application of the generalized Oldroyd model to a variety of other types of fluids may be
of interest, especially concentrated suspensions with strong hydrodynamical interactions. Zinchenko and Davis [9] have applied the generalized Oldroyd equation to concentrated emulsions, and it would also be of interest to apply the model to concentrated suspensions of rigid spheroids. The calculation of the base flows for any complex fluid is sufficient to determine the parameters for the generalized Oldroyd equation, and provides a way to predict the stress for a range of kinematics.

Further questions also arise about the best way to solve for the generalized Oldroyd parameters. It may be attractive, in some cases, to use PM flow as a base flow, in place of simple shear flow. This possibility brings about the choice for the selection of the optimal $\chi$-parameter value (where $-1 < \chi \leq 1$). The choice for the optimal value of $\chi$ may vary depending on the fluid being investigated and the type of kinematics being evaluated. The exploration of using PM flow as a base flow for the generalized Oldroyd equation is an area that can be investigated further.

Further work could also be done on discovering ways to extend the range of the generalized Oldroyd equation. For dilute emulsions, the range of the generalized Oldroyd equation was limited by the range of $\zeta$, which was due to the drops breaking up above the critical capillary number. This limitation, of course, restricts the ranges that the generalized Oldroyd equation can be applied. Further methods could be explored to extend the range of the model (such as ways to account for drop breakup in emulsions, as done by Cristini et al. [10] and Windhab et al. [11]).

A further area of study is incorporation of the generalized Oldroyd equation in a program that would solve boundary-value problems. Such a plan is beyond the work of this dissertation, since the boundary-value problems in this work (flow past a macroscopic sphere, flow between two eccentric spheres, etc.) were solved based on the Stokes or Navier-Stokes equations for a Newtonian fluid (as a first approximation for the solution of the streamlines). A non-Newtonian fluid would cause perturbations away from the calculated streamlines. These perturbations would require the equations of motion to be solved based on the non-Newtonian
hydrodynamics of the flow, using the generalized Oldroyd equation as a constitutive model. The resulting system of equations (conservation of momentum, continuity, and constitutive model equations) could be incorporated into a boundary-condition solver (such as a finite element program) and solved using an iterative solver such as the generalized minimum residual (GMRES) method. Work in solving boundary condition problems involving non-Newtonian fluids has been accomplished by Tan and Masuoka [12], who solved the first Stokes’ problem for an Oldroyd-B fluid in porous half space. Khan et al. [13] performed a similar study of some magnetohydrodynamic flows using the Oldroyd-B type constitutive model, by solving boundary-value problems for a flow caused by a rigid plate, a periodic flow between two plates, and Poiseuille flow. Similar studies can be achieved by incorporating the generalized Oldroyd equation into the solution of a specified flow geometry, or by incorporating it in a general program that solves boundary-value problems for arbitrary geometries.

5.6. Final remarks

The formulation of a robust constitutive equation is necessary to model non-Newtonian fluids in a broad range of kinematics. The generalized Oldroyd equation is a robust constitutive model, which has been developed in this work and can be used to predict the Cauchy stress for non-Newtonian fluids. These stresses can be predicted in a range of arbitrary kinematics, based on the rheological functions of two base flows (simple shear and PE). This dissertation has demonstrated the utility of the generalized Oldroyd equation for three fluids: dilute emulsions of deformable drops, suspensions of rigid spheroids subject to Brownian rotations, and dilute emulsions in the presence of surfactants. Further analysis of the generalized Oldroyd equation can also be accomplished by seeking ways to extend its range and accuracy. Overall, the generalized Oldroyd equation was shown to be a robust model that can be further incorporated in solving boundary-value problems in complex geometries.
5.7. References


Bibliography


