A constitutive model for dispersive mixtures

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Abstract

A model for the spatial evolution of a dispersed phase microstructure is developed and combined with a rheological description of the liquid-liquid systems. The former, is accomplished by coupling pre-existing models of coalescence and breakup with the kinematics of mixing processes. The rheological model is based on unifying the theory of the present phenomenological models and by applying the description of the dispersed phase microstructure to remove the adjustable parameters presently in the rheology models.

1 Introduction

There are two general approaches to modeling the evolution of morphology during liquid-liquid mixing. One method uses kinetic equations to describe the evolution of a droplet size distribution [1], effectively embedding the dependence of the process on material parameters and mixing into rates of breakup and coalescence. The other method applies principles from fluid mechanics to predict the drop size based upon the flow and the material parameters of the fluids [2]. Neither of these models predicts the spatial statistics of dispersed phase morphology.

A first step towards understanding the interplay between mixing and breakup/coalescence is the two-zone mixing model of Janssen [2]. Janssen envisions the mixing processes as consisting of weak and strong zones. In weak zones, droplets coalesce, and, in strong zones, droplets extend into filaments and eventually breakup into several smaller droplets. The model gives a good approximation of the morphology in a dispersion. Moreover, it provides a framework for analyzing breakup/coalescence processes. More work is, however, necessary to tie this model with the dynamics of mixing processes which are frequently chaotic and oversimplified by the two-zone mixing model.

One goal of this work is to develop a model for the spatial evolution of dispersed phase microstructure, and to illustrate the physical basis for the breakup and coalescence models incorporated into our overall model. The former is accomplished by coupling the framework of Janssen [2] with tools used to analyze chaotic mixing process. We provide the latter by revisiting much of the earlier work of Janssen [2] from a slightly different perspective. We focus on systems composed of viscous fluids which can be described by the Stokes equations.¹

¹In many applications, the dispersion is rheologically complex, and also further complicated by interfacial phenomena resulting from surfactants or compatibilizers. Some of the influences of viscoelasticity and surfactants are discussed in [2, 3, 4]. Idealizations are however necessary as the problem becomes intractable when all complexities are included. We neglect non-Newtonian effects and interfacial phenomena, thus, highlighting the physics central to coalescence and breakup.
The second goal is the development of a model the macroscopic rheology of liquid-liquid systems. Although a system of two Newtonian fluids is considered, non-Newtonian effects are predicted as a result of the presence of the dispersed phase. We improve upon the Lee-Park model [5] for the rheology of a blend. Our analysis provides further understanding by deriving the Lee-Park model with a different approach, and examining the principles on which the theory is based. The Lee-Park model requires prediction of the interfacial area between the two phases with a rather ad hoc kinetic equation. We use our model of liquid-liquid mixing, to determine the interfacial area of the dispersed phase, and, thus, reduce the number of unknowns appearing in the Lee-Park model.

2 Basics of mixing

Kinematics The motion of a passive particle in a flow is described by

$$\frac{dx}{dt} = v(x, t)$$

in which $v(x, t)$ is the Eulerian velocity field, at the position $x$ and time $t$.

The amount of stretching $\beta$ is frequently used to characterize the quality of mixing.

$$\beta \equiv \lim_{L \to 0} \frac{d|l|}{d|L|}$$

where $l$ and $L$ are the present and initial length of the material filament, respectively. The orientation of the filament is given by $m = l/|l|$. The equations describing the stretching and orientation of a material filament are

$$\frac{d \ln(\beta)}{dt} = D : mm$$

and

$$\frac{dm}{dt} = m \cdot [\nabla v - I(D : mm)]$$

respectively, where $D$ is the rate-of-deformation tensor. The stretching efficiency $e_\beta$ is defined as the rate of stretching normalized by a factor proportional to the square root of the local dissipation of energy

$$e_\beta \equiv \frac{D : mm}{\sqrt{D : D}}$$

When $\nabla \cdot v = 0$, i.e. incompressible flow, $e_\beta$ is less than or equal to $\sqrt{1/2}$ in two dimensional flows, or $\sqrt{2/3}$ in three dimensional flows.

The local characterization of a flow can be simplified via linearization. The velocity field with respect to a frame moving with a material element can be written in the form of an expansion as

$$v = x \cdot \nabla v + \text{higher order terms}$$

The velocity gradient tensor, $\nabla v$, defines the nature of the flow. If there exists at least one positive eigenvalue of $\nabla v$, then the flow yields exponential stretching, and is referred to as a strong flow. On the other hand, simple shear flow produces approximately linear stretching and is classified as a weak flow. Other, more rotational flows are also weak.
In complex flows, the mixing may be enhanced by the presence of a “horseshoe map” which produces stretching and folding. Horseshoe maps are indicative of chaos, and produce exponential stretching. An excellent physical picture is provided by the periodic cavity flow [6]. The stretching in the steady cavity flow is linear for long times. However, in the periodic cavity flow, the crossing of streamlines produces folds. The folding leads to doubling in the number of material filaments and, thus, exponential stretching.2

Capillary number The deformation and breakup of an initially spherical drop in a flow is characterized by the capillary number defined as

\[ Ca \equiv \frac{\mu_c \dot{\gamma} R}{\sigma} \]  

(7)
in which \( \mu_c \) is the viscosity of the continuous phase, \( \sigma \) is the interfacial tension, \( R \) is the drop radius, and \( \dot{\gamma} \), referred to as the shear-rate, is \( \sqrt{2D : D} \). Experimental [7] and computational [8] work indicate that when \( Ca \) is less than some critical value, \( Ca_{\text{crit}} \), the droplet reaches a stable ellipsoidal shape. If the capillary number is larger than \( Ca_{\text{crit}} \) then no stable shape exists, and the droplet stretches until the flow is stopped and/or the droplet breaks. A strong flow, which tends to stretch fluid elements, yields a lower \( Ca_{\text{crit}} \) than a flow which is more rotational in nature, like a shear flow.

Drop deformation When \( Ca > \kappa Ca_{\text{crit}} \), where \( \kappa \) is a flow dependent constant (approximately two in shear and about five in planar elongational flows [2]), the droplet stretches as a material element (“affine deformation”) in the bulk flow, while the cross-section, remains circular due to interfacial tension. For \( Ca_{\text{crit}} < Ca < \kappa Ca_{\text{crit}} \) the stretching of a droplet is more complicated. Similar phenomena can also be observed in a more complex flow [9].

The extending fluid filament can be described for long times by

\[ \frac{L}{R_0} \sim \dot{\gamma} t, \text{ and } \frac{R_f}{R_0} \sim (\dot{\gamma} t)^{-1/2} \] 

(8)
in simple shear flow, and by

\[ \frac{L}{R_0} \sim \exp(\dot{\gamma} t), \text{ and } \frac{R_f}{R_0} \sim \exp(-\dot{\gamma} t/2) \] 

(9)
in elongational flow. \( L \) and \( R_f \) are the length and radius of the thread, respectively, \( R_0 \) is the initial radius of the droplet. The long slender filament undergoing this deformation generally breaks up due to capillary forces.

The previous discussion addresses initially slightly deformed droplets, but the initial drop shape and orientation also influence behavior. For instance, Khakhar and Ottino [10] have shown that the resistance to deformation of a low viscosity ratio droplet decreases as it becomes longer and more slender. Very long, low viscosity ratio droplets stretch and rotate as passive fluid elements.

Modes of breakup The breakup of a long slender filament in a quiescent flow differs significantly from breakup of modestly extended droplets, commonly occurring when \( Ca_{\text{crit}} < Ca < \kappa Ca_{\text{crit}} \). The breakup of a filament of fluid is driven primarily by capillary instabilities. The initial growth

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2Principles from chaos theory are already applied in industrial mixing. For example, the baker’s map—an idealization of the horseshoe map—is the basic concept behind static mixers, and time periodicity is applied to enhance the mixing in extruders and stirred tanks.
of the disturbance can be described by linear stability analysis [11], however, its predictions have been shown to be more general [2]. The dimensionless growth rate and dimensionless wavelength of the fastest growing disturbance—termed the dominant growth rate, \( \Omega_m \), and the dominant wavelength, \( \lambda_m \)—are both unique functions of the viscosity ratio [2]. Based on conservation of mass, the average radius, \( R_{\text{ave}} \), of droplets resulting from capillary breakup can be approximated as

\[
R_{\text{ave}} \approx \left( \frac{3}{4} \lambda_m(p) \right)^{1/3} R_f
\]

where \( R_f \) is the initial radius of the filament. The dominant growth rate gives the time until breakup as

\[
t_{\text{break}} \approx \frac{\mu_c R_f}{\sigma \Omega_m(p)} \ln \left( \frac{\sqrt{2/3} R_f}{\alpha_0} \right)
\]

Here, \( \alpha_0 \) is the initial amplitude of the disturbance, which depending upon the conditions may vary from \( 10^{-7} \) to \( 10^{-9} \) m [2]—the lower value obtained by assuming thermal fluctuations of the interface, and the higher observed in experiments.

The breakup of a fluid filament in a linear flow is also dominated by capillary breakup, and can be described by linear stability theory [12]. A detailed analysis of this problem can be found in [2, 9]. The critical radius of a filament in an elongational flow can be approximated by the correlation

\[
R_{\text{crit}} \approx 0.02 \alpha_0^{0.1} \left( \frac{\mu_c \epsilon \beta \gamma}{\sigma} \right)^{-0.9} p^{-0.45}
\]

provided that \( \epsilon \beta \) is relatively constant and positive [9], and \( \mu_c \epsilon \beta \gamma \alpha_0 / \sigma \) is less than some value dependent upon the viscosity ratio [2]. The average drop radius resulting from breakup is

\[
R_{\text{ave}} \approx \left( \frac{3 \pi}{2} \right)^{1/3} R_{\text{crit}}
\]

Long extended filaments also breakup by a mechanism referred to as “end-pinching” [4]. The end of a filament forms a bulbous shape and a neck develops between the bulbous end and the rest of the filament. The neck then thins until the end separates from the filament. After breakup, the process begins again.

The behavior of a modestly extended droplet, \( L/R_0 < 15 \), with \( Ca < \kappa C \alpha_{\text{crit}} \) differs from that of a filament. When \( L/R_0 \) is very small, the droplet will retract into a sphere if the flow is stopped; otherwise, the droplet extends until breakup by one of three mechanisms: end-pinching, “tip-streaming” [4], or “necking” [7], none of which are completely understood. Other mechanisms may also play a role in complex flows or in highly concentrated dispersion. For instance, in complex flows, “fold-pinching” may occur at the bend in a filament created by stretching and folding [9]. And, an interaction between a filament and a droplet, sometimes seen in concentrated dispersions, may result in breakup of the filament [2]. Relatively little is known about these mechanisms of breakup, and our first order approximation assumes that breakup is dominated by capillary breakup and necking.

**Coalescence** A large capillary number implies that breakup is important, for a low capillary number, droplets may come into contact and coalesce. Here, a view of coalescence is provided which allows relatively simple modeling. Coalescence occurs if the film, formed between the two
droplets, slowly thins from $h_0$, the distance at which hydrodynamic interactions first influence the process, to the thickness $h_{crit}$, at which film rupture is inevitable. In pure liquids, $h_{crit}$ is the distance at which attractive van der Waals forces begin to dominate [13]. Thus,

$$h_{crit} \approx \left( \frac{HR_{eq}}{8\pi\sigma} \right)^{1/3}$$  \hspace{1cm} (14)$$

where $H$ is the Hamaker constant, and $R_{eq}$, termed the equivalent droplet radius, is $2R_1R_2/(R_1 + R_2)$, where $R_1$ and $R_2$ are the radii of the colliding droplets. If the film thickness does not decay to $h_{crit}$ during the collision, then the droplets glance off each other and separate in the flow.

The collision frequency, $C$, between randomly distributed droplets of radii $R_1$ and $R_2$ in a shear flow can be approximated with Smoluchowski’s theory [14]

$$C_{12} = \frac{2}{3}n_1n_2\gamma (R_1 + R_2)^3$$ \hspace{1cm} (15)$$
in which $n_1$ and $n_2$ are the concentration of droplets of radii $R_1$ and $R_2$, respectively. The function $C_{12}$ can also be determined for other linear flows [3]; however, equation (15) serves as a reasonable approximation for all flows. The rate of coalescence, $J_{12}$, can be described by

$$J_{12} = E_{12}C_{12}$$ \hspace{1cm} (16)$$
in which, $E_{12}$, is the collision efficiency.

The collision efficiency, $E_{12}$, of rigid droplets is a known analytical function of the viscosity ratio and relative radii of the droplets [15]. When the droplets are not rigid, the collision efficiency may be approximated by

$$E_{12} \approx \exp(-t_{drain}\gamma)$$ \hspace{1cm} (17)$$

where $t_{drain}$ is the time necessary for the film to drain from $h_0$ to $h_{crit}$, and $1/\gamma$ characterizes the time of the collision. The form of $t_{drain}$ is dependent upon the mobility of the interface [13]. For “partially mobile” interfaces, probably the most practical model [2], the time for the film to drain is

$$t_{drain} \approx \frac{\pi \mu_d F^{1/2}}{2(2\pi\sigma/R_{eq})^{3/2}} \left( h_{crit}^{-1} - h_0^{-1} \right)$$ \hspace{1cm} (18)$$
in which $\mu_d$ is viscosity of the droplets or dispersed phase, and $F$ is the force exerted by the flow, driving the droplets together. Other models for film drainage can be found in [2, 3, 13]. Equation (18) for drainage time assumes that $F$ is nearly constant. The force exerted by the flow can be approximated with the Stokes drag as

$$F \approx 6\pi\mu_c\gamma R_{eq}^2$$ \hspace{1cm} (19)$$

Other, more accurate forms of $F$ are available [3, 16], but predictions based on the Stokes drag are consistent with those from a more detailed analysis [13].

Analysis of coalescence can be simplified by characterizing the droplet size distribution with an average size\(^3\). The frequency of coalescence, assuming that $h_0 \gg h_{crit}$, can be written as

$$J \approx \exp \left( -\frac{\sqrt{3}R}{4h_{crit}pCa^{3/2}} \right) \frac{4}{\pi} \gamma \phi n$$ \hspace{1cm} (20)$$

Here, $\phi$ is the volume fraction of droplets, and $R$ and $Ca$ are the characteristic droplet radius and the capillary number, respectively.

\(^3\)More complete descriptions require using cumbersome populations balances, however, models based on an average droplet radius have been used with some success [2].


3 Liquid-liquid mixing in complex flows

The spatial evolution of the morphology of a dispersion may be predicted by the following approach. The system is discretized in time by taking time intervals of $\Delta t$ and spatially by dividing into elements of volume $\Delta V_j$. The dispersion is divided into $N$ sub-populations, each with the same constant volume of dispersed phase, but different pre-defined locations. Utilizing constant volume sub-populations insures conservation of volume.

Every sub-population consists of either droplets or filaments, but not both. Sub-populations consisting of droplets are characterized by the position vector, $x_k$, the average droplet radius, $R_k$, and the volume fraction of droplets, $\phi_k$, with the subscript $k$ denoting the sub-population between 1 and $N$. Filament sub-populations are characterized by the position vector, the orientation vector, $m_k$, parallel to axes of the filaments, the average filament radius, $R_k$, and the disturbance amplitude, $\alpha_k$, which grows from $\alpha_0$.

The algorithm used is illustrated in Figure 1. Starting at $t_i$, the flow advects each sub-population as a passive fluid element until $t_{i+1}$. This approximation has been shown to be reasonable [9] for a system with conditions similar to those of interest here.

![Figure 1: Hierarchical methodology for determining morphology.](image)

Capillary numbers $Ca_{k,i}$—the first subscript refers to the sub-population, and the second to the time—is determined. Droplet sub-populations are considered before filaments sub-populations. The critical capillary number is taken from two dimensional elongational flow, and therefore $\kappa = 5^4$.

In a sub-population with $Ca < Ca_{crit}$ coalescence occurs. Using equation (20), the rate of change in the characteristic radius of the sub-population is described by

$$\frac{dR_k}{dt} = \exp \left( -\frac{\sqrt{3}R_k}{4Na_{crit}} pCa_k^{3/2} \right) \frac{4}{3\pi} \gamma \phi_k R_k$$

(21)

With capillary numbers from $Ca_{crit}$ to $\kappa Ca_{crit}$ breakup occurs via necking. Little is known about necking; however, experimental data from [7] suggest that the time for breakup by necking for a spherical droplet in a steady two dimensional flow for $Ca = Ca_{crit}$ can be approximated by the

4 More complete analysis, involving calculating vorticity, does not seem appropriate as little is known about $Ca_{crit}$ and $\kappa$ in three dimensional flows.
Assuming that the rate of necking for $Ca$ between $Ca_{crit}$ and $\kappa Ca_{crit}$ increases linearly with shear-rate, the evolution of the characteristic radius of a necking sub-population can be approximated by

$$\frac{dR_k}{dt} = -3.91 \times 10^{-3} p^{-0.45} Ca_{crit}^{-1} \gamma Ck R_k + r_{coalesce}$$

in which $r_{coalesce}$ is the right-hand side of equation (21). The coalescence term is unimportant unless $R/(H/\sigma)^{1/2} < 10 p^{-9/8}$. We neglect $r_{coalesce}$, because it is small and probably over-estimates the rate of coalescence of deforming drops. The linear dependence of the rate of necking on shear-rate is consistent with another model based on a different theory [1].

For $Ca_k > \kappa Ca_{crit}$ affine deformation occurs and droplets change to filaments. From equations (3) and (4) the stretching, and thus the characteristic radius of the sub-populations can be determined

$$\frac{R_{k, i+1}}{R_{k, i}} = \sqrt{\frac{\beta_{k, i}}{\beta_{k, i+1}}}$$

Sub-populations of filaments are divided into two categories: those being stretched, and those in a relatively stagnant part of the flow. If $\beta_{k, i+1} > \beta_{k, i}$ and

$$Ca_{k, i} > 0.001/\sqrt{p}$$

the sub-population is stretching—sub-populations of newly formed filaments are in this group—otherwise the filament is considered relatively static. The relation (25) results from assuming that the radius of a static thread is much less than the critical filament radius from equation (12).

The critical radius of a stretching sub-population is found using equation (12) with

$$e_{\beta \gamma} = \ln(\beta_{k, i+1}/\beta_{k, i})/\Delta t$$

and $\alpha_0 = 10^{-9}$. If $R_{k, i+1} < R_{crit}$, then the filament sub-population disperses into a droplet sub-population with $R_{k, i+1}$ calculated from equation (13). This assumes that the time necessary to stretch a droplet to $R_{crit}$ is much greater than the time for the disturbance to grow from $\alpha_0$ to $R_k$. Furthermore, this approximation becomes more accurate as $\Delta t$ approaches the disturbance growth time. Static sub-population breakup is modeled by assuming that a disturbance with a dimensionless wavelength of $\lambda_m$ grows on the surface of a filament at the dimensionless rate $\Omega_m$. Thus, the amplitude of a disturbance at $t_{i+1}$, $\alpha_{k, i+1}$, is approximated by

$$\alpha_{k, i+1} \approx \alpha_{k, i} \exp \left( \frac{\sigma \Omega_m}{\mu_c R_{k, i} \Delta t} \right)$$

where $\alpha_{k, i}$ is $\alpha_0$ if the sub-population was “stretching” during the previous time increment. If $\alpha_{k, i+1} > \sqrt{2/3} \alpha_{k, i+1}$ [2], the sub-population becomes a droplet sub-population with $R_{k, i+1}$ found with equation (10).

Having tracked each individual sub-population from $t_i$ to $t_{i+1}$, and determined whether it consists of droplets or filaments and its characteristic radius, we now determine the spatial properties

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5The correlation (12) assumes that $e_{\beta \gamma}$ is positive.
of the dispersion, by calculating the average properties for each element \( j \) of volume \( \Delta V_j \). In each element, the average radius of the droplets is calculated by determining the total surface area and total volume of droplets in the element. The average radius of the droplets in the element is defined as three times the ratio of total volume to total surface area. The volume fraction of droplets in the element \( j \) is calculated by summing up the volume of droplet sub-populations in \( j \) and dividing by \( \Delta V_j \). For the next timestep, each of the droplet sub-populations in this element assume the volume fraction of droplets in the element, while the characteristic radii of the sub-populations remain unchanged. The next set of calculations are not dependent upon the volume fraction of the filaments, as volume fraction only influences coalescence, and filaments are not allowed to coalesce—it is more likely that filaments breakup upon collisions [2]. Furthermore, it is not advantageous to calculate an average filament radius for an element. The calculations are repeated for each consecutive timestep until the process is finished.

4 Preliminary results for the dispersive mixing model

The model is tested for dispersion in a prototype flow: the so-called journal bearing flow (jbf) which can be easily manipulated to produce both regular and chaotic flows [17]. Analytic streamfunctions, which allow for tractable computations are available [18]. The most important aspects of the mixing process can be captured by examination of just two protocols for the motion of the boundaries, both alternating counter-rotating. A period is defined by rotating the inner for a quarter period, the outer is rotated a half period, and again, the inner for a quarter period. Total displacement per period of the inner and outer cylinder are equal. One mixing protocol (angular displacement of the outer cylinder is 720°) produces a globally chaotic system and is considered “well-mixed”, while the other (angular displacement 180°) produces a regular region separated from a chaotic region and is referred to as “poorly-mixed”.

Mixing flows are inherently difficult to analyze with spatial averages, as islands are often present in flows. Nevertheless, it is helpful to define the following average quantities to characterize the system: the characteristic radius, \( \langle R \rangle \) is three times the ratio of the volume to total surface area of the dispersed phase, and \( \langle \dot{\gamma} \rangle \equiv U/(a_o - a_i) \), in which \( U \) is the linear velocity at which the boundaries rotate.

Examination of our models of coalescence and breakup shows that the characteristic radius is dependent upon \( p \), \( \phi \), and the three lengthscales: \( \sigma/\mu_c \langle \dot{\gamma} \rangle \), \( \alpha_0 \) and \( (H/\sigma)^{1/2} \). The three lengthscales characterize: the the maximum droplet radius stable to breakup, the initial amplitude of a disturbance on a thread, and the thickness of the liquid-liquid interface, respectively. Higher values of \( (H/\sigma)^{1/2} \) yield higher collision efficiencies. Provided dispersed phase loadings are low and surfactants are absent, the ratio of \( \alpha_0 \) to \( (H/\sigma)^{1/2} \) is relatively invariant from one dispersion to the next. Thus, we need only two of the three lengthscales to define the system. As capillary breakup is only weakly dependent upon \( \alpha_0 \), \( (H/\sigma)^{1/2} \) and \( \sigma/\mu_c \langle \dot{\gamma} \rangle \) are used to describe the system. We define the dimensionless quantities

\[
\langle Ca \rangle = \langle R \rangle \mu_c \langle \dot{\gamma} \rangle /\sigma \quad \text{and} \quad S = (H/\sigma)^{1/2} \mu_c \langle \dot{\gamma} \rangle /\sigma
\]

Here, \( S \) is termed the flow strength. Based on dimensional analysis, we expect that for a given flow system—morphology in a globally chaotic flow will differ significantly from that in a regular flow—\( p \), \( \phi \) and \( S \) will determine \( \langle Ca \rangle \).

First, we consider the behavior of \( \langle Ca \rangle \) in the well-mixed system. The evolution of \( \langle Ca \rangle \) is dependent upon the viscosity ratio. When \( \langle Ca \rangle_{\text{initial}} > \kappa \langle Ca \rangle_{\text{crit}} \) the droplets initially stretch into filaments which eventually break. In systems with viscosity ratios greater than one, the filaments stretch until breakup into droplets with \( \langle R \rangle \) considerably less than the steady state \( \langle R \rangle \), after
which the average radius increases until coalescence is balanced by breakup. Our simulations show this type of behavior, termed over-emulsification, becomes more pronounced as viscosity ratio increases. Systems with \( p < 1 \) do not exhibit over-emulsification, i.e., \( \langle R \rangle \) monotonically decreases to a steady value.

The steady state values of \( \langle R \rangle \) are also influenced by viscosity ratio. Figure 2 shows \( \langle Ca \rangle \) at steady state for the well-mixed system with \( \phi = 0.05 \) as a function of \( S \) and \( p \). For all values of \( S \), the average steady state droplet radius decreases with increasing viscosity ratio.

![Figure 2: The average steady state capillary number \( \langle Ca \rangle \) versus the viscosity ratio, \( p \) in the well mixed flow. The the values for very large viscosity ratios are effective steady state values, as coalescence in this regime is very slow and simulations were run only for 100 periods. The different curves from top to bottom are+ for \( S \) of \( 10^{-3} \), \( 10^{-4} \), \( 10^{-5} \), and \( 10^{-6} \). While \( \langle Ca \rangle \) increase with \( S \), \( \langle R \rangle \) decreases with \( S \).

However, we note that the results for viscosity ratios above ten may be misleading, because simulations were run for a maximum of 100 periods, and the rate at which \( \langle R \rangle \) approached a steady state decreased with viscosity ratio. Figure 2 also illustrates that the steady state \( \langle Ca \rangle \) increases with \( S \). However, \( \langle Ca \rangle / S \) and the average droplet radius, which can be written as

\[
\langle R \rangle = (H/\sigma)^{1/2} \langle Ca \rangle / S
\]

(29)
generally decreases with increasing \( S \).

Figure 3 shows the influence of volume fraction on the steady state average radius for \( p = 0.1 \) and \( S = 10^{-4} \). The steady state average radius increase with volume fraction, due to an increase in the rate of coalescence (see equation (20)).

A spatial description of the well-mixed and poorly-mixed systems can be seen in Figure 4. The well-mixed system shown after two periods has only a few small regions with dispersed phase volume fraction significantly higher than the mean volume fraction. In the poorly-mixed system after eight periods (total shear equal to that of the well-mixed system after two periods), there is a region with a very high dispersed phase volume fraction. The presence of the region with high volume fraction is expected as it coincides with the regular region in the flow. On the other hand, the droplet radius in the well-mixed flow does vary throughout the flow. This is due to the fact that droplet radius is also dependent upon the shear-rate which varies spatially in the flow, in spite of the global mixing. The spatial variation in droplet radius is even more pronounced in the poorly-mixed flow. Some droplets only experience low shear-rates, characteristic of the regular region in the flow. These droplets are much larger than the droplets in chaotic regions of the flow which experience high shear-rates.
Figure 3: Average steady state capillary number versus volume fraction.

Figure 4: Spatial descriptions of the well mixed and poorly mixed systems for the conditions of $\sigma = 0.005 \text{N/m}$, continuous and dispersed phase viscosities of 1 and 2 Pa $\cdot$ s, respectively, $\langle \dot{\gamma} \rangle = 10 \text{s}^{-1}$, and $\phi = 0.05$. The initial conditions are a dispersion with $R_0 = 10^{-6} \text{m}$ and $\phi_0 = 0.7$. (a) Volume fraction for the well mixed flow after 2 periods. (b) Volume fraction for the poorly mixed flow after 8 periods. (c) Droplet radius in m for (a). (d) Droplet radius in m for (b).

The differences between the morphology in the well-mixed system and in the poorly-mixed system can also be seen in the droplet size distributions. Figure 5 shows the cumulative mass fraction of droplets with a radius less than $R/(\bar{R})$ of the well-mixed system after two periods and for the poorly-mixed system after eight periods. In all cases, the initial capillary number is much greater than $Ca_{crit}$ for elongational flow.

At this early stage in the mixing we expect that the process is dominated by breakup, indicating that the droplet size distributions might be self-similar (see the appendix covering scaling concepts). The solid, dashed and dotted lines are for viscosity ratios: 10, 1 and 0.1, respectively. The distributions for different viscosity ratios collapse onto one curve. However, the curve for the poorly-mixed system differs significantly from that of the well mixed system. This type of scaling
behavior has been observed by Ottino and co-workers [3, 19]. As implied previously, the size distribution for the poorly-mixed system is bimodal, with a number of droplets of relatively large radius and several smaller radius droplets.

5 Macroscopic Rheology

Next, we consider the macroscopic rheology of liquid-liquid systems. While in the first part, non-Newtonian effects were not considered, here the non-Newtonian rheology resulting from the presence of the dispersed phase is dealt with. Still, we do not consider the influence of the rheology on coalescence and breakup.6

Here, we improve upon the Lee-Park model [5] for the rheology of a blend. Our analysis provides further understanding of the rheology of a blend, by deriving the Lee-Park model with a different approach, and examining the principles on which the theory is based. The Lee-Park model requires prediction of the interfacial area between the two phases with a rather *ad hoc* kinetic equation. We use our model of liquid-liquid mixing, discussed in part one, to determine the interfacial area of the dispersed phase, and, thus, reduce the number of unknowns appearing in the Lee-Park model.

The study of the rheology of a dispersion dates back to Einstein’s [20] work yielding the effective viscosity of a dilute suspension of solid spheres,

$$\mu_e = \mu_c (1 + 2.5\phi)$$  \hspace{1cm} (30)

in which $\phi$ is the volume fraction of the dispersed phase. Later, Taylor [21] found the effective viscosity for a dispersion containing spherical droplets. The effective viscosity—like Einstein’s relation—has the form

$$\mu_e = \mu_c \left[ 1 + 2.5\phi \left( \frac{p + 0.4}{p + 1} \right) \right]$$  \hspace{1cm} (31)

6Janssen [2] proposes a relatively simple approach to this problem. In the models discussed in part I, each $\mu_e$ in the coalescence and breakup models, excepting the $\mu_e$ describing the viscosity of the film draining between two droplets, should be replaced by an effective viscosity. Janssen [2] also discusses possible forms of the effective viscosity, $\mu_e$.  

Figure 5: Cumulative mass fraction versus $R/\langle R \rangle$. This demonstrates the scaling relationship for stretching and breaking droplets. The poorly and well mixed systems are reflected by the bimodel and wider distributions, respectively. The dashed, dotted and solid lines are for viscosity ratios of 0.1, 1, and 10.
where \( p = \mu_d / \mu_c \) is termed the viscosity ratio. As Taylor notes, the term inside the parentheses is similar to a term which corrects the Stokes drag to allow for drag on a spherical droplet of fluid.

Schowalter et al. [22] consider the influence of the first-order deformation of the droplets on the rheology of the dispersion. The analysis assumes a dilute emulsion of two highly viscous Newtonian fluids and droplets with \( C a \ll C a_{\text{crit}} \). The macroscopic rheology of this type of emulsion exhibits elastic properties with normal stress differences resulting from the deformation of the droplets. A more advanced work by Choi and Schowalter [23] determines the rheology of a nondilute dispersion of Newtonian fluids with slightly deformed droplets. The results show that the macroscopic rheology can be described by a special case of the Oldroyd 8-constant model [24], and that dropping non-linear terms in the rate-of-deformation tensor yields the convected Jeffreys model [24].

Palierne [25] also derives an expression for the linear viscoelastic modulus of a dispersion. The analysis allows for linear non-Newtonian behavior of the two fluids and for dynamic interfacial tension. Still, the model does not allow for deformation of the droplets. The Palierne model is equivalent to the Jefferys model when the droplet size distribution is monodisperse.

An alternative method of determining the rheology of a liquid-liquid system focuses on the evolution of the interface between the two fluids. An early study from this perspective [26] considers a system of two Newtonian liquids with the same viscosities and densities, mixed in nearly equal ratio. The Reynolds number is also low. Only three parameters characterize the system: viscosity, volume fraction and interfacial tension. The characteristic radius of the droplets is conspicuously absent from this analysis; however, the average droplet radius is not a material parameter as it is dependent upon the shear-rate. The model determines the characteristic droplet radius. This approach allows for stretching of the droplets, coalescence and breakup.

Lee and Park [5] extended this model to allow for a wider range of blend properties. Here, we derive the Lee and Park model with a slightly different approach, yielding a more exact constitutive equation, in tensor notation, containing the dispersed phase interfacial area as a dependent parameter. This interfacial area can be approximated by our model for dispersed phase microstructure. According to Mellema and Willemse [27], who adopted Batchelor’s [28] approach, the the bulk stress in a dispersion, \( \langle T \rangle \), can be written for Stokes flow as,

\[
\langle T \rangle = -P I + 2\mu_c (D) + T_s + T_\mu
\]  

(32)

where the angular brackets \( \langle \rangle \) denote a quantity averaged over the local volume \( V \), having the limitations that it contains many droplets and that its statistical properties vary negligibly [28]. \( T_s \) is a structure dependent stress resulting from interfacial tension, and \( T_\mu \) is referred to as the “viscosity ratio term” [5], but it too is structure dependent.

The viscosity ratio term can be written in terms of a series of surface integrals as

\[
T_\mu = (\mu_d - \mu_c) \frac{1}{V} \sum A_i (u n + n u) \, ds
\]  

(33)

in which \( A_i \) is the interfacial area of an individual droplet in \( V \), \( ds \) is an differential element of the droplet interface, \( n \) is the unit normal to the interface directed into the continuous phase, and \( u \) is the local fluid velocity—including disturbance terms due to the dispersed phase—of the flow. The summation indicates that the quantity is taken over all the droplets, indexed by \( i \), within \( V \).

The structure dependent stress, \( T_s \), reflecting the anisotropy of the disperse phase microstructure, can be expressed as [27, 28]

\[
T_s = \frac{\zeta}{V} \sum A_i \left( \frac{1}{3} I - n n \right) \, ds
\]  

(34)
This form appears in [27], but differs slightly from that of Batchelor [28]. Equation (34) is the deviatoric part of Batchelor’s [28] expression; the isotropic terms can be incorporated into the pressure. This structure dependent stress is zero for “perfectly” spherical droplets [29].

The structure dependent terms, $T_\mu$ and $T_s$, can be determined analytically for a handful of simple cases. For instance, considering one droplet in the dispersion, we can write [27]

$$
\begin{align*}
(\mu_d - \mu_e) \int_{A_i} (u_n + n u) \, ds + \sigma \int_{A_i} \left( \frac{1}{3} I - n n \right) \, ds \\
= \int_{A_i} \left[ (T_c \cdot n) y - \mu_e (u n + n u) \right] \, ds
\end{align*}
$$

(35)

where $T_c$ is the local stress in the continuous phase, and $y$ is the position on the droplet interface. The right-hand side of this equation can be evaluated for a nearly spherical droplet. Schowalter et al. [22] use this approach to determine a rheological equation for a dilute dispersion of droplets slightly deformed by the flow.

Based on this work, Mellema and Willemse [27] show that for nearly spherical droplets

$$
T_\mu = \frac{6 p - 1}{5 p + 1} \mu_e \phi D_0 + \text{second-order terms in } D_0
$$

(36)

and

$$
T_s = \frac{19 p + 16}{5(p + 1)} \mu_e \phi D_0 + \text{second-order terms in } D_0
$$

(37)

with the subscript “0” denoting the corresponding tensor of the flow undisturbed by the dispersed phase. Note that the undisturbed rate-of-deformation tensor is not necessarily equal to the average rate-of-deformation tensor in equation (32). In fact, Mellema and Willemse [27] and Schowalter et al. [22] disagree on this point. Nevertheless, $\langle D \rangle$ is generally approximated with $D_0$. Substituting the two relations above for the structure dependent terms into equation (32) yields Taylor’s result for effective viscosity. At first glance, this seems inconsistent, because $T_s$ is identically zero for perfectly spherical droplets, and Taylor [21] calculated the effective viscosity with the right-hand side of equation (35) assuming spherical droplets. However, the left-hand side and right-hand side of equation (35) are indeed equal. Taylor’s assumption of spherical droplets implies that $\sigma \to \infty$, and not that droplets are “perfect” spheres. The droplets are actually infinitesimally deformed.

Mellema and Willemse [27] also find for a dilute dispersion of initially spherical droplets with $\sigma \to 0$ that

$$
T_\mu = \frac{10(p - 1)}{2p + 3} \mu_e \phi D_0
$$

(38)

during the first moments of shear when the droplets are nearly spherical. Likewise, Palierne [25] obtains

$$
T_\mu = \frac{10(p - 1)}{2(1 - \phi)p + (3 + 2\phi)} \mu_e \phi D_0
$$

(39)

for a concentrated dispersion without interfacial tension in oscillatory shear flow. Equation (39) approaches equation (38) as $\phi \to 0$.

The first-order results for the structure dependent terms (36)–(39) have led others to assume that $T_\mu$ is purely viscous. We demonstrate that this assumption is incorrect. By Green’s divergence theorem, the viscosity ratio stress can also be expressed

$$
T_\mu = \frac{2(\mu_d - \mu_e)}{V} \sum_{V_i} \int_{V_i} D \, dv
$$

(40)
where $V_i$ is the volume of the $i$-th droplet in the volume $V$, and $dv$ is a differential volume element. We rewrite this as

$$
T = 2 \left( \frac{\mu_d - \mu_c}{\phi} \right) D_0 + 2 \frac{\left( \mu_d - \mu_c \right)}{V} \sum \int_{V_i} (D - D_0) dV
$$

(41)

Assuming that inertia forces due to fluctuations about the average flow are negligible, and manipulating a result from Mellema and Willemse [27], we express the disturbance in the rate-of-deformation tensor as a summation of surface integrals

$$
D(x) - D_0 = \frac{1}{8 \pi \mu_c} \sum \int_{A_i} \left[ \frac{3(x-y)(x-y)}{|x-y|^3} - \frac{I}{|x-y|^3} \right] \times (x-y) \cdot [\sigma n(y) \nabla_s \cdot n(y) - 2(\mu_d - \mu_c) D(y) \cdot n(y)] ds(y)
$$

(42)

This equation for part of the viscosity ratio term contains two contributions. One due to the interfacial tension at every point on the interface between the two fluids, and another containing the rate-of-deformation tensor. Based on this result, we assume that the last term in equation (41) can be expressed in the form of a constitutive equation dependent upon $T_s$ and $D_0$. The simplest possibility is the linear form

$$
\frac{2}{V} \sum \int_{V_i} (D - D_0) dV = \alpha D_0 + \beta T_s
$$

(43)

According to Mellema and Willemse [27], in the limiting case of a dilute dispersion of nearly spherical droplets,

$$
\frac{2}{V} \sum \int_{V_i} (D - D_0) dV = -\frac{2}{5 \mu_c} (T_\mu + T_s)
$$

(44)

For this case, we can analytically determine $\alpha$ and $\beta$, and show that

$$
T_\mu = \frac{10 (\mu_d - \mu_c)}{2 \mu_d + 3 \mu_c} \phi D_0 - \frac{2 (\mu_d - \mu_c)}{2 \mu_d + 3 \mu_c} T_s
$$

(45)

Clearly, the viscosity ratio term possesses an elastic component due to interfacial tension. Also, by setting $T_s = 0$, it is possible to verify that the rheology of spherical droplets with $\sigma \rightarrow 0$ is accurately described by equation (45). For morphologies differing from slightly deformed drops the linear approximation in (43) may not be exact, and/or $\alpha$ and $\beta$ may be different. An interesting area of further research is development of a constitutive equation for fluid filaments. One possible approach to this problem is to follow the methodology of Schowalter et al. [22], using the velocity field for long slender droplets provided by [30]. However, without a more accurate approximation, we assume that (45) is valid for all structures.

We use the results of Palierne [25] to determine that

$$
T_\mu = \frac{10 (\mu_d - \mu_c)}{2 (1 - \phi) \mu_d + (3 + 2 \phi) \mu_c} \phi D_0 - \frac{2 (1 - \phi) (\mu_d - \mu_c)}{2 (1 - \phi) \mu_d + (3 + 2 \phi) \mu_c} T_s
$$

(46)

for high volume fractions of the dispersed phase.

Consider the contribution to $T_s$ by one droplet denoted $T_i$. According to Ottino [17], the rate of stretching of an element on the interface of the droplet can be expressed as

$$
\frac{1}{ds} \frac{D ds}{Dt} = \nabla \cdot v - D : nn
$$

(47)
where \( \mathbf{n} \), the vector normal to the interface, changes as

\[
\frac{D\mathbf{n}}{Dt} = (\mathbf{D} : \mathbf{n} \mathbf{n}) \mathbf{n} - \mathbf{n} \cdot \mathbf{L}
\]  
(48)

in which \( \mathbf{L} \) is defined by \( \mathbf{L} \equiv (\nabla \mathbf{v})^T \). Assuming incompressible fluids, the first term on the right-hand side of equation (47) is zero. Thus, we can write

\[
\frac{D\mathbf{T}_i}{Dt} = \frac{\sigma}{V} \frac{D}{Dt} \int_{A_i} \left( \frac{1}{3} \mathbf{I} - \mathbf{n} \mathbf{n} \right) ds
\]

(49)

This assumes that the averaging volume, \( V \), remains constant.\(^7\) Substituting equation (48) into this equation yields

\[
\frac{D\mathbf{T}_i}{Dt} = \frac{\sigma}{V} \int_{A_i} \left[ \mathbf{L}^T \cdot \mathbf{n} \mathbf{n} + \mathbf{n} \mathbf{n} \cdot \mathbf{L} - \left( \frac{1}{3} \mathbf{I} - \mathbf{n} \mathbf{n} \right) (\mathbf{D} : \mathbf{n} \mathbf{n}) \right] ds
\]  
(50)

An important, simplifying assumption \([26]\) is that \( T_s \) can be split into a term dependent upon the flow and another accounting for interfacial tension. That is,

\[
\frac{D\mathbf{T}_i}{Dt} = \frac{D\mathbf{T}_i}{Dt}^{\text{flow}} + \frac{D\mathbf{T}_i}{Dt}^{\sigma}
\]  
(51)

A similar assumption is made about interfacial area. The flow dependent part of \( \mathbf{T}_s \) is evaluated by assuming that the interface is passive \([26]\). Therefore, we replace \( \mathbf{D} \) and \( \mathbf{L} \) with their undisturbed tensors, \( \mathbf{D}_0 \) and \( \mathbf{L}_0 \), to determine

\[
\frac{D\mathbf{T}_i}{Dt}^{\text{flow}} = - \left[ \mathbf{L}_0^T \cdot \mathbf{T}_i + \mathbf{T}_i \cdot \mathbf{L}_0 \right] + \frac{2Q_i \sigma}{3} \mathbf{D}_0 + \frac{1}{3} (\mathbf{D}_0 : \mathbf{T}_i) \mathbf{I}
\]  
(52)

where \( Q_i \) is the interfacial area of the \( i \)-th droplet divided by \( V \). Following Doi and Ohta \([26]\), the last term on the right-hand side is approximated by assuming that

\[
\int_{A_i} \mathbf{D}_0 : \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} ds \approx \frac{1}{VQ_i} \int_{A_i} \mathbf{D}_0 : \mathbf{n} ds \int_{A_i} \mathbf{n} ds
\]  
(53)

in which, the factor \( 1/VQ_i \) accounts for the presence of the extra surface integral on the right-hand side. This closure approximation obeys the condition that

\[
\text{tr} \left( \int_{A_i} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} ds \right) = \int_{A_i} \mathbf{n} ds
\]  
(54)

Equation (53) is however incorrect for nearly spherical droplets. As noted by Frankel and Ac-rrivós \([31]\), for a spherical droplet with the surface area, \( A_i \), the surface integral

\[
\int_{A_i} n_j n_k n_l n_p e_j e_k e_l e_p ds = \frac{VQ_i}{15} (\delta_{jk} \delta_{lp} + \delta_{jl} \delta_{kp} + \delta_{jp} \delta_{kl}) e_j e_k e_l e_p
\]  
(55)

\(^7\)In some circumstances, the dispersed phase volume fraction will change during mixing and \( V \) will effectively increase. It is possible to show that the final constitutive equation does not change if this effect is considered.
in which $n_j$ is the $j$-th component of $n$, and $e_j$ is the unit vector of the $j$-th coordinate. The fourth-order tensor resulting from this surface integral demonstrates that cross terms appear in the last term of equation (52). Examining (55) and recalling that

$$\int_{A_i} nnds = \frac{VQ_i}{3} I$$

for a sphere, suggests another possible closure approximation of the form

$$\int_{A_i} D_0 : nmnnds \approx \frac{3}{5VQ_i} \left[ (D_0 : \int_{A_i} nnds) \int_{A_i} nnds + 2 \int_{A_i} nnds \cdot D_0 \cdot \int_{A_i} nnds \right]$$

This closure approximation does not satisfy equation (54).

Other possible corrections to allow for spherical droplets could be formed by adding a linear combination of the traceless tensors $D_0$ and $(T \cdot D + D \cdot T) - 2(T : D)I/3$ to equation (54). Here, we use the closure

$$\int_{A_i} D_0 : nmnnds \approx \frac{1}{VQ_i} \int_{A_i} D_0 : nnds \int_{A_i} nnds + \frac{2VQ_i}{15} D_0$$

(58)

giving the correct result for spherical droplets and satisfying the condition (54). Inclusion of other traceless terms might be necessary to accurately describe more deformed droplets. A possible starting point for determining a more accurate closure is provided by Larson [32], who shows

$$T^s \propto C^{1/2}$$

(59)

where $C$ is the Cauchy strain tensor, and $T^s$ is the stress tensor for a foam or a dispersion of droplets which deform passively. Larson’s constitutive equation is difficult, in its present form, to incorporate into a model which allows for viscous dissipation and droplet shape relaxation due to interfacial tension.

Substituting (58) into equation (52) and expressing the surface integrals in terms of $T_i$ yields

$$\frac{DT_i}{Dt} \bigg|_{\text{flow}} = - \left[ L_0^T \cdot T_i + T_i \cdot L_0 \right] + \frac{2Q_i}{15} D_0 + \frac{2}{3} (D_0 : T_i) I - \frac{D_0 : T_i}{Q_i} T_i$$

(60)

Summing this equation over all the droplets in the local volume, $V$, and assuming that these droplets possess a similar structure, allows, as a first-order approximation, substitution of $T_s$ and $Q$, where $Q$ is the total interfacial area per volume $V$, for $T_i$ and $Q_i$.

In order to complete the constitutive equation, we determine the interfacial tension contribution to $T_s$. As noted by Doi and Ohta [26], the degree of anisotropy of the dispersed phase can be represented in terms of the ratio of $T_s/Q$. Since elastic forces resulting from interfacial tension tend to restore droplets to spheres, we assume that

$$\frac{D}{Dt} \left( \frac{T_s}{Q} \right) \bigg|_\sigma = -c_1 ET_s$$

(61)

The constitutive equation for a foam under shear is shown by Reinelt [33] to be very similar to the predictions of the Doi-Ohata model. Reinelt’s analysis is based on a discrete version of equation (34). It assumes that the foam structure consists of tetrakaidecahedras, and, thus, the surface integral in (34) can be written in terms of a summation over the fourteen surfaces of a tetrakaidecahedra.
in which 
\[ E = \left( \frac{5\mu_c}{2(1 - \phi) \mu_d + (3 + 2\phi) \mu_c} \right) \]  (62)

We note that the Lee-Park model assumes that this rate of structure relaxation is proportional to \( T_s \). This is not an issue in the Doi-Ohta model, because \( T_s \) is equal to the elastic part of \( T_\mu + T_s \) when the viscosity ratio is one. Our correction to the Lee-Park model allows for the fact that higher viscosity ratio droplets relax slower than low viscosity ratio droplets. Dimensional analysis shows that 
\[ c_1 = \frac{1}{\lambda \phi \mu_c} \]  (63)

The volume fraction is included in this relation to make the resulting constitutive equation consistent with Taylor’s effective viscosity, but \( \lambda \) may be a function of \( \phi \), and structure\(^9\).

Applying equation (63) and assuming that the change in interfacial area can be expressed in terms of a flow contribution and an interfacial tension contribution, like equation (51) for the structure related stress, we rewrite equation (61) as
\[ \frac{D T_s}{D t} = -\frac{E \sigma Q}{\lambda \phi \mu_c} T_s + \frac{1}{Q} \left( \frac{D Q}{D t} \right)_{\text{flow}} T_s \]  (64)

Analysis of the interfacial area similar to that for the flow dependent terms in \( T_s \) shows that
\[ \frac{D Q}{D t} \bigg|_{\text{flow}} = \frac{1}{\sigma} D_0 : T_s \]  (65)

Using equations (51), (60), (64) and (65) we determine that
\[ T_s^{(1)} = -\left( \frac{E \sigma Q}{\lambda \phi \mu_c} - \frac{1}{Q} \frac{D Q}{D t} \right) T_s + \frac{8\sigma Q}{15} D_0 + \frac{2}{3} (D_0 : T_s) I - \frac{2(D_0 : T_s)}{\sigma Q} T_s \]  (66)

where \( T_s^{(1)} \) is the covariant (or lower) convected derivative of \( T_s \). In order to determine \( \lambda \) for nondilute concentrations, we approximate the relaxation time, \( \tau \), with that for a nondilute dispersion of spherical droplets, shown by Graebling [34], to be
\[ \tau = \frac{3 \phi (19\mu_d + 16\mu_c) [2(1 - \phi)\mu_d + (3 + 2\phi)\mu_c]}{8\sigma Q} \frac{5(1 - \phi)\mu_d + (5 + 2\phi)\mu_c}{5(1 - \phi)\mu_d + (5 + 2\phi)\mu_c} \]  (67)

This relaxation time is not constant, as the interfacial area in our model is dependent upon the flow. We determine that
\[ \lambda \approx \frac{15}{8} \left( \frac{19\mu_d + 16\mu_c}{5(1 - \phi)\mu_d + (5 - 2\phi)\mu_c} \right) \]  (68)

We write the final constitutive equation in terms of \( T_\sigma \equiv ET_s \), as
\[ \langle T \rangle = -P I + \left[ 1 + \frac{10(\mu_d - \mu_c)}{2(1 - \phi)\mu_d + (3 + 2\phi)\mu_c} \phi \right] \mu_c D_0 + T_\sigma \]  (69)

\(^9\)The constant \( \lambda \) is likely to depend upon the structure. However, when \( \lambda \) is structure dependent, the constitutive equation becomes significantly more complex, containing timescales for different structures. Also, the stresses for each of these timescales are coupled, because the initial stresses of a structure are related to the stresses in the preceding structure. According to [24], constitutive equations with coupled timescales are ill-advised for solving fluid flow problems.
with
\[
T_\sigma + \tau T_\sigma^{(1)} - \tau \frac{D \ln(Q)}{Dt} T_\sigma = \frac{19\mu_d + 16\mu_c}{E [5(1 - \phi)\mu_d + (5 + 2\phi)\mu_c]} \phi \mu_c D_0 + 2\tau \frac{(D_0 : T_\sigma)}{E \sigma Q} (D_0 : T_\sigma) T_\sigma
\]

Equation (69) is suggested by Lacroix et al. [35] for describing the rheology of a blend in oscillatory shear. However, these authors have not properly derived this equation, and, hence, do not determine the correct coefficients in the relation (70) for \( T_\sigma \). Our corrections for \( T_\sigma \) are negligible for Lacroix et al. [35], because they studied small deformations. These authors note that this equation properly fits their experimental work, but they cannot provide any further insight.

We rewrite equation (70) in terms of the Jaumann derivative, \( D/Dt \), as
\[
\frac{D T_\sigma}{Dt} + \tau \frac{D \ln(Q)}{Dt} T_\sigma = \frac{19\mu_d + 16\mu_c}{E [5(1 - \phi)\mu_d + (5 + 2\phi)\mu_c]} \mu_c \phi D_0 + \frac{2\tau}{3} (D_0 : T_\sigma) I - \frac{2\tau}{E \sigma Q} (D_0 : T_\sigma) T_\sigma
\]

for comparison with the results of Schowalter and co-workers [22, 23] and Frankel and Ac- rivos [31] for slightly deformed droplets. The constitutive equations for nearly spherical droplets are in terms of droplet radius, while the length scale, \( \phi/Q \), appearing in equation (71) allows for more deformed structures. This difference aside, equation (71) is very similar to constitutive equations for slightly deformed droplets. The relaxation times and effective zero-shear viscosities are the same. We forced the relaxation time by approximating it with the relaxation time from one of these models, but the viscosity is not forced. This similarity in the effective zero-shear viscosities supports our result. The traceless second term on the right-hand side of our constitutive equation is not present in constitutive equations for slightly deformed droplets; however, if our constitutive equation (71) is expressed in terms of \( \langle T \rangle \), then a traceless second-order term in \( D \) appears due to this second term. This term also appears in the constitutive equation for nearly spherical droplets, but the coefficient is different. For this reason, we have included the dimensionless constant \( \nu \) to allow for more flexibility, as these terms may be influenced by the closure. However, our present analysis yields \( \nu = 1 \). The last terms on the left and right sides of (71) do not appear in equations for slightly deformed droplets, because \( Q \) is approximately constant is this case, and third-order terms do not appear in the equation for slightly deformed droplets.

6 Interfacial Area

In order to apply equation (70), one must determine the interfacial area. To this effect, Lee and Park [5] use the rather \textit{ad hoc} relationship
\[
\frac{D Q}{Dt} = \frac{1}{\sigma} D_0 : T - \lambda c_2 \frac{\mu_c}{\mu_c} Q^2 - \lambda c_3 \frac{\mu_c}{\mu_c} T : T
\]

in which \( c_2 \) and \( c_3 \) are dimensionless constants, which are essentially adjustable parameters. On the right-hand side, the first term is the change in interfacial area due to the passive stretching of the interface, the second term accounts for coalescence, and the last term accounts for the relaxation of the surface due to interfacial tension, which includes breakup.

In some cases, this approach gives reasonable results [5, 35, 36], but there are limitations. According to (72), \( Q \) approaches zero when the flow is stopped and \( t \to \infty \). Therefore, the approximation is only valid for co-continuous phases, or \( \phi \sim 0.5 \). This limitation is generally corrected by assuming \( c_2 \propto \sqrt{T : T} \), i.e., interfacial area stops decaying when the droplets are
spherical. Furthermore, as discussed in two recent notes [37, 38], equation (72) cannot predict phenomena resulting from hysteresis.

An alternative means of determining interfacial area is to apply our model for dispersed phase morphology. The interfacial area of filaments, or droplets with $\kappa C_a < C a$ is easily determined by assuming passive fluid stretching. It is slightly more difficult to find the the interfacial area of droplets with $C a < C a_{\text{crit}}$, because or model does not inherently predict the degree of droplet deformation. Nevertheless, for flows in which the dispersed phase reaches a pseudo-steady state much faster than the timescales over which the flow changes, interfacial area can be approximated by a model proposed by Vinckier et al. [36], assuming ellipsoidal droplets. In more transient flows, one must also know the time necessary for a droplet to reach the steady state discussed in part I. Also for similar reasons, we cannot directly apply our model to predict the the interfacial area of droplets in the range $C a_{\text{crit}} < C a < \kappa C a_{\text{crit}}$, because relatively little is known about droplet behavior in this intermediate range. As a first order approximation, one could use an equation similar to (72) to predict the interfacial area of droplets in this regime. We note that using equations (69) and (70) with the interfacial area determined by our model from part I allows prediction of phenomena resulting from hysteresis.

7 Preliminary results for the constitutive model

Here, we demonstrate coupling our constitutive equation with our model for dispersed phase morphology in the prototype journal bearing flow. We assume that the velocity field in the flow is negligibly influenced by the dispersed phase, but that the stresses in the flow are dependent upon the flow. This allows us to use analytical velocity fields for the flow. This approximation is a reasonable approximation for very low Deborah numbers, and is consistent with a second-order fluid [24]. In order to simplify the computations, we make two very crude approximations: droplets with $C a < \kappa C a_{\text{crit}}$ remain spherical, and filaments with $C a > \kappa C a_{\text{crit}}$ stretch passively. The latter approximation is relatively accurate. We use the former to avoid the use of ad hoc rules. We note that even with this crude approximation the coupling is a difficult computational problem, because the interfacial area approximated by our model is not continuous. While we obtained reasonable results, further work in this area requires development of a special integration scheme which probably smoothes the discontinuous interfacial area.

Figure 6: Local mechanical power $\langle H \rangle : D_0/2 \mu_c D_0 : D_0 - 1$ for the well mixed flow after one period. The conditions are $\sigma = 0.005 N/m$, continuous and dispersed phase viscosities of 20 and $10 Pa \cdot s$, respectively. $\langle \dot{\gamma} \rangle = 10 s^{-1}$, and $\phi = 0.05$. The initial conditions are a dispersion with $R_0 = 10^{-4} m$ and $\phi = 0.7$. 
Figure 6 shows the distribution of the second normal stress difference. Clearly, the effect of the dispersed phase on the stresses is demonstrated. In figure 7 the local distribution of the increase in mechanical power, when compared with a flow without a dispersed phase, is shown.

Figure 7: The local second normal stress difference coefficient, defined as $\frac{1}{2} \left[ T_{zz} - (T_{xx} + T_{yy})/2 \right]/2D_0 : D_0$, for the same conditions as Figure 6.

8 Conclusions

We have rederived the Lee-Park model with a new approach, making several corrections to the existing model. A new closure approximation has been proposed for the fourth-order moment in equation (52). The closure is clearly more accurate for slightly deformed droplets, but is unproven in the case of filaments. Interfacial area is a dependent parameter in our constitutive equation. Generally, the interfacial area is determined with an approximate kinetic equation containing several adjustable parameters. However, we have demonstrated that this can be avoided by using our model for dispersive mixing to calculate the interfacial area. This methodology allows prediction of phenomena resulting from hysteresis.

References


