Simulation of Droplet Breakup by
Dissipative Particle Dynamics (DPD)

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A senior thesis submitted to the

Senior Project Committee, Department of Physics,
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May 2, 2012
Table of Contents

1) Executive Summary 3
2) Introduction 4
3) Background 4
4) Literature Review 9
5) Objectives 11
6) Concept and Methods 12
7) Results 15
8) Discussion 25
9) Conclusion 28
10) References 29
14. **Executive Summary**

Coarse grained (CG) simulation methods, such as CG molecular dynamics and Stokesian dynamics, are normally used to gain a better understanding of mesoscopic phenomena. Hoogerbrugge and Koelman proposed a new simulation method called Dissipative Particle Dynamics (DPD) in 1992, which has a variety of applications, including Newtonian fluids, colloidal suspensions, emulsion, polymer solutions, polymer melts, polymer blend, diblock copolymer, polymer nano-composites, and so on [1]. Specifically, DPD is well suited to address the problem of droplet breakup, which is important for mixing operations in industrial production, cosmetics, pharmaceuticals, and food as well as oil recovery and cleanup operations. Droplet breakup was experimentally quantified by Grace in the 1980’s, but the behavior has not been fully reproduced using simulation [7]. This thesis applies a new DPD simulation method recently developed by the Maia group, whose coarse-grained level is tunable, to capture the physics of droplet breakup in micro- and nano-emulsions [4]. The droplet breakup phenomenon is described based on the viscosity ratio of the phases and the capillary number, a ratio of viscous stresses to interfacial tension. Viscosity was modified by taking advantage of the Fluctuation-Dissipation theorem. We have found that DPD can qualitatively reproduce the Grace plot for Newtonian fluids under shear.
2. Introduction

Mixing is an important step in the processing of materials. In particular, the dispersion of incompatible polymers can pose a formidable problem in the design of materials. Since the flows are often complex and not analytically solvable, simulation must be used to study this behavior theoretically. The molecular behavior must be preserved while studying large systems and large time scales, so coarse grained (CG) simulation methods, such as CG molecular dynamics and Stokesian dynamics are usually used. However, a new simulation technique was introduced by Hoogerbrugge and Koelman in 1992 called Dissipative Particle Dynamics (DPD), which is a coarse grained technique that can be used to study transient and equilibrium behavior at long time scales because it uses softer potentials than other methods. It can be used to model systems involving Newtonian fluids, colloidal suspensions, emulsions, polymer solutions, polymer melts, polymer blends, diblock copolymers, and polymer nano-composites.

It is hoped that mixing operations can be studied and modeled using DPD. Previous work has established a proof-of-concept for viscosity measurements, droplet breakup, and flow characterization. The goal of this study is to fully reproduce the experimental Grace plot for Newtonian fluids under shear flow. We hope that this approach can eventually be extended to include entangled polymers and extensional flows.

3. Background

Dissipative Particle Dynamics

DPD was created by Hoogerbrugge and Koelman in 1992 to study mesoscopic phenomena [1]. Similar to molecular dynamics (MD), it conserves forces, forming a thermodynamic ensemble that can be used to simulate non-equilibrium dynamics and incorporates Navier-Stokes hydrodynamics [2]. In order to reproduce proper hydrodynamics, it
is necessary to include the solvent particles explicitly [3]. The advantage of DPD over atomistic methods such as MD is that coarse graining reduces the number of interactions necessary to compute and the softer potentials used in DPD make large time steps, several orders of magnitude larger than MD, possible. The relation between coarse grained particles and atomistic particles is shown in Figure 1. Since the size of the coarse-grained particle can be defined arbitrarily, DPD is dimensionless with the length scale defined in terms of the bead radius. The time scale is also defined relative to the bead radius. The energy scale is defined in terms of the thermostat used.

Fundamentally, DPD is governed by the Langevin equation, which is a coupled stochastic first order differential equation that described the position and the velocity of the particles as

$$\frac{\partial r_i}{\partial t} = v_i$$  \hspace{1cm} (1a)

$$m_i \frac{\partial v_i}{\partial t} = F_i,$$  \hspace{1cm} (1b)

where $r_i$ is the position vector, $v_i$ is the velocity vector, $m_i$ is the mass, and $F_i$ is the sum of the forces acting on the $i^{th}$ particle. The forces acting on particles are typically chosen as

$$F_i = \sum_{j \neq i} \left( F_{ij}^R + F_{ij}^D + F_{ij}^C \right),$$  \hspace{1cm} (2a)

where $F_{ij}^R$ is the random force, $F_{ij}^D$ is the dissipative force, and $F_{ij}^C$ is the conservative force acting between particles $i$ and $j$. The random force is defined as

$$F_{ij}^R = \sigma_{ij} \omega^R (r_{ij}) \theta_{ij} \mathbf{\hat{r}}_{ij},$$  \hspace{1cm} (2b)
where $\sigma$ is the strength of the random force, $\omega^R$ is a weighting function, $\theta_{ij}$ is a delta-correlated Gaussian random variable with $\langle \theta_{ij}(t) \rangle = 0$ and $\langle \theta_{ij}(t)\theta_{k\ell}(t') \rangle = \delta_{ij\ell} \delta_{k\ell} \delta(t - t')$. The dissipative force is defined as

$$F_{ij}^D = -\gamma_{ij} \omega^D(r_{ij})(\mathbf{r}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{r}_{ij},$$

(2c)

where $\gamma$ is the strength of the dissipative force and $\omega^D$ is a weighting function. The weighting functions are constrained by the relations

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2$$

(3a)

$$\frac{\sigma^2}{2\gamma} = k_b T = \tau,$$

(3b)

in order to maintain a constant temperature $\tau$ in the system. Typically, it is chosen such that

$$\omega^D(r_{ij}) = f(x) = \left\{ \begin{array}{ll} \left(1 - \frac{r}{r_c}\right)^2, & r < r_c, \\ 0, & r \geq r_c. \end{array} \right.$$  

(4)

The relation in (3b) is frequently referred to as the Fluctuation-Dissipation theorem since it relates the strength of the random thermal fluctuations to the strength of viscous dissipation.

Finally, the conservative force is usually defined as

$$F_{ij}^C = \left\{ \begin{array}{ll} a_{ij} \left(1 - \frac{r}{r_c}\right), & r < r_c, \\ 0, & r \geq r_c, \end{array} \right.$$  

(2d)

where $a_{ij}$ is the interaction parameter that depends on the species involved. In Figure 2, the cut-off radius $r_c$ is indicated by the dashed red line and the interaction radius or distance $\mathbf{r}_{ij}$ is indicated between the center of the particle being considered and a particle within the cut-off radius. At the cut-off radius, the ratio $\frac{r}{r_c}$ is 1.
and the magnitude of the conservative force goes to 0, which ensures continuity in the conservative force.

Together the random and dissipative forces form a complete NVT thermodynamic ensemble. So, the conservative force is not required, but is traditionally used since it mimics Newton’s 3rd law of motion. In fact, Yaminoi et al. replaced the conservative force with an entanglement force in order to mimic the behavior expected from the reptation theory for entangled polymers and to prevent bond crossing [4]. However, the conservative force in (2d) is used to control the surface tension between the phases because same phase and different phase interactions can have different conservative force constants.

Groot and Warren determined useful parameter ranges for simulations and related these parameters to the Flory-Huggins chi parameter, extending the range of experimental research accessible to DPD [5]. Spenley further extended the capabilities of DPD by determining the scaling relationships between the degree of coarse graining and explicit model parameters [6]. Now, the computational speed can be changed based on the accuracy of the coarse graining and we can have different size DPD particles in the system after including the coarse grain tunable extension proposed by Yamanoi et al [4].

**Physics of Droplet Breakup**

Droplet breakup is described in terms of two dimensionless numbers: the viscosity ratio and the capillary number. Dimensionless numbers are useful because they define a mapping or similitude between different systems that should behave similarly in the characteristics in the ratio defining the dimensionless number. The viscosity ratio is defined as the ratio of the droplet’s viscosity to the viscosity of the surrounding matrix. Generally, the viscosity of fluid $\eta$ is defined as
\[ \eta(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}}, \quad (5a) \]

where \( \sigma \) is the shear stress and \( \dot{\gamma} \) is the shear rate or rate of strain. For Newtonian rheology, the viscosity \( \eta \) is constant and independent of the shear rate:

\[ \eta = \frac{\sigma}{\dot{\gamma}}. \quad (5b) \]

The capillary number represents the ratio of the viscous forces to interfacial or surface tension. Explicitly, the capillary number is defined in experimental studies as

\[ Ca = \frac{\eta_m \dot{\gamma} R}{\Gamma}, \quad (6) \]

where \( \eta_m \) is the viscosity of the matrix, \( \dot{\gamma} \) is the shear rate or rate of strain, \( R \) is the radius of the droplet, and \( \Gamma \) is the interfacial tension. At breakup conditions, the capillary number is called the critical capillary number. For a given set of materials for the droplet and matrix, the viscosity ratio and interfacial tension are specified; so, the only free parameter in (6) is the shear rate. Since higher shear rates require greater power from the mixing instrument, the critical capillary number is a measure of the effective power necessary to cause breakup of the droplet.

**Experimental Droplet Breakup**

The conditions necessary to cause breakup of a droplet in a matrix with viscosity ratios between \( 10^{-6} \) and around 10 was investigated by Grace [7]. His results are summarized in Figure 3, which shows regions that cause breakup above the curve. From Figure 3, it is clear that it is generally not possible to breakup droplets that are more viscous than the matrix (viscosity ratio > 3.5) using simple shear. The y-axis is similar to the capillary

![Figure 3. Grace Plot (droplet breakup under simple shear) [7]](image-url)
number, a dimensionless parameter that describes the ratio between the viscous and interfacial forces.

4. Literature Review

Since droplet breakup is a mesoscopic and macroscopic phenomenon, it is virtually impossible to study with atomistic methods such as molecular dynamics or quantum calculations. Attempts have been made to characterize the effects of droplet breakup using finite element methods (FEM) and DPD. FEM studies are primarily limited by their inability to model fracture since that would destroy the calculation mesh. On the other hand, DPD studies are not limited in this way and their primary limitation is lack of study.

Finite Element Methods

The effect of confinement on capillary number was observed using the bound integral method [8]. Through comparison with experimental results, binary breakup was observed at low confinements in agreement with the unconstrained situation, but ternary breakup was observed for higher confinements. They found that confinement had no effect on the capillary number for a viscosity ratio of 1. Lower viscosity ratios actually had higher capillary numbers, while higher viscosity ratios had lower capillary numbers. This indicates that it should be possible to breakup droplets with viscosity ratios of 3.5 using confined spaces. In another study, Moldenaers’ group related the capillary number was related to orientation of the deformed droplet and a linear fit was obtained [9]. Alternatively, Hulsen’s group studied the stresses on droplets as they went through a capillary rheometer with a contraction ratio of 5 [10]. However, no comparison was made to the Grace plot in these studies.
Dissipative Particle Dynamics

Visser et al. demonstrated that the viscosity of a fluid could be modified isothermally by changing both gamma and sigma in the Fluctuation-Dissipation theory (Figure 4), but that the resulting viscosity versus gamma plot is non-symmetric [11].

Similar to the confinement work done with FEM, Jones et al. studied a droplet adhered to a surface using DPD, but they studied a constant viscosity ratio in terms of the contact angle under shear [12]. Clark et al. performed proof-of-concept work, showing unconstrained breakup in multiphase systems [13]. Extensional flows were modeled to mimic the separation from a pendant droplet under gravity. Shear flows were also studied and similar structures were obtained to those observed experimentally. However, the range of possible viscosity ratios was not explored to compare with the Grace plot.

![Figure 4. Relation between gamma and viscosity at different temperatures [11].](image-url)
5. Objectives

In this study, we hope to reproduce the Grace plot for Newtonian droplets under shear using DPD to demonstrate that the behavior observed is physically meaningful. Specifically, we intend to use the capillary number and viscosity ratio to reproduce Figure 5 along with droplet shape. Agreement with experiment would indicate that this method could be used to study more complex systems and eventually predict complex flows using non-Newtonian fluids.

From the review of the literature, it appears that DPD is the simulation technique best suited to study this phenomenon since it can study long time scales, reproduce hydrodynamics, and describe chemical interactions, but is not limited by the continuity of meshes as in FEM. In particular, the smooth potentials, coarse graining, cut-off radius, and large time steps make DPD ideal for screening materials computationally before they are experimentally tested. Proof-of-concept work has been performed by Clark et al. indicating that it should be possible to study droplet breakup under shear and extension [13].

![Grace plot](image)

*Figure 5. Grace plot in terms of the capillary number and viscosity ratio. Droplet shape is indicated at various points [14].*
6. Concepts and Methods

In order to reproduce the Grace plot in Figure 5, measurements need to be in place to measure the terms in the capillary and the viscosity. The capillary number is defined in (6). In order to measure the viscosity as defined in (5a), the shear stress and shear rate or strain rate needs to be measured. The shear rate can be measured as

\[
\sigma_{xy} = \frac{1}{V} \left( \sum_{ij} r_{ij,x} F_{ij,y} \right) + \frac{m}{V} \left( \sum_i v_{i,x} v_{i,y} \right),
\]

where \( V \) is the volume of the system, \( m \) is the mass of the particles, \( r_{ij} \) is the distance between particles \( i \) and \( j \), \( F_{ij,y} \) is the \( y \)-component of the forces acting between particles \( i \) and \( j \), and \( v_i \) is the velocity of particle \( i \) for flow in the \( y \) direction acting on the \( x \) normal plane [12]. For our purposes, the mass of the particles has been set to 1 and the measurement is per particle in a unit volume. The interfacial tension \( \Gamma \) is related to the pressure difference \( \Delta P \) by the Laplace equation

\[
P_{in} - P_{out} = \Delta P = \frac{\Gamma}{R},
\]

where \( R \) is the radius of curvature formed by the droplet due to the pressure imbalance. The pressure can be measured using DPD as

\[
P = \frac{1}{V} \sum_{i,j} F_{ij,x} r_{ij,x} - \frac{1}{2} (F_{ij,y} r_{ij,y} + F_{ij,z} r_{ij,z}),
\]

where \( x \) is the direction of flow [12]. \( F_{ij} r_{ij} \) can be thought of as the compressive work done by the pressure. The radius is measured by monitoring the extreme points of the droplet in each direction and fitting them to the equation of a sphere. This result is valid for small deformations.
While measuring the viscosity and interfacial tension are convenient experimentally, the measurement of these properties computationally introduces several errors. An alternative method that reduces these errors is to simplify (6) using the known relations. Substituting (5b) into (6), we get

\[ \text{Ca} = \frac{\sigma}{\Gamma}, \]  

(10)

which is still true for both Newtonian and non-Newtonian rheology. Additionally, the interfacial tension and radius can be substituted by the pressure difference by combining (8) with (10) to give

\[ \text{Ca} = \frac{\sigma}{\Delta P}. \]  

(11)

Again, this is done without a loss of generality because it is from the definition of interfacial tension. Thus, calculation of the capillary number has been reduced to quantities that can be measured directly from the simulation.

Additionally, the interactions between particles of different phases need to be considered if the dynamics of experimental systems are to be reproduced accurately. The conservative force parameter \( a \) has been related to the Flory-Huggins \( \chi \) parameter by Groot and Warren [5]. They found that the self-interaction term \( a_{ii} \) is related to the temperature by

\[ a_{ii} = \frac{75}{\rho} k_b T = \frac{75}{\rho} \tau, \]  

(12)

where \( \rho \) is the density of the phase, \( k_b \) is Boltzmann’s constant, \( T \) is the temperature, and \( \tau \) is the fundamental temperature. The different phase interaction term \( a_{ij} \) is

\[ a_{ij} = \frac{75}{\rho} k_b T + \Delta a = \frac{1}{2} (a_{ii} + a_{jj}) + \Delta a \]  

(13)

where \( \Delta a \) is related to the Flory-Huggins \( \chi \) parameter by

\[ \chi = \frac{\Delta a (\rho_i + \rho_j)}{k_b T} = \frac{\Delta a (\rho_i + \rho_j)}{\tau} \]  

(14)
and $\rho_i$ refers to the density of phase $i$. These measurements all assume that the fluid represented has the isothermal compressibility of water ($\kappa^{-1} = 16$), which is related to the conservative force parameter by the relation

$$\kappa^{-1} = \frac{1}{k_b T} \frac{dP}{d\rho} = 1 + \frac{2\alpha a \rho}{k_b T}, \quad (15)$$

where $\alpha = 0.101$ is the mean field value of the pressure for the DPD system and $\rho$ is the density of the system. More specifically, the compressibility refers to the osmotic isothermal compressibility. This assumes the equation of state

$$P = \rho k_b T + aa\rho^2, \quad (16)$$

where $P$ is the pressure, and $a$ is the conservative force parameter [5].

Also, the interactions of particles in the dissipative and random forces need to be considered. Visser et al. compared different averaging techniques and discovered that the most effective method for minimal computational cost was to use a harmonic mean for the different phase interactions [11]. This means that the different phase random force parameter would be calculated as

$$\sigma_{ij} = \frac{1}{2} \left( \frac{1}{\sigma_{ii}} + \frac{1}{\sigma_{jj}} \right) \quad (17)$$

and the same is true for the dissipative force parameter $\gamma$.

The system studied in this thesis will be in the NVT ensemble with periodical boundary conditions. The droplet is a collection of 500 DPD beads and the matrix is 100,000 DPD beads. The system is allowed to thermally equilibrate for 100 time steps before imposing shear for 500 time steps. The system is integrated for $\Delta t = 0.01$ using the Verlet leapfrog algorithm [5]. In order to prevent the droplet connecting with itself through the periodical boundary condition and forming an infinite column, the simulation box in direction of shear is twice as long as the other
two dimensions. All changes of sigma and/or gamma will be quantified in terms of the effect on temperature as a result of the Fluctuation-Dissipation theorem. Also, the conservative force parameter will be adjusted using (12) as temperature is changed. The default parameters for the one parameter model are \( \sigma = 5.61, \gamma = 3.35, a_{ii} = 12.5, a_{ij} = 30 \). The default parameters for the two parameter model are \( \sigma = 10, \gamma = 4.4721, a_{ii} = 12.5, a_{ij} = 30 \).

7. Results

Given the Fluctuation-Dissipation theorem in terms of sigma, gamma, and temperature, there are two clear ways to change viscosity: change one parameter and hold the other one fixed, allowing temperature to change; or hold temperature constant by changing the two parameters. Since the goal of this study is to first determine if it is possible to describe droplet breakup in DPD, we will use simplest computational method first. Namely, changing gamma and holding sigma fixed, which will change temperature (“one parameter method”). While the physical interpretation of these results is unclear since a viscosity ratio would be constructed by putting two materials with different temperatures together, it is useful in letting us know if it is worth pursuing more complex and physically meaningful methods. Based on the results of the one parameter method, we will try to extend the method using the two parameter method, where both sigma and gamma are changed to hold temperature constant. In this system, the temperature of both fluids will always be the same, which has a direct physical interpretation.

General Material Properties

Before trying to recreate the Grace plot, it is important to define the properties of the material we are modeling in order to ensure that we are meeting the assumptions for the Grace plot. Namely, we need a fluid with Newtonian rheology that can be deformed by simple shear and responds to changes in temperature in a physically meaningful way. Fluids behaving
physically have a constant interfacial tension with regards to changes in shear rate, but should strongly decrease as temperature is increased in a critical range and then plateau at high temperatures when the thermal energy is large enough for the molecules to overcome the repulsion energy barrier causing phase separation. By definition, Newtonian fluids do not change viscosity with shear rate. However, physical fluids have an Arrhenius-type activation energy behavior in terms of viscosity changes as a result of temperature changes. Namely, the viscosity should decrease exponentially as temperature increases.

**Viscosity**

The viscosity was studied using only one phase. The shear stress measured using (7) and the shear rate was an input to the simulation. The measured shear stress at different strain rates is shown in Figure 6. The slope is linear with an adjusted $R^2 = 0.9997$, which indicates that a
constant linear slope is an appropriate description for this system as assumed in (5b) for Newtonian rheology. The change of viscosity with temperature is shown in Figure 7. The red curve is a fitted line because the Arrhenius equation is

\[ \eta = A e^{\frac{E_a}{RT}}, \]

(18)

where \( \eta \), \( A \) is a fitted pre-exponential constant, \( E_a \) is the activation energy, \( R \) is the ideal gas constant, \( k_b \) is Boltzmann’s constant, and \( T \) is the temperature in Kelvin. The exponential is a good fit to the data with an adjusted \( R^2=0.9997 \). The fitted activation energy is about 200 \( \text{j/(particle K)} \), which corresponds to about 15 \( \text{kJ/(mol K)} \) for a small molecule such as hexane with a molecular weight of 84 g/mol. This is in the right ballpark since NIST reports data for hexane of about 10 \( \text{kJ/mol} \) [15]. This rough agreement gives us confidence in the physical realism of this result. A further verification of the Newtonian properties and activation energy
behavior is given by examining the shear stress plots in Figure 8. Both of these graphs show the shear stress versus temperature as in Figure 7. The same trend is observed in both graphs, indicating that there is only a shift in magnitude by increasing the shear rate from 0.05 to 0.50. This is expected since the fluid is Newtonian, which means that the ratio of shear stress to strain rate is independent of strain rate. As the strain rate increases, the shear stress increases in order to maintain a constant viscosity at constant temperature. The overall curve recovered is also an exponential decay with temperature or an exponential increase with the inverse of temperature as expected from the activation energy behavior for the fluid. Thus, the fluid has been shown to have Newtonian rheology and follow an activation energy model.

**Interfacial Tension**

The interfacial tension at constant temperature, but different shear rates is shown in Figure 9. It is clear that the interfacial tension is constant because the constant line is within the error bars for all of the measurements. The change in interfacial tension with temperature is
Figure 9. Interfacial tension versus shear rate at constant temperature shows a constant interfacial tension regardless of shear rate.

Figure 10. Interfacial tension changes with changes in temperature shows a physically expected trend.
shown in Figure 10. The interfacial tension strongly decreases as temperature is increased for temperatures below \( k_b T = 1 \) and then plateau at high temperatures to around 1. This makes physical sense as argued before because the molecules have enough energy to overcome the repulsion energy barrier causing phase separation at high temperatures.

**One Parameter Method**

The first concern in creating the Grace plot is what range of viscosity ratios is open. From Figure 7, it is clear that there are at least three orders of magnitude easily accessible. There is no reason to suggest that greater viscosity ratios are inaccessible; however, the major characteristics of the Grace plot all occur within 2 orders of magnitude from unity. Thus, the different viscosities measured can be put together as droplet and matrix pairs. For several viscosity ratios, the shear rate was varied to pin down the critical capillary number, which is the region where the system goes from not breaking up to breaking up. The resulting capillary numbers are plotted versus viscosity ratio along with snapshots of the droplets at different regions of the plane in Figure 11. The slope of the critical capillary line decreases gently from the left towards a viscosity ratio of one. There is a minimum around a capillary number of one at a viscosity ratio of about one. Then, the critical capillary line increases more sharply to the right past a viscosity ratio of one. These are the important qualitative features of the experimental Grace plot in Figures 3 and 5. Additionally, the snapshots of the droplets appear similar to the inset sketches in Figure 5. In particular, there is no deformation at low capillary numbers of all viscosity ratios. At low viscosity ratios, the droplet breaks up through the S-shaped figure shown with the small neck at roughly 45 degrees while the main droplet bodies are parallel to the shear. At viscosity ratios around unity, stress is best transferred from the droplet to the matrix as evidenced by the lower capillary number required to breakup the droplet. This
causes the droplet to deform smoothly before it breaks up as shown in the snapshots. At higher viscosity ratios, the matrix is more easily deformed than the droplet, which means that when the droplet breaks up it will be closer to 45 degrees since greater stress is needed to breakup the droplet. Experimentally, it was measured that for viscosity ratios greater than 4, the droplet could not be broken up. However, there is some question as to whether or not this part of the Grace plot is physical or a limitation of the experimental apparatus since a less easily deformed droplet with poor stress transfer is more likely to act like a barrier, which causes deformation of the flow, which leads to extensional flows in the matrix only for the concentric cylinders apparatus used in the experiment. So, it is not very concerning that the high viscosity ratio

Figure 11. One parameter Grace plot is qualitatively correct. It has a gentle slope from the left, a minimum near a viscosity ratio of one, and a sharper increase after.
region of Figure 11 is not as sharp as experimentally measured. Overall, the qualitative features of the Grace plot are captured by this method.

**Two Parameter Method**

The success of the one parameter method gives us confidence that DPD can reproduce the Grace plot, which motivated us to examine the more physically meaningful, but computationally more complex two parameter method. Again, the first concern is what viscosity ratios are accessible using this method. According to the literature result in Figure 4, the viscosity changes slowly for high gamma values, but increases sharply for small gamma values. This

![Figure 12. Changes in viscosity as a result of changes in gamma using the two parameter method.](image-url)
figure is reproduced in Figure 12, which validates our implementation of the two parameter method. It is more useful for our purpose to view this trend on logarithmic axes, which is shown in Figure 13. The viscosity slowly increases for gamma greater than 10, which is not useful for our purposes. To the left, the viscosity increases sharply, but systems with gamma less than 0.02 are unstable, meaning that the droplet flies apart and does not have a stable temperature. So, we are limited a two order of magnitude range of viscosities, which means that we can simulate from viscosity ratios of 0.01 to 100. This is sufficient since all of the key features can be identified within two orders of magnitude of a viscosity ratio of one.
The grace plot that is constructed using this range of viscosities is shown in Figure 14. The capillary number curve decreases from the left towards a minimum around one. However, the minimum actually occurs at a viscosity ratio of three or four. The sharp increase to the right is completely missing from the graph. This is by far the biggest problem with Figure 14. Additionally, it appears from the snapshots that the droplet breaks up the same way for all viscosity ratios. The S-shaped droplet is not observed at low viscosity ratios, which is an indication that there are more problems with this method.
8. Discussion

At low viscosity ratios, the droplet breaks up through the S-shaped figure shown with the small neck at roughly 45 degrees while the main droplet bodies are parallel to the shear. This is because the maximum stress components of the shear occur at 45 degrees to the strain in the matrix, which deforms the droplet more in the center because stress is poorly transferred between the droplet and the matrix [16]. At viscosity ratios around unity, stress is best transferred from the droplet to the matrix as evidenced by the lower capillary number required to breakup the droplet. This causes the droplet to deform smoothly before it breaks up as shown in the snapshots. At higher viscosity ratios, it is harder to breakup the droplet because there is again poor stress transfer from the matrix to the droplet. Here, the matrix is more easily deformed than the droplet, which means that when the droplet breaks up it will be closer to 45 degrees since greater stress is needed to breakup the droplet. Experimentally, it was measured that for viscosity ratios greater than 4, the droplet could not be broken up. However, there is some question as to whether or not this part of the Grace plot is physical or a limitation of the experimental apparatus since a less easily deformed droplet with poor stress transfer is more likely to act like a barrier, which causes deformation of the flow, which leads to extensional flows in the matrix only for the concentric cylinders apparatus used in the experiment. This reduces the stresses felt by droplet further, which makes the observed capillary number higher than it would be in a non-confined apparatus such as an extruder. Additionally, thermal gradients or impurities in the experimental apparatus could disrupt the systems and stress transfer mechanisms. Thus, it is not concerning that we do not perfectly reproduce the Grace plot at high viscosity ratios.
The one parameter method (Figure 11) was able to correctly reproduce the Grace plot at least qualitatively. The qualitative agreement between the shape of the critical capillary number curve and the snapshots indicate that stress transfer is being correctly modeled. In particular, we are able to produce different types of breakup in terms of droplet morphology. Thus, the droplet breakup phenomenon can be correctly described using DPD. Physical interpretation of the one parameter requires a reinterpretation of the meaning of temperature in the system. Obviously, it does not make sense physically to have a droplet at different temperature in contact and equilibrium. Since we are using temperature to control the viscosity of the system, it makes more sense to interpret the temperature of the system as an “internal temperature” representing the viscosity of the system. Other simulation methods, most notably the Lennard-Jones potential, have required measurement of physical constants in order to relate the simulation results to physical results. So, it is not completely reasonable to suggest that the “temperature” of the system could be a measured or fitting parameter based on the viscosity of the system at the temperature of interest. The behavior of a fluid would then be modeled by viscosity at a given temperature and the “internal temperature” of the system, which could be used to control the activation energy.

Unfortunately, the two parameter system (Figure 14) was not able to correctly reproduce the Grace plot. The biggest problems are that the critical capillary number curve does not have the sharp increase to the right of unity viscosity ratio and does not have the correct droplet breakup morphology as indicated by the snapshots. Clearly, there is a problem with how the system models interactions. Based on the axes plotted in the Grace plot, it makes sense to examine the viscosity and interfacial tension. We reproduced the viscosity change with gamma from the literature (Figures 4 and 13); so, it is unlikely to be the viscosity control. Thus, the
interfacial tension is most likely the problem. The interfacial tension is primarily controlled by the temperature (Figure 10) and the conservative force parameter. The conservative force parameter is updated with regard to temperature based on (12) and (13). Since the one parameter change correctly reproduced the droplet breakup phenomenon, it is unlikely to be the temperature relation. However, the other contributions to the conservative force parameter are more significant in the two parameter method because temperature is not changing. Thus, the way that the conservative force parameter is related to the Flory-Huggins chi parameter (14) may be to fault. In deriving this relation, Groot and Warren used isothermal compressibility (15) to say that the fluid modeled was incompressible by setting its isothermal compressibility equal to that of water. It is possible that the compressibility of the fluids used by Grace were more compressible than water, which would indicate a higher conservative force parameter. In particular, this definitely the case for larger chained molecules such as oils and polymers that have radius of gyrations that can be changed based on hydrostatic pressure. This free volume does not really exist in water, but is significant even in the sorts of oils that were used to measure the experimental Grace plot. This would cause greater interfacial tension and phase separation. As a result, stress transfer would be worse at viscosity ratios further from unity, which leads to higher critical capillary numbers as previously discussed.

Ultimately, we were able to achieve our goal of reproducing the Grace plot for the droplet breakup phenomenon under shear using DPD. The success of the computationally simple one parameter model validates our hypothesis that it is possible, but the two parameter model shows that there are additional complexities that need to be addressed before implementing a DPD model that has a direct physical interpretation.
This work is significant in that this is the first time that the full Grace plot has been reproduced computationally. With work on the two parameter model, it is possible to have a model with a direct physical interpretation. This opens the door for using DPD as a screening tool for determining if a given materials will be processable and dispersed using certain processing conditions. In a more complex application, DPD could potentially be used to describe the full behavior inside processing equipment, which could allow for optimization of processing equipment for different materials in ways that other techniques such as FEM could not because the parameters in DPD can account for the chemical nature of the materials. More direct extensions of this work include the study of extensional flows, non-Newtonian rheology such as shear thinning and shear thickening, and studying polymeric chains.

9. Conclusion

The droplet breakup phenomenon was described using DPD. The one parameter method allowed us to verify that it is possible to study the droplet breakup phenomenon in a computationally simple way. Qualitative agreement in the critical capillary number curve and the droplet morphology indicate that we are correctly capturing the main characteristics and physics of the phenomenon. Extension of this approach to a more physically meaningful case in the two parameter system was not as successful. In particular, the droplet morphologies all appear to be roughly the same and the sharp increase to the right of unity viscosity ratio is missing. This may be a result of the incompressibility assumption used to determine the conservative force parameter, which is most significant in the two parameter system. Future work will include studying extensional flows, non-Newtonian rheology, and polymeric chains.
10. References


