SHEAR THICKENING OF SILICA ROD SUSPENSIONS

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ABSTRACT

Colloidal particles in a liquid such as silica rod suspensions exhibit non-Newtonian behaviors like continuous shear thickening (CST) and discontinuous shear thickening (DST). These rheological behaviors of suspensions of spherical particles have been widely studied and abrupt shear thickening is known to be a result of the increasing interparticle frictional interactions with the increase of particle volume fraction and stress. These behaviors in suspensions of rod-like particles, however, have only recently been investigated due to the complexity of the rod-like particle suspensions under shear. While the role of the interparticle frictional forces has been explored, the contribution of the aspect ratio and size of the particles to shear thickening has mostly remained unknown. Here, we synthesize silica rods with a tunable aspect ratio in water/glycerol solution. We then perform rheological measurements to study the shear thickening behavior on several aspect ratios and sizes of the rod-like particles with various volume fractions. We demonstrate a decrease in the critical volume fraction for DST with increasing aspect ratio. With the Wyart and Cates model (W-C model), we can obtain the frictionless jamming fraction, $\phi_0$, and the frictional jamming fraction, $\phi_m$. We also investigate the effect of temperature on shear thickening and show that the flow curves of the relative viscosity under temperatures from 0 to 35 °C collapse onto a single curve.
INDEX WORDS: Physics, Condensed Matter, Soft Condensed Matter, Materials Science, Complex Fluids, Dissertations, Theses (academic)
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CHAPTER 1

INTRODUCTION

Rod-like particles can provide strength and integrity to certain materials as fiber reinforcement so they are often used to change the rheological properties of a solution, such as the viscosity of the materials [1,2]. They play an important role in a variety of commercial materials such as paper, food, pharmaceuticals, and other consumer products [3–6]. For example, in the paper industry, anisotropic particles like kaolin, clays, and precipitated calcium carbonate (PCC) are added to the suspensions to help improve paper opacity in the paper making process [7]. However, with the addition of rod-like particles to the solution, the suspension can undergo a non-Newtonian fluid behavior called shear thickening [8]. This phenomenon is what we are interested in studying here.

One of the well-known examples of shear thickening is cornstarch in water [9]. The suspensions undergoing shear thickening will experience increasing viscosity with ascending applied shear stresses. That is the reason why a person can walk on the cornstarch solution without sinking in [10]. This process, however, could sometimes be harmful in industrial applications. For example, shear thickening in suspension can lead to damage to the equipment, such as shear jamming [7]. Therefore, with a wide range of applications in the industries, a better understanding of shear thickening on rod-like particle suspensions is important.

However, despite the large quantities of studies that have been done on the suspensions of spherical particles [11–13], there is still a lack of understanding of high aspect ratio particles in terms of
their flow-induced shear thickening. It is known for spherical particles, it experiences shear thickening when volume fractions increase [12,14]. High aspect ratio particles exhibit this same behavior. However, it is believed with higher aspect ratios, the colloidal suspensions would undergo shear thickening at lower volume fractions compared to its spherical counterparts [8,15–17] and it is partly due to the lower random packing densities for higher aspect ratios [18]. Volume fractions here are defined as the volume of the solid particles over the total volume of the solids plus liquids. However, for rod-like particles, unlike their spherical counterparts, there is a phase transition happening with the change of aspect ratio and volume fraction. A phase transition between isotropic and nematic phase when aspect ratio and volume fraction increase would also affect the shear thickening behavior of the liquid, which makes the research on high aspect ratio particles much more complicated than their spherical counterparts [19]. In our research, we are using various aspect ratios of silica rods with different volume fractions to study the shear thickening process.

Silica rods are rod-like materials with aspect ratios that are easily tunable. Here, we are using one pot wet chemistry method to obtain silica rods [20]. By simply changing the synthesis conditions such as the amount of chemical contents, temperatures, etc. we can obtain well-dispersed silica rods with different aspect ratios within a certain amount of polydispersity. Therefore, it is a great material to be used to study the effect of aspect ratios on rheological properties of suspensions, such as shear thickening [20,21]. We use SEM to characterize the particles and rheometer to perform the rheological measurements.

We are studying how the aspect ratio of rod suspensions would affect its shear thickening behavior
under different volume fractions [8,15,22,23]. In our results, we show the flow curves of silica rods with aspect ratios of 2, 6, and 9 with various volume fractions. We can see that above a certain volume fraction, the silica rod suspensions start to show continuous shear thickening behavior (CST). And at a critical volume fraction, the suspension would undergo discontinuous shear thickening (DST). Both of these volume fractions for CST and DST decrease with increasing aspect ratio. However, the sizes of the particles will also affect shear thickening. Using the Wyart and Cates model (W-C model), we can obtain the frictionless jamming fraction, $\phi_0$, and the frictional jamming fraction, $\phi_m$. We also investigate the effect of temperature on shear thickening and show that the relative viscosity collapses onto a single curve, which is consistent with previous work on spherical particles [16].
CHAPTER 2

BACKGROUND

2.1 SHEAR FLOW AND VISCOSITY

Shear flow is a type of laminar flow caused by applied shearing forces. In a simple shear flow, when an external force is applied to the fluid, fluid at different heights of the solution moves at a constant velocity. Its value is proportionate to the height and its gradient direction is perpendicular to the flow direction [24].

One of the simplest shear flows is called Couette flow. In the Couette flow, the liquid is placed between two parallel plates, as shown in figure 2.1. The bottom plate is fixed while the top plate is moving at a constant speed along the x-axis. If we imagine the fluid consists of multiple layers, each of these layers within the fluid moves at a speed proportionate to their height. This causes the velocity gradient along the y-axis. Moreover, the different velocities between the adjacent layers result in a frictional force resisting the relative movement between them. And this is the cause of viscosity. In particular, the fluid near the top plate has a force in the direction opposite to the movement of the plate, and there is an equal but opposite force on the bottom plate. Therefore, an external force is required to keep the top plate moving at a constant speed.
Figure 2.1: Configuration for Couette flow with two infinite plates. Here, the external force is applied on the top plate with a constant velocity \( u \), and the bottom plate is stationary. Velocity is on the x-axis and the velocity gradient is on the y-axis.

There are three directions when we discuss a shear coordinate system. As shown from the figure 2.2, we define x as the flow direction, y as the gradient direction, and z as the vorticity direction.

To simplify the matrix, with the choice of axes, there is a velocity only in the x direction and zero velocity in y and z directions, as shown below. The strain rate tensor can be shown as below, with only one non-trivial component:

\[
\Gamma = \begin{pmatrix}
\partial_x u_x & \partial_y u_x & \partial_z u_x \\
\partial_x u_y & \partial_y u_y & \partial_z u_y \\
\partial_x u_z & \partial_y u_z & \partial_z u_z
\end{pmatrix} = \begin{pmatrix}
\dot{\gamma} & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]  \hspace{1cm} (2.1)

Here, \( \dot{\gamma} \) is the shear rate under the flow direction along the x-axis.
As we mentioned earlier when under shearing, fluids with different viscosities have resistance to this shearing motion. The stress $\sigma$ applied by the fluid in resistance to the shear is proportional to the shear rate $\dot{\gamma}$. This proportional constant is called dynamic viscosity $\eta$, as defined below:

$$\sigma_x = \eta \dot{\gamma}$$ (2.2)

Newtonian fluids are fluids where stresses are linearly proportional to the local strain rate at any given point. That is equivalent to saying that viscosity for these fluids is constant no matter what stresses are applied. For Newtonian liquids, the viscosity is an intrinsic material parameter and is independent of the shear rate [13,22].

Adding small particles in a Newtonian liquid, however, can cause the liquid to have non-Newtonian behavior. In this case, the viscosity may vary with the shear rate, and the viscosity is given as a function of shear rate. In some instances, viscosity decreases with increasing shear rate, resulting in a rheological behavior called shear thinning. In other cases, the increasing shear rate
has the opposite effect on the viscosity. The viscosity of the liquid increases with the shear rate, resulting in shear thickening, which will be discussed in more detail in the shear thickening section [4,22].
2.2 Brownian Motion

Brownian motion is a random fluctuation of particles in a suspension that collide with their surrounding fast-moving liquid particles. There is no preferential direction for the particles when the liquid is at thermal equilibrium.

Figure 2.3: Three tracings of colloidal particles of radius 0.53 µm, as seen under the microscope. Successive positions every 30 seconds are joined by straight line segments (the mesh size is 3.2 µm). Reproduced from the book of Jean Baptiste Perrin, Les Atomes.

For colloidal particles, since the particle sizes and suspension viscosities here are sufficiently small, thermal fluctuations are relevant here. Therefore, we need to take into the account of Brownian motion. To compare with experimental results, it is desirable to express physical quantities in dimensionless units. For suspensions that are under shear, thermal fluctuations are characterized by the dimensionless Peclet number.
For rods, there are translational diffusion coefficients and rotational diffusion coefficient. Translational diffusion coefficients are used to determine the fluctuations of the positions of particles in space while rotational diffusion coefficient is used to determine the changes in orientation of the particles. For spheres, since there is no need to consider orientations, we would only consider translational diffusion coefficients when we calculate the Peclet number. For rods, however, the rotational diffusion coefficient is more important when it compares to relaxation time. Therefore, the Peclet number for rods is the shear rate in units of the rotational diffusion coefficient of the rods, which is defined by the ratio of advective transport rate to diffusive transport rate for rods:

\[
P_e = \frac{\text{advective transport rate}}{\text{diffusive transport rate}} = \frac{\dot{\gamma}}{D_r}
\]  

(2.3)

Where \(D_r\) is the rotational diffusion coefficient, \(\dot{\gamma}\) is the shear rate. Here, we also employ the rotational diffusion coefficient \(D_r^0\) at infinite dilution. The expression for diffusion coefficient is:

\[
D_r^0 = \frac{3k_BT}{\pi \eta L^3} \ln \left( \frac{L}{d} \right) - \frac{2}{3}
\]

(2.4)

Here, \(L\) is the length of rods, \(d\) is the effective diameter and \(\eta\) is the solvent viscosity. [25]

In the case that shear rate is high enough, as we can see from the above equation, the Peclet number would be large, which means that the suspension becomes non-Brownian. On the other hand, when Peclet number is zero, meaning the suspension is not subjected to any form of shear, under certain
concentration, suspension can order into nematic and smectic phase, which we will discuss in section 2.6.
2.3 **Measurement Setup**

For our experiment, we measure the rheological properties, such as viscosity, normal force, etc. of our samples using rheometer 302 from Anton Paar. The setup of the 302 and physical components are shown in the figure below.

![Figure 2.4: Setup of Anton Paar Rheometer 302 and the physical components for the measuring system. Left: the setup of Anton Paar Rheometer 302. Right: the physical components for the measuring system. It includes a quick connector, a measuring tool, and a base mount. (Figure from Anton Paar Rheometer 302 manual.)](image)

There are primarily three measuring geometries: concentric cylinders, cone-plate, and parallel-plate, as shown in figure 5. For concentric cylinders, the measuring tool is completely immersed in the liquid to be measured. The advantage of this geometry is it is useful for measuring low
viscosity liquids, it is easy to handle (by simply filling the cup with liquids to a certain mark and lowering the tool) and has good thermal stability. The disadvantage is that it requires a lot of liquid and it is usually not realistic to use a lot of samples in the experiment as samples might be difficult to obtain in a large quantity. The second measuring system is cone-plate. It is shaped like a cone with a certain angle and a cut off plateau on the center of the tool. The advantage of cone-plate is that it gives consistent shear conditions, which means the shear rate and shear stress are a constant number throughout the fluid sample. Moreover, it requires a relatively small sample volume and has a fast temperature equilibration. The disadvantage is that since the center of the gap is relatively small, it can only be used to measure solution with particle size less than 10 µm. The third measuring system is parallel-plates. It is recommended for highly viscous materials and it has an adjustable gap. The disadvantage is that it uses a relatively larger amount of samples compared to cone-plate and subjects the sample to a range of shear rates.

Figure 2.5: Three measuring geometries for rotational and oscillatory rheometer. The geometries from left to right are concentric cylinders, cone & plate, and parallel plates. (Figure from Anton Paar Rheometer 302 manual.)
After the samples are loaded, the measuring tool can be lowered to the required position according to the type of tools used and the amount of desired sample. A spatula is used to trim the excessive amount of sample. This is an important step since the excessive amount of liquid would affect the results of the measurements. And as needed, mineral oil can also be applied to prevent the evaporation of the samples. All kinds of experiments can be carried out using the software RheoPlus or RheoCampus, such as flow curves, etc.

The setup for a confocal rheometer is different from the setup of the rheometer 302 that is shown in the right panel of figure 2.4. Instead of a solid base mount, a stage with a certain shape of holes cut out on the bottom is used. A glass cover slide can be placed on top of the stage with a secured ring. An objective is placed below it. The other settings and procedures of the experiment are the same. However, with the addition of the objective, we can observe the localized movements of the solution using fluorescent beads, which otherwise would not be possible with a regular rheometer.

There are two kinds of tests that we can perform on a Rheometer: rotational tests and oscillatory tests. For the rotational test, different rotational speeds are set to determine the shear rate. Using this method, the rheometer can determine the required shear stress $\tau$ according to the viscosity equation $\eta = \tau/\gamma$. It is considered destructive for internal structures of materials under the rotational test if the destruction of the internal structures is irreversible. Therefore, it is primarily used for characterizing the viscous properties of materials with a relatively simple internal structure.

For the oscillatory test, the sinusoidal oscillations are used in the way to explore the sample's
viscoelastic properties at its linear regime. When the test is performed in a sample’s linear-viscoelastic range, it is deemed as “non-destructive” as its applied forces do not disturb or destroy the microstructure of the material. Therefore, it is mostly used for investigating the stability of materials with a complex structure.
2.4 Continuous Shear Thickening and Discontinuous Shear Thickening

As we mention earlier, when certain solid particles are dispersed in a Newtonian fluid suspension, they can change the viscosity property of the suspension and transform it into a Non-Newtonian fluid. When the volume fraction of the silica rod suspension is above a threshold, the fluid will undergo shear thinning at lower shear stresses and shear thickening at higher shear stresses [28]. The focus of my research is on the shear thickening part of the flow curve so here we are going to focus on that. When the fluid is shear thickening, it will undergo a dramatic increase with increasing stresses [12]. As we can see from figure 2.6, a person could run across the surface of a suspension of cornstarch in water without sinking in [22]. Moreover, this shear thickening process is reversible, unlike shear-induced aggregation [26]. When the applied stress is removed, the suspension would go back to the fluid state [27].

Figure 2.6: A person running on top of a dense suspension of cornstarch and water. The fluid can temporarily hold up the person’s weight like a solid. [22]
There are two types of shear thickening. When we plot viscosity with shear rate, we can see that when the volume fraction of the suspension is modestly high, the suspension undergoes continuous shear thickening (CST), where the viscosity of the suspension increases smoothly with increasing shear rate [28]. While at higher volume fraction, the suspension would undergo discontinuous shear thickening (DST), where the viscosity jumps abruptly over several orders of magnitude when the shear rate is above a critical point as shown in figure 2.7 [29,30]. When we plot viscosity with stress, we can see that for Newtonian fluid, the slope of the flow curve is zero. For Non-Newtonian fluid in CST regime, the slope of log viscosity versus log strain rate of the flow curve is above zero and under one. When the fluid is in DST regime, the slope of the flow curve is one.

The theory of the reason non-Newtonian fluids undergoing shear thickening from previous studies is based on two types of particle interactions, frictional and hydrodynamic forces, which we will discuss further in Wyart-Cates model section [15,31–33].
Figure 2.7: Flow curve of cornstarch in a solution of 85% glycerol and 15% water with different mass fractions. [22]

The samples being used in figure 2.7 is cornstarch in a solution of 85% glycerol and 15% water with different mass fractions. In the first flow curve of shear stress versus shear rate as seen in figure 2.7, shear thickening is defined by the region with a slope greater than 1. The development of apparently discontinuous viscosity curves can be seen as the mass fraction increases toward a critical volume fraction called $\phi_c$. Above $\phi_c$, the suspension becomes a yield stress fluid, which means if below the yield stress, the fluid acts like a solid and it needs stress above the yield stress to shear the fluid. If the same data are replotted as viscosity versus shear stress, it shows the gradual evolution of the increasing slope in the shear thickening regime, confined in the stress range between $\tau_{\text{min}}$ and $\tau_{\text{max}}$. When plotted as $\eta(\tau)$, a slope greater than zero corresponds to shear
thickening, and a slope of 1 corresponds to a discontinuous jump in stress [22].
2.5 W-C Model

Recent studies and simulations have shown that shear thickening behavior occurs with applied shear stresses on the suspension. In the past, researchers proposed that the transition between continuous shear thickening and discontinuous shear thickening was due to the transition from hydroclusters to frictional forces [34,35]. These hydroclusters are aggregated particles compressed together momentarily, forming irregular shape of particle groups. Simulations and experiments are suggesting that shear thickening is due to the formation of hydroclusters when the short-range hydrodynamic lubrication forces overcome the interparticle repulsive forces under shear flow [36].

However, studies have been done in recent years using shear reversal protocol, as seen in figure 2.8 [11]. For a contact dominated fluid, contact forces would drop to zero immediately upon reversal of an applied shear strain. Hydrodynamic forces, however, would stay the same in magnitude and only the direction of the forces would be the opposite. With these studies, the researchers argue that the transition from frictionless to frictional inter-particle contacts dominates in the regime of both continuous and discontinuous shear thickening [37,38].

Based on this, Wyart and Cates developed a model (W-C model) to make predictions of shear thickening behavior of colloidal particles based on contact forces theory with various parameters, such as the fraction of frictional contacts f. Several studies have shown that the W-C model can reliably reproduce the experimental rheological behavior for spherical particles [16,33,39]. However, it has its limitations when it comes to rod-like particles. In this section, we will discuss the WC model and its shortcomings.
Figure 2.8: Scheme of shear reversal protocol. (a): the applied shear strain is a triangle wave with an amplitude of 10 and the shear rate is a corresponding square wave. (b): green line is the instantaneous stress response of a viscous fluid while red line is the response for a contact-dominated fluid [11].

Here, we describe a published investigation of polymethylmethacrylate (PMMA) sphere suspensions with diameter $d=4\mu m$ to illustrate the application of the W-C model [40]. Figure 2.9(a) shows the flow curves of PMMA sphere suspensions at various volume fractions. As we can see from the curves, suspensions undergo shear thickening when the volume fraction is above the critical volume fraction threshold. Moreover, at a fixed shear stress, relative viscosity increases with volume fraction. Viscosity for different volume fractions at different stresses from these flow curves can be expressed as:
Here, $\eta$ is the viscosity measured by rheometer, $\eta_f$ is the solvent viscosity, $\phi$ is the sample volume fraction and $\phi_J$ is the stress dependent jamming volume fraction. The fitting parameter $\beta$ here is generally taken to be 2 [41–43]. However, others have taken this number to be 1.8 as well [17].

$$\frac{\eta}{\eta_f} = \left(1 - \frac{\phi}{\phi_J}\right)^{-\beta} \tag{2.5}$$

Figure 2.9: Relative viscosity and jamming volume fractions. (a) Relative viscosity vs. shear stress at different volume fractions for PMMA spheres with diameter 3.78um. (b) Values of relative viscosity under different shear stress are plotted at various volume fractions. Lines are fits plotted using the equation (2.5). Blue and red lines correspond to low stress and high stress viscosity plateaus. (c) Jamming volume fractions $\phi_J$ are plotted at different shear stress. [40]

If we replot these data points with volume fraction as the x-axis and relative viscosity as the y-axis, relative viscosities under different volume fractions with the same shear stress can be fitted using equation (2.5), as shown in figure 2.9(b). The volume fraction, under which the relative viscosity
diverges, is the jamming fraction \( \phi_j \). Specifically, \( \eta_0 \) is the low stress viscosity plateau (blue line) at low shear stress. Here, they are the values of the viscosities under 0.1Pa stress for all volume fractions. And \( \eta_m \) is the high viscosity plateau (red line) at high shear stress. They are taken as the plateau values under 200Pa.

At a fixed volume fraction, the relative viscosity increases with increasing shear stress as shown with a vertical black arrow in figure 2.9(b). Hence, \( \phi_j \) can be plotted as a variable of \( \sigma \) as shown in figure 2.9(c) for various values obtained from figure 2.9(b). As we can see from figure 2.9(c), \( \phi_j \) is dependent on \( \sigma \). It is higher with lower shear stresses and decreases when shear stresses increase between the range of \( \phi_0 \) and \( \phi_m \).

In the W-C model, contacts between particles are either lubricated, with friction coefficient \( \mu = 0 \), or frictional, with \( \mu > 0 \). The fraction of the frictional contacts is called \( f \), and it increases with shear stress \( \sigma \) since higher shear stress forces more particles to encounter each other. And W-C posit a repulsive force that must be overcome for particles to come in contact.

In the W-C model, jamming volume fraction can be expressed as a function of \( f \) only:

\[
\phi_j^{WC} = f \phi_m + (1 - f)\phi_0
\]  

changing linearly from random close packing, \( \phi_0 \), at \( f = 0 \) to frictional jamming, \( \phi_m \), at \( f = 1 \). Thus, \( \phi_j^{WC}(f(\sigma)) \) decreases with \( \sigma \).

As we discussed earlier, viscosity is dependent on stress \( \sigma \) and volume fraction \( \phi \). Therefore, according to equation 2.5 and 2.6 above, the viscosity should be determined by three factors: \( \phi_0 \),
\( \phi_m \) and \( f \). Here, \( \phi_0 \) and \( \phi_m \) are the limiting frictionless and frictional jamming points, which can be obtained by fitting the flow curves at low and high stress plateaus. \( f \) can be determined by the equation below:

\[
    f(\sigma) = \exp\left[-(\sigma^*/\sigma)^\beta\right]
\]

(2.7)

Here \( \sigma^* \) is the critical shear stress where the flow curves start its shear thickening and \( \beta \) is generally taken as 0.85.

Therefore, the logic of the W-C model for shear thickening can be shown in figure 2.10. First, we obtain the relationship between the jamming volume fraction and shear stress by combining their relationships with a mutual faction of frictional contact \( f \) with equations 2.6 and 2.7. Then with equation 2.5, we can, therefore, plot the flow curve.
Figure 2.10: Fraction of frictional contacts $f$ and jamming volume fraction. (a) Fraction of frictional contacts $f$ as a variable of $\sigma/\sigma_0$. (b) $\Phi_{WC}^J(f)$ as a linear equation between $\phi_0$ at $f=0$ and $\phi_m$ at $f=1$. Combining the two plots, we can get (c) $\Phi_{WC}^J(f(\sigma))$ as a function of $\sigma/\sigma_0$. Using relationship between $\Phi_{WC}^J(f(\sigma))$ and $\eta / \eta_f$ according to equation, we can get plot (d), which shows the flow curves of shear thickening. And this flow curve would be the simulated flow curve that we get from the W-C model. We can plot a bunch of these flow curves on top of the experimental data and see how good the simulated flow curves that the model predicts fits the real data [40].

However, the W-C model is accurate when used to predict flow curves for spherical particles, but it has some limitation when it comes to rod-like particles. And we can see this from the model itself. The size or shape of the particles does not play a role in the W-C model. However, researchers have found that the onset stress $\sigma^*$ would decrease with particle size [40]. Moreover, the model can only be used to predict the behaviors in the shear thickening regime. It cannot be
used to explain the shear thinning part of the flow curves.

Figure 2.11: Failure of the W-C model for bidisperse PMMA spheres. The fractions of small particles are 0, 0.2, 0.5, 0.65, 0.8 and 1. Symbols: flow curves for different fractions. Lines: simulations from the W-C model [40].

Guy et al. found that the W-C model fails to predict the flow curves when the particles of the suspension are bidisperse (size ratio = 1:4), as shown in figure 2.11 [40]. They argue that it is because the W-C model only has one fraction of frictional contact $f$. And in this case, when there are two sizes of particles present, there are three kinds of contacts: large-large (‘11’), large-small (‘12’), and small-small (‘22’). Figure 2.12 shows that the fraction of frictional contacts $f_{11}$, $f_{12}$, and $f_{22}$ are very different compared to original fraction of frictional contact calculated by the W-C model.
**Figure 2.12:** Fraction of frictional contact $f$ calculated by the W-C model. $f_{11}$, $f_{12}$, and $f_{22}$ are three kinds of frictional contacts taken into the fraction of small particles [40].
2.6 Phase Diagram of Silica Rod Suspension with Different Volume Fractions

It is well known that rod-like colloids with sufficiently large aspect ratios show a transition from the isotropic to the nematic phase with increasing colloid volume fraction [19]. Onsager showed that at sufficiently high densities, hard rods must form a nematic liquid crystal phase [44]. Figure 2.13 shows the scheme of particle arrangements for isotropic phase, nematic phase, smectic phase, and liquid crystal phase.

Figure 2.13: Schemes from left to right shows the particle arrangements for the liquid crystal phase, the smectic phase, the nematic phase, and the isotropic phase. [45]

Bolhuis et al. used simulation to predict transitions between different phases theoretically at different volume fractions as a function of the aspect ratio L/d, where L is the rod length and d the rod diameter, using hard spherocylinder model [19]. Here, the length to width ratio of
spherocylinder is defined as $L/d+1$. In this way, hard spheres have the length to width ratio of 1. The model provides a good estimate for rodlike colloidal particles with short-range repulsive interactions. However, we need to keep in mind that the behavior between rodlike colloidal particles and hard spherocylinders might be different. And it is largely because a lot of rodlike colloidal particles are not perfectly rigid like spherocylinders here or that colloid-colloid interaction is not truly a hardcore repulsion.

Figure 2.15 shows the equilibrium phase diagram of hard spherocylinder particles over a wide range of aspect ratios. As we can see, the region of isotropic-nematic coexistence for the hard spherocylinder particles is very narrow. The coexistence region widens when there is an attractive interaction between the rods. Phase separation under shear, however, is a much more complex problem when compared to equilibrium phase separation. The non-equilibrium behavior of suspensions of rod-like colloids in shear flow is much less known.
Figure 2.14: Summary of the phase diagram of hard spherocylinders with L/D between 0 and 100. To give equal emphasis to all parts of the phase diagram, we have plotted the reduced density as a function of log(L/D+1). [19]

Figure 2.14 shows the phase diagram of hard spherocylinders. The y-axis is reduced density $\rho^* = \rho/\rho_{cp}$, which is the density relative to the density of regular close packing of spherocylinders. The equation used to calculate $\rho_{cp}$ is as followed [19]:

$$\rho_{cp} = 2/(2^{1/2} + (L/d)^{3/2})d^3$$

The phase behavior for long rods is depicted as a function of log(L/D+1) to give equal emphasis to the different parts of the phase diagram. For larger values of L/D, the I-N transition moves to lower densities. In contrast, the density of the nematic-smectic transition is not very sensitive to
the shape anisotropy of the rods and approaches the finite limit $\rho^* = 0.47$. Similarly, the smectic-to-solid transition exhibits only a weak dependence on L/D and occurs at $\rho^* = 0.66$ [19].

The above discussion focuses on the equilibrium phase transition for rods with a certain aspect ratio and volume fraction. However, when the rod suspensions are under shear, the situation can be much more complicated. Recent studies suggest that there are shear-induced microstructural changes that occur within the fluid. Hoffman group argued that shear thickening is due to the order-disorder transition within the suspension [46]. When the particles are under low shear rates, they tend to align with each other, causing shear thinning. However, at higher shear rates, the increasing collisions between particles would cause misalignment of rods resulting in shear thickening. Shear thickening of suspensions of spheres and rods will be discussed in detail in section 2.8.
2.7 PACKING FRACTION OF RODS

We have a better understanding of how volume fractions affect the shear thickening of spherical particles with previous researches [14]. However, the effects of shear thickening for rod-like particles with various aspect ratios are still not well studied. To better understand the rheological behavior of rod-like particles, not only do we have to emphasize the phase transition that is caused by the increase of aspect ratio and volume fraction of the particles as we discussed in the previous section, but we also need to pay close attention to the random packing of rod-like particles with the increasing volume fraction. In this section, we will discuss how aspect ratio affects random packing and whether the phase transition from isotropic phase to nematic phase for the rod suspension would occur before the solution reaches the jammed state.

Ferreiro-Cordova et al. used simulation to study the random packing of hard spherocylinders [18]. Random packing is a system in which the particles are disordered. While a random sediment for spherical particles can be obtained via centrifugation, the experimental approach of a random packing for rod-like particles is difficult to achieve because of the isotropic-nematic transition. Figure 2.15 shows the final configurations for spherocylinders with aspect ratios of 0.5, 5, 10, and 30. The different colors of the particles represent the angle of these particles to the positive z-axis. They found that the packing fraction decreases from 0.699 for aspect ratio of 0.5 particles to 0.209 for aspect ratio of 30 particles.
Figure 2.15: Configurations for different aspect ratios and the packing fractions for the spherocylinders. Aspect ratios: (a) 0.5, (b) 5, (c) 10, and (d) 30. Packing fractions for these rods: (a) 0.699, (b) 0.556, (c) 0.440, and (d) 0.209. The colors of the particles represent the angle of these particles with respect to the positive z axis. [18]

As shown in figure 2.16, the phase diagram that we discussed in the previous section is plotted in the same graph with packing fraction for various aspect ratios of rods reported by different researchers. Various studies have different results, and this illustrates the difficulty to reliably simulate random packing for rod-like particles. However, one thing worth noting here is that packing fraction from every study shows that with a certain aspect ratio, the rod-like particles will transition from isotropic phase to nematic phase before it reaches a jammed state. Moreover, from the graph, we can see that the packing fraction decreases with increasing aspect ratio.

For high aspect ratio anisotropic particles under shear, the effect of shear flow is more pronounced
due to the orientation of the particles that depends on the shear flow compared to spherical particles [47]. The volume fraction required for the solution to possess shear thickening behavior should be lower [15]. It is also attributed to excluded volume effects. With increasing anisotropy, particle motion would be significantly hindered, so the system could not reach maximum close packing fraction [48].

Figure 2.16: Comparison of the phase diagram and volume fraction of spherocylinders as a function of the aspect ratio L/D. [18]
2.8 SHEAR THICKENING OF ROD SUSPENSIONS

As we discussed in the previous section, the rheological response of shear thickening behavior for colloidal particle suspensions, both spheres and rods depend on volume fraction. With the increasing volume fractions, the suspensions can undergo continuous or discontinuous shear thickening. For rod suspensions, however, we would need to take into account the aspect ratio as well. Recent studies show that higher aspect ratio particles can experience shear thickening at lower volume fractions and suggest that this is due to the decreasing random packing densities of the higher aspect ratio particles as we discussed in the last section [15]. In this section, we would compare rheological results from multiple studies that have been done on spheres and various aspect ratios of rod-like materials.

![Diagram](image)

**Figure 2.17:** Viscosity vs. stress flow curves for suspensions of 1 um diameter silica spheres of various volume fractions. The numbers on the left side of the graph are the volume fractions of the silica sphere suspensions. The $\beta$ values on the right side represent the slopes of the curves [14].
Studies have been done on spherical particles and their rheological behaviors on shear thickening are mostly understood [9,31,49]. Rathee et al. used silica spheres with a radius of 0.48 to study the shear thickening behavior for spherical particles. The results have shown when the volume fraction is larger than 0.3, the measured viscosity as a function of the applied shear stress becomes non-Newtonian. As shown in figure 2.17, for $\phi = 0.35$, the suspension experienced a moderate shear thinning followed by a Newtonian plateau and shear thickening with slope of the flow curves $\beta = 0.5$. $\beta$ here, as we mentioned in section 2.4, is a calculated value to determine the existence of shear thickening. For Newtonian fluid, $\beta = 0$; for discontinuous shear thickening, $\beta = 1$. With the increase of volume fraction, we can see $\beta$ increases as well. At 0.58 volume fraction, discontinuous shear thickening can be observed [14]. The critical shear stress, $\sigma_c$, which is the onset shear stress for suspension to start experiencing shear thickening, does not show significant volume fraction dependence [16,39,50].

![Figure 2.18: SEM images of precipitated calcium carbonate (PCC) particles with aspect ratios of 2, 4, and 7. [15]](image)
As we mentioned earlier, the aspect ratio of the rods plays an essential role in shear thickening as well and we need to take that into account. Egres and Wagner performed rheological measurements for acicular precipitated calcium carbonate (PCC) colloidal rods with aspect ratios of 2, 4, and 7 suspended in poly(ethylene glycol) dimethyl ether (PEG) as shown in figure 2.19 [15]. The lengths of the rods range from 500nm to 1300nm and the diameters range from 200nm to 200n. They
observed a trend of decreasing volume fraction for shear thickening with increasing aspect ratio. The critical volume fraction, $\phi_c$, is the onset volume fraction for discontinuous shear thickening. Its value decreases from 0.454, 0.378 to 0.308 for aspect ratio of 2, 4 and 7 PCC particles. And they are all lower than the critical volume fraction for spheres, $\phi_c = 0.58$ [51].

One thing worth noting here is that the critical volume fractions, $\phi_c$, for these rods here are higher than the maximum random packing fractions for rod-like particles [52]. They argued that this is consistent due to the high alignment of rods in a nematic phase. However, the critical shear stress, $\sigma_c$, is close in magnitude despite the distinct differences in particle aspect ratio.

![Figure 2.20: SEM images for the two shapes of rods.](image)

**Figure 2.20: SEM images for the two shapes of rods.** Left: aspect ratio of 9 with dimensions of (266.5 ± 0.6 μm) by (29.9 ± 0.5 μm) by (31.4 ± 0.4 μm); Right: aspect ratio of 6 with dimensions of (139.5 ± 0.7 μm) by (24.9 ± 0.6 μm) by (30.2 ± 0.4 μm). [8]

Brown and Jaeger have studied the effect of different shapes of particles on shear thickening [8]. The particles are fabricated in the molds to desired shapes with aspect ratios of 9 and 6, as shown in figure 2.20. These particles are also suspended in the PEG solution. They found that for different shapes of particles, the critical volume fraction, $\phi_c$, depends on particle shape. For their rod particles specifically, $\phi_c = 0.37$ for aspect ratio of 6 rods and $\phi_c = 0.35$ for aspect ratio of 9 rods.
We know that these numbers are lower than $\phi_c = 0.58$ for spheres as well. However, they argued that the differences in critical volume fraction are due to the shapes of the particles as well.

![Flow curves for various volume fractions with aspect ratios of 9 (left) and 6 (right).](image)

**Figure 2.21:** Flow curves for various volume fractions with aspect ratios of 9 (left) and 6 (right). The solid black lines have a slope of 1 corresponding to the discontinuous shear thickening. We can see that the critical volume fraction decreases with a higher aspect ratio. [8]

James et al. used the silica rods to study the role of aspect ratio on shear thickening [17]. They used one pot method (see section 3.1) to synthesize silica spheres (average diameter of 280nm), and silica rods with aspect ratios of 8 (average length of 2.0um) and 11 (average length of 2.8um), as shown in figure 2.22. Above aspect ratio of 11, their synthesis produces irregular shapes of rods [44]. Their solvent for the particles is 70% glycerol and 30% water with 15 mM NaCl. NaCl here is to facilitate the hydrogen bonding between the silica rod particles with silanol surface groups [53].
As shown in figure 2.23, the spheres start to show shear thickening at $\phi = 0.36$ discontinuous shear thickening at $\phi_c = 0.48$; Aspect ratio 8 rods has mild shear thickening at $\phi = 0.28$ and DST at $\phi_c = 0.40$; Finally, aspect ratio 11 rods shows mild shear thickening at $\phi = 0.18$ and DST at $\phi_c = 0.30$. Compared to results from other experiments on spheres with $\phi_c = 0.58$, this system has a lower critical volume fraction to below 0.50 for its sphere system.

Figure 2.23(D) shows the comparison of flow curves of different aspect ratios at volume fraction $\phi = 0.34$. we can see that shear thickening increases slightly from spheres to aspect ratio 8 rods but experiences a significant jump for aspect ratio 11 rods.
Figure 2.23: Flow curves for spheres, aspect ratio 8 rods, and aspect ratio 11 rods at various volume fractions. (A) spheres, (B) aspect ratio 8 rods, and (C) aspect ratio 11 rods. (D) Comparison of flow curves at $\phi = 0.34$. [17]
Figure 2.24: Low and high shear viscosities as a function of volume fraction. (A) (B) The frictionless jamming volume fraction $\phi_0$ and the frictional jamming volume fraction $\phi_m$ is determined from the linear least square analysis. (C) Relationship between jamming volume fraction range $\phi_0-\phi_m$ and aspect ratio [17].

Moreover, they use silica rods with different aspect ratios to show the application of the W-C model as shown in figure 2.24. They plot the rescaled viscosities against the volume fraction and use equation (2.5) and the least square analysis to fit the experimental data to find the frictionless and frictional jamming volume fractions.

Recently, Rathee et al. showed some experimental data on how the orientation of the rods changes
under shear flow [54]. They argued that unsteady flow behavior arises under constant shear stress and shear rate because of the strong coupling between shear flow and particle orientation. They demonstrated that the orientation of rods fluctuates around the flow direction when they are under a small applied stress. However, a transition from this small fluctuation state to a disordered state is observed with the increase of applied stresses. And the boundary stress microscopy on shear thickening of the rod suspensions shows that this disordered orientation of rods results in the heterogeneous stresses under applied shear stresses.
2.9 Boundary Stress Microscopy

A technique we use here is Boundary Stress Microscopy (BSM). It is a direct measurement of local stresses transmitted to the surface of the suspension, which is spatially resolved localized boundary stresses at specific locations in addition to the system-averaged bulk viscosity versus time [55]. The previous research of shear thickening has been done in spherical particles in Newtonian fluid [14]. However, there are still not a lot of studies on shear thickening of rod suspensions and since rods have much higher aspect ratios compared to spheres, it shows more interesting and complicated experimental results when we investigate the localized stresses.

For spherical particles dispersed in a Newtonian fluid, under continuous shear thickening regime, well-defined dynamic heterogeneous stress regions will occur when the applied stress is above a certain point. These localized stress regions have boundary stresses that are much higher than the applied stress. These heterogeneous boundary stresses propagate along the shearing direction and are largely dependent on the gap distance between the two shearing surfaces [14,19].

Under the shear thickening regions, as the applied stress is increased, these heterogeneous stress regions become a larger fraction of the total surface area and the occurrence is more frequent. Figure 2.25 shows the uniform area when there is no applied stress compared to the heterogeneous high shear stress regions when there is applied stress [14]. Previous studies on shear thickening generally focus on the bulk rheology of the liquid and how the viscosity of the liquid responds to
increasing shear rates. However, with the use of boundary stress microscopy, we can study the localized heterogeneous forces under discontinuous shear thickening.

**Figure 2.25:** Snapshots of uniform stress with Newtonian fluid and the heterogeneous boundary stress in the velocity direction. Captured at 0.56 volume fraction of suspension of 1um silica spherical particles and 1000Pa shear stress [14].

The way that BSM works is by attaching an object to an elastic substrate and using microscopy to image the potential induced substrate deformations. With a substrate that has known mechanical properties, such as stiffness, the measured deformations can be converted into traction forces. BSM has recently been adopted in the realm of physics for studying problems such as wetting, contact mechanics, fracture, adhesion, and friction. [55]

As seen in figure 2.26, BSM measures the forces by how much a sample deforms an elastic substrate [56]. This is similar to measure the force on a spring by using Hooke's law. We can obtain the force through its extension. If we have a force on the substrate, it will have a displacement. Here the amount a substrate deformed under the force would depend on its properties such as stiffness, thickness, and compressibility.
In BSM, one way to measure the displacements is through tracking the movements of tracer particles, usually fluorescent beads, embedded on top of the substrate. Once the displacements of the beads are obtained, traction stresses can be calculated by solving a boundary-value problem.

Figure 2.26: Schematic diagram of a BSM substrate. A soft substrate (light grey) is bonded to a rigid base (dark grey). Fluorescent beads (yellow, red) are embedded at the substrate base, and near its surface. A discrete force, $F$, is applied to a finite patch (dark grey circle) of the substrate displacing it a distance $u$. The continuous stress distribution is applied by a contractile sample. [56]

The substrate used here can be crucial. It should be soft enough so that the deformation caused by traction forces on the substrate can be accurately measured. However, at the same time, it should be stiff enough so the strain here would not exceed its linear response regime. Also, in the practice, if the substrate is too soft, traction forces that are large enough in the region can tear apart the substrate here.
CHAPTER 3

METHODS

3.1 SYNTHESIS OF THE RODS

To obtain rod particles with tunable aspect ratio, we use one pot wet chemistry method to synthesize the silica rods, as shown in figure 3.1 [20]. We mix 30 gm of polyvinylpyrrolidone (PVP) and 300ml of pentanol in the flask, then sonicate for two hours until the PVP is fully dissolved. After that, we prepare 0.18M of sodium citrate dihydrate (0.529 gm in 10 ml DI water) and mix 2ml of it, 30ml ethanol, and 8.4ml water. After sonicating it in water for 10 minutes, we add 6.75ml of ammonia and 3ml of tetra-ethyl orthosilicate (TEOS) to the solution. Upon the addition of TEOS, silica rods start to grow. The flask with the solution is placed in the water bath of a certain temperature overnight to allow the growth of rods. Samples are centrifuged and cleaned with ethanol and water three times. The supernatant is removed and the particles in the sediment are redispersed in ethanol. In this process, different lengths of silica rods can be separated and we can get a suspension that is more monodispersed.

Figure 3.1: One pot wet chemistry method for synthesis of silica rods. Chemical contents are added step by step and the parameters are changed accordingly to achieve the synthesis of the rods with a desired aspect ratio.
<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>25</th>
<th>25</th>
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<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP amount (g)</td>
<td>30</td>
<td>30</td>
<td>15</td>
<td>15</td>
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<tr>
<td>Time (h)</td>
<td>12</td>
<td>24</td>
<td>24</td>
<td>24</td>
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<tr>
<td>Results (length)</td>
<td>~2um</td>
<td>~4um</td>
<td>~6um</td>
<td>~20um</td>
</tr>
</tbody>
</table>

Figure 3.2: The lengths and diameters of rods under different synthesis conditions. On the left graph, it shows the lengths of the rods increase with the increase of synthesis time. On the right graph, it shows that the synthesized particles are spheres when there is no presence of PVP content. However, with the increase of PVP content, the lengths of the rods decrease instead [20]. The table shows my experimental results to obtain lengths of 2, 4, 6 and 20um silica rods with different synthesis conditions.

By changing the synthesis conditions like temperature or the amount of chemical contents, we can obtain different aspect ratios of rods. For example, with the increase of the reactive temperature, rods can grow longer. But since the diameters of the rods depend mostly on the droplet of the water dispersed in PVP solution so they stay almost constant during the synthesis process, which would result in rods with different aspect ratios. We are going to discuss the growth mechanism and the
characterization method in the next section so that we will have a better understanding of how the change of certain parameters affect the aspect ratios of the rods.

Different synthesis conditions have been tried out here to obtain different aspect ratio rods. The table above shows three different synthesis conditions with various temperatures and PVP amount. We can see rods grow longer with the increase of temperature and decrease of PVP amount. The lengths of rods range from 2um to 20um with diameters about 270nm, which results in aspect ratios from 7 to 70. However, by further decreasing the PVP amount to zero would produce spherical particles instead of rods. The explanation for this result is the presence of PVP in the droplet of water is essential for the growth of rods.
3.2 GROWTH MECHANISM AND CHARACTERIZATION

To better tune the aspect ratios of the silica rods to our purpose, we need to understand the mechanism for their growth. And one way to do this is to use equipment such as Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) to characterize the silica rods.

To be able to see the rods under confocal microscopy, we let the silica rods stay in glycerol and water solution (Glycerol: water = 8:2) to make it index match. Also, the index matching solution is very close to the density match, which would slow the process of rod settlement. Alternatively, different concentrations of salt NaCl was added to the samples.

![Figure 3.3: The growth of rods under TEM.](image)

(a) is a water droplet in the pentanol solution. (b) to (f) show the growth of the rod after TEOS enters the droplet to fuel the growth. [20]
Figure 3.3 shows the TEM images of different stages of rod growth [20]. After we mix water with PVP and pentanol solution and sonicate it, water would form a lot of droplets with fully dissolved PVP in the mixed solution. The rods would not grow with the lack of PVP presence in the water droplets. The diameter of the water droplets would determine the diameter of the rods and that is the reason that despite the change of the lengths, the diameters of the rods remain relatively the same. The role of sodium citrate is to stabilize the water droplets during the growing process of rods. Without it, the sizes of the rods would be more polydispersed. Upon adding TEOS, rods start to grow. TEOS would enter the water droplets and make the rods grow on one side. During this process, if we increase the synthesis time, the lengths of the rods would increase accordingly as we discussed in the previous section. If we increase TEOS, it would also result in longer rods. At the end of the growth process, the rods would lose the other end of the water droplet and form a shape of a bullet.
3.3 **Volume Fraction Calculation**

![Diagram](image)

Figure 3.4: The procedures for determining the weights needed to calculate the volume fraction.

As we mentioned in the previous chapter, volume fractions play an important part in the shear thickening of silica rod suspension. Suspension undergoes continuous and discontinuous shear thickening based on various of volume fractions. A slight change of volume fraction can hugely affect the shear thickening regime. Therefore, the determination of volume fractions is essential in our experiments. Our calculation of volume fractions is based on the weights of the samples. The advantage of using weight instead of volume is that weight can be precisely measured while it is much harder to do so when it comes to volume. Therefore, we would reach our desired volume by
dividing the weight with density.

The procedures for calculating the volume fraction is shown in the figure above. We dry the rods on top of a hot plate at 100 degrees Celsius for 2h or until the rod suspension completely dry out. Then we measure the weight of the dried rods. Calculate its volume by dividing the weight by density of silica, 1.9g/cm³. We then add a certain amount of water by its weight and calculate the volume. To fully dissolve the dried rods in the water, we sonicate the solution for 2h. After sonication, we centrifuge the solution for half an hour. Remove a certain weight of supernatant (water) and calculate the remaining volume of water. According to the volume of water, calculate the weight of four times the volume of glycerol. Centrifuge the solution for 90 min. Remove a certain amount of the supernatant (water: glycerol = 20%:80%) according to the desired volume fraction using the density of 1.208g/cm³. Sonicate the suspension for half an hour.
3.4 Fluorescently Label the Rods

Some of the experiments require the rods to be fluorescently labeled, therefore, this procedure is to dye the rods. After the last cleaning step, redisperse rod particles in 100ml of ethanol. Mix 25mg of FITC, 35ul of APS, and 5ml of ethanol together overnight. Under magnetic stirring, 12ml of ammonia, 10ml of water, 1ml of TEOS, and the mixed solution with FITC in it were added. After reacting for several hours the mixture was centrifuged and washed with ethanol three times.

This procedure would add a fluorescent shell outside the original rods. Therefore, the diameters and aspect ratios of the rods would change slightly.
3.5 Rheology

Rheological measurements are essential to our research here for understanding the behaviors of shear thickening for rod suspensions. To better perform the measurement, we need to pay close attention to the preparation of the samples and the conditions of the testing.

As we mentioned in section 3.2, silica rod particles are kept in the water/glycerol solution. Before loading the samples, the solution is sonicated in water for half an hour to ensure the complete dispersion of the particles and to avoid any evaporation that might occur due to the extended duration of the sonication that would affect the volume fraction. After the sonication, the solution is carefully pipetted onto the rheometer stage to avoid any bubbles as they would possibly affect the rheology of the samples.

Rheological measurements are conducted using a controlled stress rheometer (Anton Paar MCR 301) with a cone and plate geometry. After the measuring tool is lowered onto the sample, we would trim the excessive fluid and place an oil ring around the sample to avoid evaporation. The following preshear protocol is performed on the sample before conducting any of the experiments reported to eliminate any effects of sample loading:

1. After loading, a preshear stress ramp from 0.1 to 1000 Pa is performed.
2. After the preshear, a second stress ramp from 0.1 to 1000 Pa in 300s and back to 0.1 Pa in 300s is conducted to show the reversibility of any shear thickening observed in the suspension.
Ascending and descending stress sweeps are performed on samples from 0.1 Pa to a maximum stress of 1,000 Pa. Due to the rate limitations of the rheometer, the results from this maximum stress are not reliable for samples with lower particle volume fractions. Ascending and descending flow curves show that the hysteresis is minimal and the critical stress for shear thickening is independent of stress sweep direction.
3.6 **Boundary Stress Microscopy (BSM) Setup**

As we mentioned in the previous section, to understand the rheology of the suspension better, not only do we need the bulk rheology provided by the Rheometer, we also need a method to study its localized stresses. Boundary stress microscopy (BSM) is a way to measure the localized stresses.

![Setup of boundary stress microscopy (BSM)](image)

**Figure 3.5: Setup of boundary stress microscopy (BSM).** A glass coverslip is coated with a thin, uniform PDSM gel with fluorescent beads sitting on top of it. The sample is placed on top of the gel and the measuring tool on top of the sample. We can observe the movements of the beads using the objective under the glass coverslip [14].

The PDMS gel is mixed with a curing agent (Sylgard 184) at a ratio of 35:1. The mixture is stirred thoroughly and degassed until there are no visible air bubbles. A glass coverslip with a diameter of 40mm (Fisher Sci) is plasma cleaned and rinsed with ethanol and deionized water. The coverslip is spin-coated with a thin, uniform film of the mixed PDMS gel with a thickness of 35um. Afterward, the coated coverslip is cured at 100 °C for an hour. The PDMS is functionalized with 3-aminopropyl triethoxysilane (Fisher Sci) using vaporized deposition for ~40 min in a desiccator.
after the PDMS is fully cured. Fluorescent beads with a diameter of 1.04\textmu m and excitation/emission of 480/520 nm are dispersed in a solution mixed with 3.8 mg/mL sodium tetraborate, 5 mg/mL boric acid, and 0.1 mg/mL 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (Sigma-Aldrich). The mixed fluorescent bead solution is pipetted on the top of the PDMS gel and rinsed with water after 6 minutes. The treated coverslip with PDMS gel and fluorescent beads on top is placed on the stage of the confocal rheometer and secured with a ring [57]. The rod suspension is placed between the gel and measuring tool.

We use 25 mm cone-plate geometry here to ensure a uniform average shear rate. The tool has a flat bottom surface and an angled cone. An objective of 10x is placed under the glass coverslip to capture the images. The rheological measurements are the same as in section 3.5.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF SILICA RODS WITH VARIOUS ASPECT RATIOS

Figure 4.1: SEM images and confocal images of AR9 rods and AR6 rods. (a): SEM image of AR9 rods (~2.15μm in length, ~250nm in diameter, aspect ratio ~9); (b): AR6 rods (~3.26μm in length, ~550nm in diameter, aspect ratio ~7); (c) Confocal image of AR6 rods in suspension of 0.1 volume fraction; (d) Confocal image of AR6 rods in suspension of 0.2 volume fraction; (e) Confocal image of AR6 rods in suspension of 0.3 volume fraction.
Scanning Electron Microscope (SEM) and image analysis are the methods we use to characterize the sizes and shapes of the rod particles. This is a reliable way we could analyze the polydispersity of the rod particles. Rod particles are not strictly monodispersed after we synthesize and clean them. Therefore, we would obtain the SEM images of the rods and use image processing to analyze the distribution of the aspect ratios for the rod particles.

The SEM images in figure 4.1 show various aspect ratios of the rods. The lengths are ranging from 2um to 3.5um. However, while the lengths of the rods are almost doubled, so are the diameters of the rods. Therefore, the overall aspect ratios only change slightly from around 6 to 9. However, this is also an interest for us since it would help us understand whether the rheological properties of a suspension are solely dependent on the aspect ratios of the particles in the liquid or the dimensions of the particles play a role as well, as Brown and Jaeger argued in Section 2.8 [51]. The lengths are due to the growth mechanism of rods explained in Section 3.2 and the diameters are determined by the water droplets.

As we can see from the images, the rods are relatively monodispersed. This is largely due to the cleaning process (see Section 3.3), which can get rid of larger or smaller rods using the centrifuge technique. Hence it results in much more monodispersed samples that we can use to perform the rheological tests. By centrifuging the solution under different speeds and separating the sediments and supernatants, we can select different lengths of rods and make the lengths of rods more monodispersed. This is important for our following experiments because the polydispersibility can significantly affect the rheological behaviors of the rods [40].
Figure 4.2: Histograms of lengths and diameters for AR2, AR6, and AR9 rods.
To get a better sense of the monodispersity of the rod samples we used in our experiments, we quantify the lengths and diameters of the rod samples with different aspect ratios using histograms before the rheological experiments. We took SEM images of rods with different aspect ratios at various locations and used ImageJ to measure the lengths, diameters, and the corresponding aspect ratios of the rods. The histograms are shown in figure 4.2. The average length and diameter for all three aspect ratios are shown below.

**Table 1: Average lengths and diameters for silica rods with aspect ratio of 2, 6 and 9.**

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Average Length (µm)</th>
<th>Average Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.58</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>3.26</td>
<td>0.56</td>
</tr>
<tr>
<td>9</td>
<td>2.15</td>
<td>0.25</td>
</tr>
</tbody>
</table>
4.2 **Flow Curve of Shear Thickenning with Different Aspect Ratios**

We conduct a series of stress-controlled rheological measurements on various aspect ratios of silica rods to investigate how volume fractions and aspect ratios affect the rheology of the suspension. Ascending and descending shear stress sweeps are performed on each sample. Here, volume fractions of the suspension in my system can be changed and decided by the method mentioned in Section 3.3. Silica rods that we use are stable enough to not be affected by the processes of concentrating and redispersion. Therefore, the same batch of rods can be reused to achieve the desired volume fraction to keep the aspect ratio of the sample consistent.

The tool that we are using is a 25mm diameter con-plate. The rheometer that we are using here is Anton Paar MCR 302. The rods are dispersed in water/glycerol (20%/80%) solution and the experiments are carried out under room temperature (25 °C).

4.2.1 **AR2 Silica Rods**

Figure 4.3 shows the flow curves of AR2 silica rod suspension (average length = 0.58μm and average diameter = 0.37μm) under different volume fractions. As we can see from the figure, the bottom blue line is a mix of 20% water and 80% glycerol with no rods in the suspension. This is the background viscosity and it gives us an idea of the initial viscosity and it is important for the calculation of relative viscosity in the W-C model. By increasing the volume fraction, we can see the Newtonian plateau of the viscosity increases as well, which is what we expected. Moreover, the 0% flow curve is supposed to be a flat line throughout the shear stress sweep due to the nature
of a Newtonian fluid. However, in this case, we can see shear thinning below 0.1Pa from the graph. This tells us that the tool limit of the rheometer and for a viscosity that is low enough, these data points are likely not trustworthy (see Section 3.5).

![Graph showing viscosity versus shear stress for different volume fractions of aspect ratio 2 rods. Volume fraction from bottom to top: 0, 0.10, 0.20, 0.30, 0.40, 0.50.]

**Figure 4.3: Flow curves of viscosity versus shear stress for different volume fraction of aspect ratio 2 rods.** Volume fraction from bottom to top: 0, 0.10, 0.20, 0.30, 0.40, 0.50.

From 0.30 volume fraction, the viscosity of silica rod suspension undergoes a moderate shear thinning, followed by a Newtonian plateau and afterward increases significantly from around 30Pa. During the shear thickening regions, we cannot see a significant hysteresis between ascending and descending shear stress sweeps, which suggests that the shear thickening is reversible. For 0.10 and 0.20 volume fraction, however, shear thickening is not obvious. For 0.50 volume fraction, the suspension is still under continuous shear thickening regime.
Figure 4.4: Flow curve of discontinuous shear thickening for 0.55 volume fraction of AR2 rods. The blue line is the first run after loading the sample from 0.01 to 500Pa. The red and green lines are the ascending and descending stress sweeps.

As we can see from the figure 4.4, for the 0.55 volume fraction AR2 rods, the viscosity undergoes a moderate shear thinning, followed by a Newtonian plateau and afterward increases significantly from around 40Pa and above of shear stress. The slope of the flow curve $\beta = 1$, which means that it is discontinuous shear thickening (DST) under this volume fraction. This critical volume fraction is slightly lower than the results of the spherical particle with $\phi_c = 0.58$ [14]. This is consistent with what we expect from an aspect ratio of rods that is slightly higher than spheres. As we discussed in the previous sections, aspect ratio plays an important role in affecting shear thickening behavior. With the increase of aspect ratio, the critical volume fraction should be lower particles to undergo shear thickening. Therefore, in the following experiments, we would compare this result to AR6 and AR9 rods.
Figure 4.5: Reproducibility of flow curves from different samples. (a): flow curves for volume fractions of 0.30 AR2 rod suspensions; (b): flow curves for volume fractions of 0.50 AR2 rod suspensions; (c): the reproducibility of viscosity and slope for every volume fraction.

When carrying out rheological experiments, one thing worth noting is the reproducibility of the experimental results. A change of condition, such as sonication of the suspension and bubbles introduced by the loading of the samples can dramatically change the rheological results. Therefore, we need to verify the results by performing multiple experiments under the same condition.
Figure 4.5 shows some examples of the reproducibility for AR2 silica rod particles at 0.30 and 0.50 volume fractions. Samples are from the same batch of rod synthesized. However, different runs are prepared separately. The samples are being cleaned, dried, and measured to a certain volume fraction before carrying out the corresponding measurement. As we can see from the figure, the reproducibility is very good. For volume fractions of 0.30 and 0.50, they are almost overlapping with each other on the shear thickening regime. The bottom graph in figure 4.5 shows the reproducibility for viscosities under 1,000s$^{-1}$ and the slopes of the flow curves for various volume fractions.

4.2.2 AR6 SILICA RODS

To understand how aspect ratio affects shear thickening on rod particles, we perform the following experiments on AR6 rods (average length = 3.26µm and average diameter = 0.56µm) with various volume fractions. In this section, we will discuss the results and compare them to the W-C model.
Figure 4.6: Flow curves of AR6 rods. With volume fractions: 0.31, 0.33, 0.35, 0.4, 0.44, 0.46. (a): flow curves plotted as viscosity versus shear stress; (b) flow curves plotted as shear stress versus shear rate.
Figure 4.6 shows the flow curves of AR6 rod suspensions with volume fractions of 0.31, 0.33, 0.35, 0.4, 0.44 and 0.46. As we can see, the suspension has a moderate shear thickening at $\phi = 0.31$ and discontinuous shear thickening at the critical volume fraction $\phi_c = 0.44$. This number is much lower when compared to spheres, $\phi_c = 0.58$ and AR2 rod, $\phi_c = 0.55$. It shows the suspensions undergo discontinuous shear thickening at much lower volume fraction for higher aspect ratio.

The graph of shear stress vs. shear rate is another way of presenting these flow curves as it is more intuitive to see when the transition of continuous shearing thickening to discontinuous shear thickening happens. As we can see from the graph, with a 0.44 volume fraction, the curve becomes vertical after certain shear stress, which indicates the DST regime of suspension. For volume fractions below 0.44, we can see that the onset stress, $\sigma_c$, for shear thickening stays almost the same. This corresponds to the findings in theoretical simulations. However, for volume fraction 0.46 suspension, we can see the onset shear stress shifted to a much lower stress, which is because the suspension is deep in shear thickening regime under this volume fraction.
Figure 4.7: Relative viscosity plotted against volume fractions for high and low viscosity limit for AR6 rods. The red dots are low viscosity values, and the blue dots are high viscosity values. The lines are fits from W-C model.

Figure 4.7 shows the fitting of low viscosity and high viscosity values at various volume fractions to find the frictionless jamming volume fraction $\phi_0$, and the frictional jamming volume fraction $\phi_m$ according to the W-C model (see Section 2.5). The red dots in the figure are low viscosity values, which are obtained by averaging the values of the plateau in the low viscosity regime. The blue line is the fit for these values using $\phi_0 = 0.63$. The blue dots on the other hand are high viscosity values, which are obtained as the highest value in the shear thickening regime. The orange line is the fit for these values using $\phi_m = 0.46$. As we can see from the graph, the data points are not perfectly on top of the fitting line. We suspect that this is largely because of the limitation from the W-C model as we discussed in Section 2.5.
Figure 4.8: Algorithm generated flow curves for AR6 rods using the W-C model on top of experimental flow curves to see the accuracy of the fitting.

Using the frictionless jamming volume fraction $\phi_0$, and the frictional jamming volume fraction $\phi_m$ obtained from the fitting, we can generate flow curves at various volume fractions. As seen in figure 4.8, three of the simulated flow curves are shown on top of the experimental data. We can see that for some volume fraction like 0.40, the fitting at shear thickening regime is almost overlapping with experimental data. However, for volume fractions like 0.35 and 0.33, the fittings are relatively good at the beginning of shear thickening but diverge at higher shear stresses. This could be because the high viscosity plateaus for different volume fractions that we choose earlier are not the accurate values, for example, the shear thickening might not plateau at 1000Pa yet and therefore resulting in the inaccuracy for the fitting value of frictional jamming volume fraction. And that is one of the possible reasons that the fitting values for higher shear stresses diverge from experimental data. One thing worth mentioning here is that the W-C model does not make
predictions for the shear thinning part.

4.2.3 AR9 Silica Rods

![Graph showing flow curves for AR9 rods with various volume fractions.](image)

**Figure 4.9:** Flow curves AR9 rods with volume fractions: 0.4, 0.42, 0.46, 0.47, 0.48.

Similarly, figure 4.9 shows the flow curves of AR9 rod suspensions (average length = 2.15µm and average diameter = 0.25µm) with volume fractions 0.4, 0.42, 0.46, 0.47 and 0.48. For AR9 silica rods, the aspect ratio is higher than AR6 silica rods. However, the sizes of them are smaller. We can see the volume fraction for discontinuous shear thickening is 0.47, which is very close to 0.46 for AR6 rods. However, the volume fraction of AR9 rods for moderate shear thickening, despite much lower than AR2 rods, is higher than AR6 rods. This shows that aspect ratio plays an important role when it comes to shear thickening. However, the sizes and shapes of the rods can
affect the shear thickening behavior as well [8].

![Graph showing volume fractions for high and low viscosity limit for AR9 rods.](image)

**Figure 4.10: Volume fractions for high and low viscosity limit for AR9 rods.**

Using the same method, we can use the W-C model to generate simulated flow curves for AR9 rod particles. The red dots in the figure are low viscosity values and the blue line is the fit for these values using $\phi_0 = 0.64$. The blue dots, on the other hand, are high viscosity values and the orange line is the fit for these values using $\phi_m = 0.48$, which is much lower than volume fraction for spherical particles 0.58. And compared to the value for AR6 rod suspension, which is 0.46, this number is very close. This shows that despite the difference in aspect ratio, the sizes of the rods also affect the shear thickening behavior.
Figure 4.11: Algorithm generated flow curves for AR9 silica rods using the W-C model on top of experimental flow curves to see the accuracy of the fitting.

Figure 4.11 shows the simulated flow curves for volume fractions of 0.47 and 0.46 fit very well with experimental data in the shear thickening regime. However, for other volume fractions, especially the volume fractions that are not in discontinuous shear thickening regime, the accuracy to fit the flow curves is much less. One thing worth mentioning here is that for discontinuous shear thickening, the critical shear stress has no longer stayed constant. Therefore, in our simulation using the W-C model to generate the flow curves, we would change the value of the onset shear stress accordingly.
4.2.4 **Slope Comparison for Various Aspect Ratio**

**Figure 4.12: Calculated slope of flow curves and the jamming fraction.** (a): Calculated slope of flow curves vs. volume fraction for AR2, AR6 and AR9 silica rod particles. (b): The frictionless jamming fraction, \( \phi_0 \), and the frictional jamming fraction, \( \phi_m \) for AR2, AR6 and AR9 silica rod particles.

Figure 4.12 (a) shows the slopes of the flow curves with different volume fractions for AR6 and AR9 silica rod suspensions. As we can see from it, AR2 rod suspensions have much lower slope values for the same volume fraction of AR6 or AR9. AR6 and AR9 rod suspensions, however, have relatively close slope values for the same volume fraction. However, the values of AR6 are consistently slightly higher than AR9 with the same volume fraction. We would have expected the opposite since the higher aspect ratio should possess a lower volume fraction for shear thickening. However, we must keep in mind that the sizes of the rods also play a role here.

Figure 4.12 (b) shows the comparison of the frictionless jamming fraction, \( \phi_0 \), and the frictional jamming fraction, \( \phi_m \) for AR2, AR6 and AR9 silica rod particles. As we can see, both \( \phi_0 \) and \( \phi_m \) decrease significantly from AR2 to AR6. It is expected as we mentioned in Section 2.7, the random packing volume fraction decreases with the increase of aspect ratio. Moreover, the packing volume
fractions decrease with the increase of aspect ratio since there are more rod to rod contacts for higher aspect ratio rods [52]. For AR6 and AR9, both $\phi_0$ and $\phi_m$ remain relatively unchanged. But we have to keep in mind that the size of the particles will also play a role here.
4.3 **Flow Curves under Temperature Control**

In the previous section, we explore the effect of aspect ratio and size of the particles on shear thickening behaviors. Here, we conduct a series of stress sweeps on these samples at various temperatures to understand how temperature affects shear thickening. Also, by lowering the temperature of the system, as we will discuss in detail later, we can obtain a higher viscosity under the same volume fraction and shear stress, effectively lowering the corresponding shear rate of the suspension. This is an interest for us since it will allow us to perform Boundary Stress Microscopy (BSM) more easily in the future experiments with lower shear rate.

Figure 4.13: Flow curves for volume fraction 0.40 of AR9 rods at temperature 0°C, 5°C, 10°C, 20°C, and 35°C.

Figure 4.13 shows the flow curves for volume fraction 0.40 of AR9 rods at temperature 0°C, 5°C, 10°C, 20°C, and 35°C. We use water/glycerol = 20%/80% as the solution in these suspensions. And a constant shear stress $\sigma = 10$Pa is applied for 10 minutes before the data collection. As we mentioned earlier, we are interested in temperature control because temperature affects the
absolute viscosity and shear rate of the same sample. From figure 4.13, we can see that the viscosity has increased for over an order of magnitude from temperature 35 °C to 0 °C, which means that the corresponding shear rate has decreased the same order of magnitude. This is due to the decrease of viscosity for water/glycerol solution from 0.0267Pa.s at 35 °C to 0.262Pa.s at 0 °C.

Figure 4.14: Collapse of flow curves with adjusted relative viscosity for volume fraction 0.40 of AR9 rods at temperature 0°C, 5 °C, 10 °C, 20 °C, and 35 °C. Relative viscosity is the value of the absolute viscosity for the suspension divided by solvent viscosity under the same temperature.

However, despite the absolute viscosity for the suspension changes dramatically with the temperature, we want to find out the relationship between their relative viscosity. The relative viscosity is defined as the absolute viscosity of the suspension divided by the solvent viscosity as shown below:

$$\eta_r(\sigma, T) = \frac{\eta_A(\sigma, T)}{\eta_s(\sigma, T)}$$

The solvent viscosity here is the viscosity of water/glycerol = 20%/80% solution under a certain temperature.
As we can see from figure 4.14, flow curves for the various temperatures almost collapse onto a single curve under the shear thickening regime, which means that these flow curves have the same slope $\beta$. There is also no significant change in the shear thickening onset stress $\sigma^*$ or the low viscosity plateau $\eta_0$ and the high viscosity plateau $\eta_m$. This means the experimental temperature of the system does not affect the shear thickening behavior. And this is consistent with the W-C model as the model does not take into account the temperature of the system. We use relative viscosity in W-C model and this takes into account of the temperature effect already.

Figure 4.15: Comparision of AR9 rods with different volume fractions (left: 0.31, right: 0.35) at temperature 0°C, 5°C, 10°C, 20°C, and 35°C.

Figure 4.15 shows the collapses of the flow curves for AR9 rods with volume fractions 0.31 and 0.35 at various temperatures. As we can see, under various volume fractions, the relative viscosity flow curves still overlap with different temperatures.
Figure 4.16: Slopes $\beta$ of the shear thickening regime for AR9 rods. $\beta$ increases with increasing volume fractions. The error bars show the variation at different temperatures under that same volume fraction.

We plot the slopes $\beta$ of the flow curves for the AR9 silica rod suspensions with various volume fractions at different temperatures here as an example to demonstrate the variation on $\beta$ under different volume fractions, as shown in figure 4.16. $\beta$ increases with increasing volume fractions, which is consistent with our previous results. The error bars here show the variation of $\beta$ at different temperatures under that same volume fraction. We can see that although the differences of $\beta$ with the same volume fraction is small, this variation broadens with the increase of volume fraction. However, this discrepancy might be because that a steady state viscosity measurements can not be performed reliably with a solid-like discontinuous shear thickening state [58].
CHAPTER 5
CONCLUSION

This thesis has explored the shear thickening of silica rod suspensions. Shear thickening is the increase of viscosity when shear rate or shear stress increases. It is a phenomenon that exists in our daily life and has a wide range of industrial applications. My research aimed to have a better understanding of this process in rod suspensions.

First, we have successfully fabricated silica rod particles with tunable aspect ratio using one pot wet chemistry method. With our knowledge on the growth mechanism of the synthesis of the silica rod particles, we can obtain the silica rods with the desired aspect ratio by changing the corresponding parameters. And with the cleaning process, reasonably monodisperse rod particles can also be achieved. With this synthesis process, however, we have found that rods with aspect ratio larger than 9 often have a curly shape.

Secondly, we have demonstrated that by adding silica rod particles to the fluid, the suspension undergoes continuous shear thickening (CST) and discontinuous shear thickening (DST) as applied stress increases. Shear thickening also strengthens with the increase of volume fraction on the rod suspensions with the same aspect ratio. $\beta$, which is the calculated slope value for the shear thickening regime of the flow curve of the silica rod suspensions, increases with the increase of volume fraction. Critical shear stress, which is the onset shear stress that the suspensions start showing shear thickening, however, is relatively independent of the volume fraction. Within this context, we have also explored the effect of aspect ratio and size of the silica rods on shear...
thickening. We have demonstrated that by increasing aspect ratio of the rod particles, the critical volume fraction for both CST and DST decreases.

Moreover, by using the spherocylinder model, we have studied the close packing volume fraction and the equilibrium phase diagram of the silica rod particles. We have calculated the reduced density for a suspension of a certain aspect ratio and volume fraction and concluded that the suspension under equilibrium is in nematic phase before it gets to a jammed state.

In addition, we have also showed the application of the Wyart and Cates (W-C) Model on our silica rod suspension rheology. We have compared the simulated flow curves using the W-C Model with our experimental results for AR2, AR6 and AR9 rods. We have explored the limitation of W-C model on rod particles and its failure to predict the shear thinning part of the flow curve in a suspension with polydispersity. Despite the shortcoming of the model, the frictionless jamming fraction, $\phi_0$, and the frictional jamming fraction, $\phi_m$ for silica rods obtained in our experiments have shown the consistency with the results from other groups. Both $\phi_0$ and $\phi_m$ decrease significantly with the increase of the aspect ratio from AR2 to AR6. AR6 and AR9 rods, however, have similar $\phi_0$ and $\phi_m$.

Lastly, we carried out the experiments on the silica rod suspensions with temperature control. We have successfully decreased the shear rate of the suspension by an order of magnitude with the decrease of the temperature from 35 °C to 0 °C. We demonstrated that the flow curves with the relative viscosity, which is the suspension viscosity divided by solvent viscosity, collapse onto a single curve. Therefore, we have concluded that shear thickening is not affected by the change of
viscosity under different temperatures.

In conclusion, the shear thickening of the silica rod suspensions is a complex and exciting field with many possible industrial applications and research directions. The results presented in this thesis have contributed to the better understanding on the mechanism of shear thickening process on the rod-like particles.
CHAPTER 6

FUTURE WORK

Based on the work that we have done on the silica rod suspension to date, there are still some questions that remain unanswered that would be worth exploring. I recommend the following plans in the future.

1. In order to get a more complete picture of how aspect ratio affects shear thickening process, rheological properties of higher aspect ratio rod suspensions can be explored, including changing the shape of the silica particles. As we know that rods with higher aspect ratios undergo shear thickening at relatively lower volume fractions when compared to its spherical counterpart despite the fact that with a shear aligned state, rods have a higher packing fraction than spheres. Therefore, it will be interesting to see if the results still hold true for higher aspect ratio rods. The challenge here is that with the current synthesis technique, it is hard to obtain rod particles with aspect ratio higher than 11 without the rods being curly in the end.

2. The surface of the silica rod particles can be altered. By adding surfactant, we can change the surface property of the silica rods, including increasing the coefficient of friction by adding bumps on the rod particles or changing the charges on the rod particle surface. Some studies have suggested the theory that a disordered contact network is formed with the particles during the shear thickening process. And we know that anisotropic particles have more contacts in a disordered state. Therefore, rods with a different surface property can
possibly increase or decrease the frictional contacts between the rods despite having the same aspect ratio.

3. Explore the heterogeneous stress generated by discontinuous shear thickening of the suspension using Boundary Stress Microscopy. As we showed in this thesis, there has been some work done previously trying to understand the relationship between the orientation of the rods under applied shear stress and the heterogeneous stresses being generated. It will be of our interest to explore whether the heterogeneous stresses increase with disorientation of the rods and the increase of aspect ratio.
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