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Understanding shear thinning using Brownian dynamics simulation

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Understanding Shear Thinning Using Brownian Dynamics Simulation

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Departmental Honors Thesis
University of Tennessee at Chattanooga
Department of Chemistry and Physics

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Abstract: In this work, we study the changes in structure during the shear thinning regime using Brownian Dynamics with a simple steady-state shear flow of binary charged colloidal suspension. Previous research has analyzed the viscosity, radial distribution, elasticity and plasticity of materials with rheo-SANS experimentation; however, less research has been conducted to replicate the experiment through computer simulations. With Brownian Dynamic Simulation, this study was able to reproduce the results obtained in a recent rheo-SANS experiment and it also explored the viscosity, radial distribution, elastic and plastic behavior of a system under different parameters. The comparison of simulated data with experimental data revealed the computer simulation to successfully generate results indicative of shear thinning behavior in both the viscosity versus shear data as well as the radial distribution data. The simulated system was also able to successfully generate systems which exhibited plastic behavior and elastic behavior.

Table of Contents

Chapter 1: Introduction

1.1 Introduction to Colloids, BDS, and our Project

A colloid is a mixture that has particles ranging between 1 and 1000 nanometers in diameter, yet are still able to remain evenly distributed throughout the solution. These mixtures are homogeneous, and the particles remain dispersed meaning that they will settle in the bottom of a container. Examples of colloids include whipped cream, mayonnaise, milk, butter, gelatin and some biological systems like blood. Such examples can begin to explain why studying colloids is necessary. Colloidal studies can benefit businesses by helping to improve product quality to then improve sales. Colloidal studies can be beneficial for safety purposes, such as studying the behavior of oil for the sake of employee safety on oil rigs. And such studies on blood can lend obvious contributions to the health sciences. Thus, many industries benefit from this colloidal and fluid focused research, such industries in food, cosmetics, pharmaceuticals and medicine [1,2]. One type of research used to study colloids is BD simulations which are used to simulate such colloidal suspensions under various parameters. In fact, some of the earlier studies regarding colloids in light of altering parameters such as particle size, shear rate, viscosity etc. were due to interest from industry. Industrial companies were curious to better understand why their procedure of coating paper, which increased the coating's viscosity in the process, was resulting in torn papers and ruined machinery [3]. Similar investigations have been conducted since then. For example, studies to observe how the viscosity changes as a function of an external force (shear) are more common [4,1]. Regardless of the subject of the colloidal studies, a major component analyzed is viscosity.

The focus of this particular research aims to recreate rheological data in a simulated manner for the purposes of comparing with experimental data. Other research has revealed that various colloids are studied under rheometers and with small angle neutron scattering with the intent to observe shear thinning behavior such as in Lanotte et. al's rheometric study on red blood cell morphology, but few have chosen opted to study the behavior with computer simulations [5].

1.2 Viscosity

When examining these colloidal systems, viscosity is a key subject analyzed. Viscosity is a fluid's resistance to flow. This tendency is modeled by Newton's Law of Viscosity which describes the relationship between shear stress and shear rate in a fluid [6]. Viscosity is given as

$$\eta = \frac{\tau}{\gamma} \qquad \textit{Equation 1}$$

Where $\tau$is shear stress,$\gamma$is shear rate, and viscosity is determined in Pascal seconds ($Pa \cdot s$) [7,8]. Trends of viscosity can be observed as a function of shear rate as seen in Figure 1.

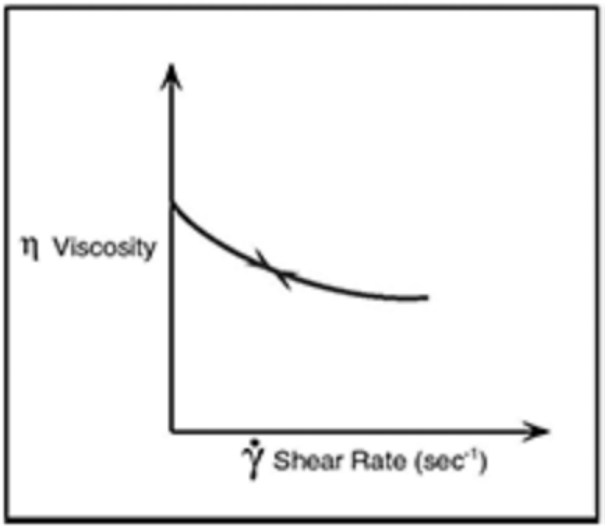

Figure 1: Graph of viscosity as a function of shear rate

Shearing occurs when internal friction of a fluid increases and the amount of force needed to overcome the friction increases [8]. This illustrates why more viscous fluids require more force to flow. Figure 2 depicts the process of shearing and is the model that was used to establish Newton's Law of Viscosity (*Equation 1*) [8].

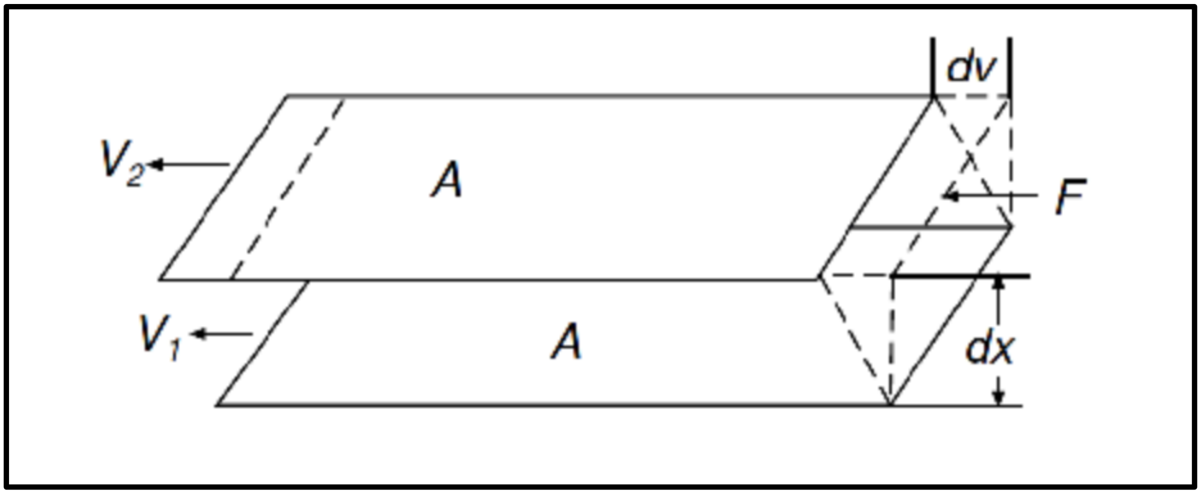

Figure 2: Diagram of shearing

Shear is the force applied to the fluid system in a specific direction. As increasing shear is applied to the fluid, the response in viscosity separates fluids into two categories: Newtonian fluids and Non-Newtonian Fluids [9].

1.3 Newtonian and Non-Newtonian Fluids

In nature, we can classify liquids in two categories. Newtonian and non-Newtonian. If the viscosity does not change as shear increases, then it is a Newtonian fluid as seen in Figure 3 [10]. Fluids such as water and alcohol fall into this category.

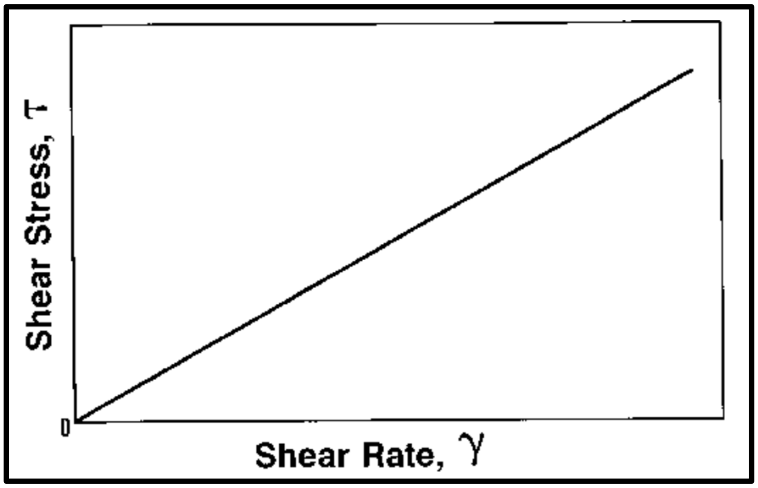

Figure 3: Graph of Newtonian fluid

In comparison, fluids whose viscosities change are Non-Newtonian fluids as seen in Figure 4 [11].

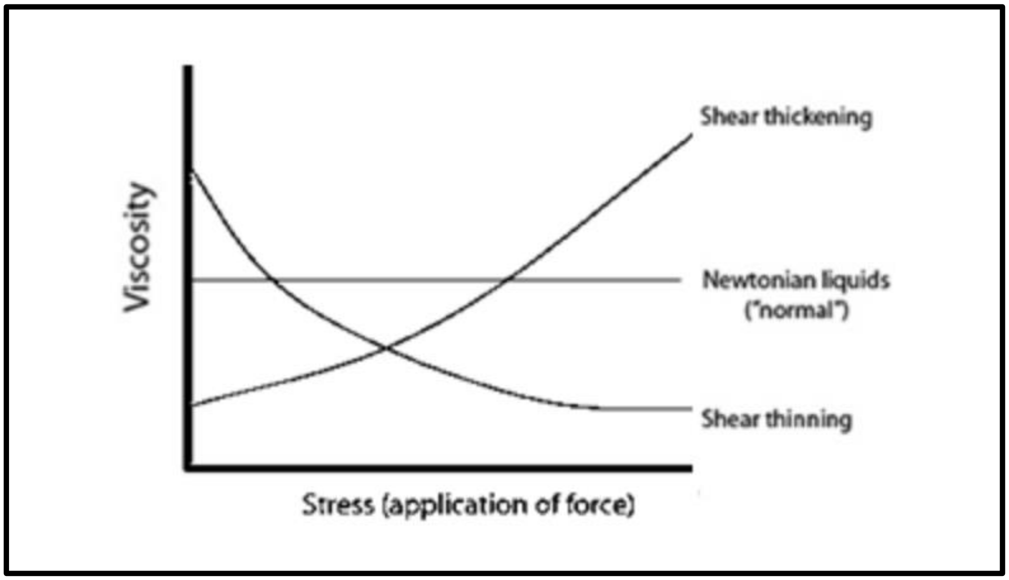

Figure 4: Graph of Non-Newtonian fluids compared to Newtonian fluids

There are two kinds of Non-Newtonian fluids: shear thinning fluids and shear thickening fluids.

1.4 Shear Thickening

If viscosity increases as shear increases, the fluid experiences shear thickening [3]. Many materials incorporate such materials into their products of their ability to dampen and absorb shock by dispersing the initial force applied [3]. Other common materials that incorporate shear thickening fluids are Kevlar vests. Shear thickening fluids help disperse the force of bullets and increase overall rigidity of the vests more efficiently [3]. This material is even incorporated into products as simple as sporting equipment. Similar to a Kevlar vest, a tennis racket aims to redirect an incoming ball, but the strings of the racket must maintain their rigidity while still dispersing the vibrations from the impact [3].

1.5 Shear Thinning

The other type of Non-Newtonian fluid is shear thinning fluids. Shear thinning fluids are the opposite of shear thickening fluids. These fluids will decrease in viscosity as shear force increases [12,2]. Ketchup is a prime example of shear thinning behavior. When turned upside down, ketchup will not readily flow from its container, so the bottle must be hit on its bottom or squeezed and once the action ceases so too does the flow. The force exerted is decreasing the viscosity of the ketchup allowing it to flow more easily, and without the added force, the ketchup resumes its initial viscosity. Other types of shear thinning materials include paints and blood [5]. Paints desire shear thinning for practical reasons.

Paints will maintain a higher viscosity under no shear while they are in their containers which prevents valuable products from accidentally running out of its container. But when a product is needed, applying small shear in the form of a squeeze to the bottle for example will decrease the product’s viscosity allowing it to be easily dispensed from its bottle.

On a more serious topic, typical shear thinning fluids can be observed in biological systems in the form of blood. Specifically, shear thinning behavior is seen in whole blood because of the aggregation and deformability of red blood cells which are a key component of whole blood [5]. Understanding this behavior in the flow of blood lends greater understanding of what is occurring during times of good health and during times of disease. For example, it is understood that without the aggregation of red blood cells, the phenomena of shear thinning would continue meaning that without clotting, blood would continue to flow too easily [5]. Figure 5 illustrates data from a study that analyzed the deformation of red blood cells in relation to the relative viscosity as a function of shear stress [13].

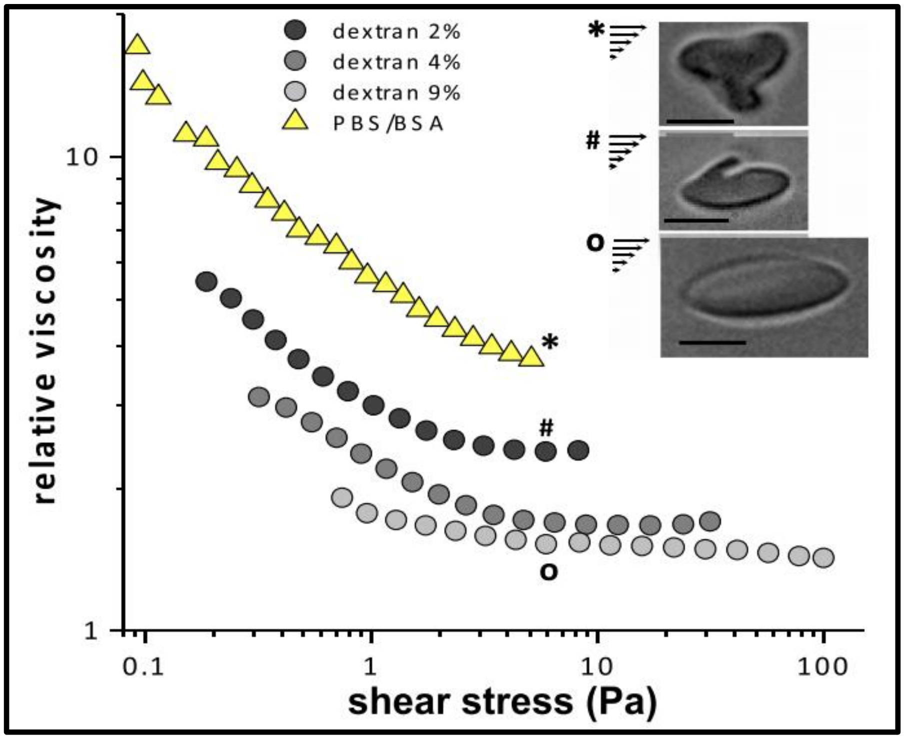

Figure 5: Data from study of red blood cell deformation

1.6 Rheology

These investigations of colloids, fluids, viscosity are considered rheological studies. Rheology is the study of the flow of liquids, gases, or even soft solids. Most materials studied in rheology are defined by a constitutive equation that relates the shear exerted (τ), the material's strain rate (γ), and Newtonian viscosity (μ) in the case of Newtonian fluids [14]. In the case of Non-newtonian fluids, the Newtonian viscosity is replaced with a ratio of the apparent viscosity in the fluid to the normalized viscosity in the fluid [14]. As discussed previously, such studies may be conducted using computer simulations like BD simulations, but they can also be conducted with Rheometers. Rheometers are instruments that measure physical parameters of a material under certain estimated rheological parameters [15]. Rheometers can "measure the viscosity, viscoelastic properties… with respect to time, temperature, frequency, and stress-strain, and transient response" [15]. The cost of such instruments are easily in the range of hundreds of thousands of dollars whereas computer simulations provide a cheaper alternative for research. But it should be noted that this particular system does not account for intermolecular interactions. If these interactions were to be studied, a different type of simulation would be used.

1.7 Elasticity and Plasticity

Beyond the occurrence of shear thinning and shear thickening in Non-Newtonian liquids, the investigation of a fluid's microstructure may be studied after the effects of an exerted shear. The concept of elasticity and plasticity commonly seen in solids may be applied to fluids. In solids, objects are composed of atoms in a defined arrangement and held at a certain distance from each other with bonds [13]. These bonds can be imagined as a connection akin to a spring where the distance between molecules can be stretched, compressed, and twisted to an extent even though a solid is considered a rigid body as illustrated in Figure 6 [13]. This behavior is referred to as elasticity.

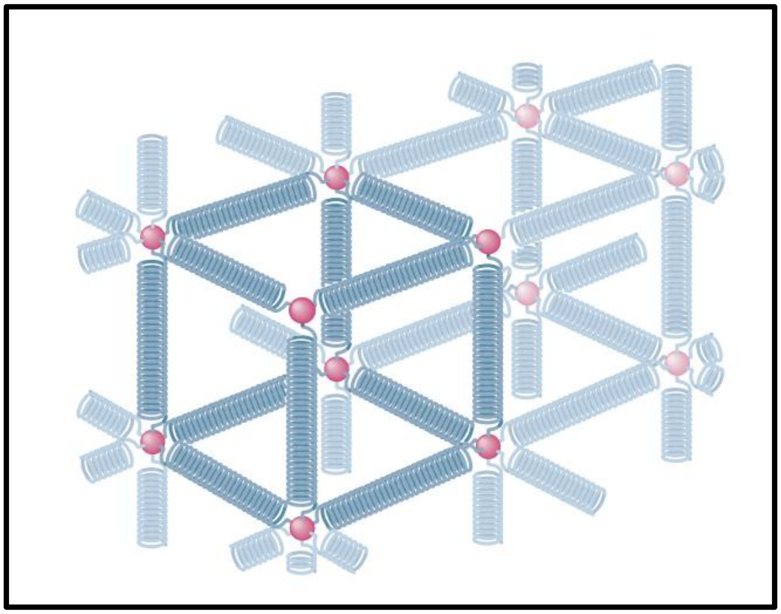

Figure 6: Image of atoms and bonds of a metallic solid

And while these bonds can move, there is a point for each solid to where the stress imposed on the solid is too great for the atoms and bonds to return to their original configuration thus resulting in permanent deformation of the solid [13]. This behavior is known as plasticity. This point of no return is known as the yield strength. To further push a solid's limits of endurance to a force, if the solid is pushed beyond its ultimate strength then the structure eventually ruptures [13]. Yield strength and ultimate strength can be observed in Figure 7.

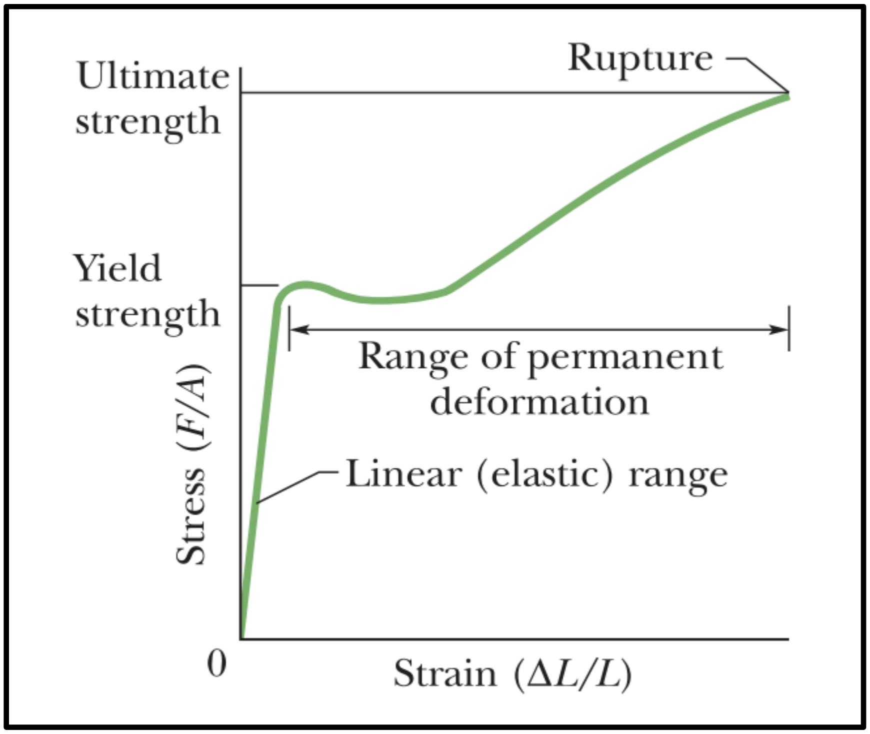

Figure 7: Example of yield strength and ultimate strength

The same principles of elasticity and plasticity can be applied to fluids as well. After a fluid's exposure to shear, the configurations of particles can either resume their original configuration or end in a differing configuration that the original. In the former situation, the fluid would exhibit elastic behavior. Consider a rubber band. After a force is applied when pulling a rubber band, the band will resume its initial structure after the force is removed. This notion describes fluids whose final particle configuration resembles its original configuration.

When the final particle configuration does not resume the initial configuration, it is reflecting plastic behavior. This is similar to applying a force to a plastic bottle. After the force is applied, the plastic bottle will not be able to return to its primary particle configuration. Rheological studies can be utilized to determine under what conditions fluids exhibit elastic or plastic behavior. The most common techniques of studying fluids in general include optical microscopy and scattering experiments with light, x-rays, and neutrons [3]. But for the purposes of this research project, the rheological study of shear thinning, and elastic/plastic behavior were investigated using Brownian Dynamic Simulations.

Chapter 2: Methodology

2.1 The Yukawa Potential

The Yukawa potential, seen in *Equation 1*, was the first component of the simulation.

$$U = \frac{Ae^{-zk(r-1)}}{r} \qquad \textit{Equation 1}$$

In the equation, U describes the intermolecular potential that causes an exponential decay of potential from some distance, r is the radius between two particles, A is the coupling parameter, and zk is the screening parameter [16]. The radius is measured as the distance between the centers between two particles where there is no overlapping of the particle spheres. This equation is also referred to as the pairwise repulsive hard-core Yukawa Potential and describes the interaction between binary colloidal particles that are charged [1]. Such an interaction was chosen as it closely represents the interaction between charged particles of silica, SiO_2, since the study would first compare its results to those experimentally obtained from Dr. Luis Sanchez-Diaz's study at Oak Ridge National Laboratory [1]. It should be noted that a single silica molecule is a neutral molecule, but the charge of these particles refers to the inevitable intermolecular charge. Also, this system considers values as unitless for ease of comparison with this preliminary code. In future studies with this code, units will be added.

2.2 Radial Distribution Function G(r)

The radial distribution function G(r) was another equation incorporated to describe our system. This function is one that describes the probability of finding a pair of atoms or particles some distance (r) apart as seen in *Equation 2* [17].

$$G(r) = \frac{V}{N^2}\left(\sum_i \quad \sum_{j \neq i} \quad \delta(r - r_{ij})\right) \qquad \textit{Equation 2}$$

Where V is volume, N is the number of molecules, i and j are the molecule indexes, and δ is Dirac delta function. The radial distribution function explains the relationship between the volume of a box and the number or particles within it. The two variables are inversely proportional, so as the number of particles within the box increases, the volume within will decrease.

2.3 Brownian Dynamics (BD)

The simulation of this study was primarily based on Brownian Dynamics (BD) which aims to describe motion of particles in a simulation as they would occur in reality. The BD simulation performed in this study used an algorithm which was first proposed by Ermak and McCammon as seen in *Equation 3* with the exception of not including hydrodynamic simulations and adding shear flow in the x direction [1,18].

$$r_i(t+\Delta t) - r_i(t) = (\gamma y_i \hat{e}_x + \beta D_0 F_i(t))\Delta t + \Delta X_i(t) \qquad \textit{Equation 3}$$

In this function, γ is the shear rate, D_0 is the short-time self diffusion of the particles in the system, t is time, $i$is a particle, $r_i(t) = (x_i(t), y_i(t), z_i(t))$ is the positional vector of a particle, $\hat{e}_x$ is the unit vector along the x axis, $\Delta X_i(t)$ is random displacement [1].

The simulations were performed in a cubic box under periodic boundary conditions. Shearing was incorporated into the boundary conditions using the ‘sliding brick’ boundary conditions of Lees and Edwards [19]. The initial configurations were generated by the following procedure: first, particles were placed randomly in the simulation box at the desired density, and then the overlap between the particles was reduced or eliminated. Once the initial configuration was constructed, several thousand cycles were performed to achieve thermal equilibrium, followed by at least two million cycles where the data was collected. We found that the results obtained were almost the same for each cycle, and that there is no systematic effect of system size in the calculation of these properties.

2.4 Viscosity as a function of Shear

With the simulation, data was acquired describing the systems viscosity under different shears. Viscosity is a fluid's resistance to flow and depending on fluid, the viscosity may change in response to the altered force. When considering this dynamic viscosity (η), it is calculated as seen in *Equation 4* in the units of $\frac{N \cdot s}{m^2}$ or in the SI unit $Pa \cdot s$ where F is force, t is time, and a is area [18].

$$\eta = \frac{F \cdot t}{a} \qquad \textit{Equation 4}$$

In other situations, viscosity may also be considered by Newton's Law of Viscosity, as discussed in Chapter 1, which describes the relationship between shear stress and shear rate in a fluid [6]. Viscosity is given as

$$\eta = \frac{\tau}{\gamma} \qquad \textit{Equation 1}$$

Where τ is shear stress, γ is shear rate, and viscosity is determined in Pascal seconds ($Pa \cdot s$) [7,8]. The function describes the proportional relationship between shear and stress within the system.

This study compared the viscosity vs shear figures with the experimental figure. The system was modeled after the experimental parameters by having a density of 0.85, screening parameter (zk) of 3.20 and coupling parameter (A) of 3.12 under shears of 0.5, 5.0, 15.0, and 20.0. Then, the system was examined with a screening parameter (zk) of 8.00, coupling parameter (A) of 1.00×10^2 at densities of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 under shears of 0.0, 0.5, 1.0, 5.0, 15.0, and 20.0. And recall that these values were considered as unitless for the purposes of the code.

2.5 Elasticity and Plasticity

The system was lastly studied to learn more about its elastic and plastic tendencies under differing densities. The system was considered at density 0.5 and 0.3, both under 20.0 and 0.0 shear. First, the system was observed at the end of a simulation run at maximum shear, 20.0, and the positions of each particle in the system was recorded. This configuration of particles was then run in a simulation without shear to see if the configuration would return to its initial configuration of remain in the configuration established at the end of maximum shear. The same process was repeated for the system at 0.3 density. The determination of the changes of configuration were made with qualitative inspections. The particles after simulation were judged as either being in an ordered state or a disordered state.

Chapter 3: Results and Discussion

3.1 Comparisons with Experimental Data

The first portion of the experiment focused on comparing simulated data with experimental data from an experiment conducted at Oak Ridge National laboratory. The results from the experiment can be seen in Figure 8. The experiment was studying silica which is considered to be a non-newtonian substance. Specifically, silica is a shear thinning material. Figure 8 reveals that for the sample, as shear rate is increasing, the viscosity decreases.

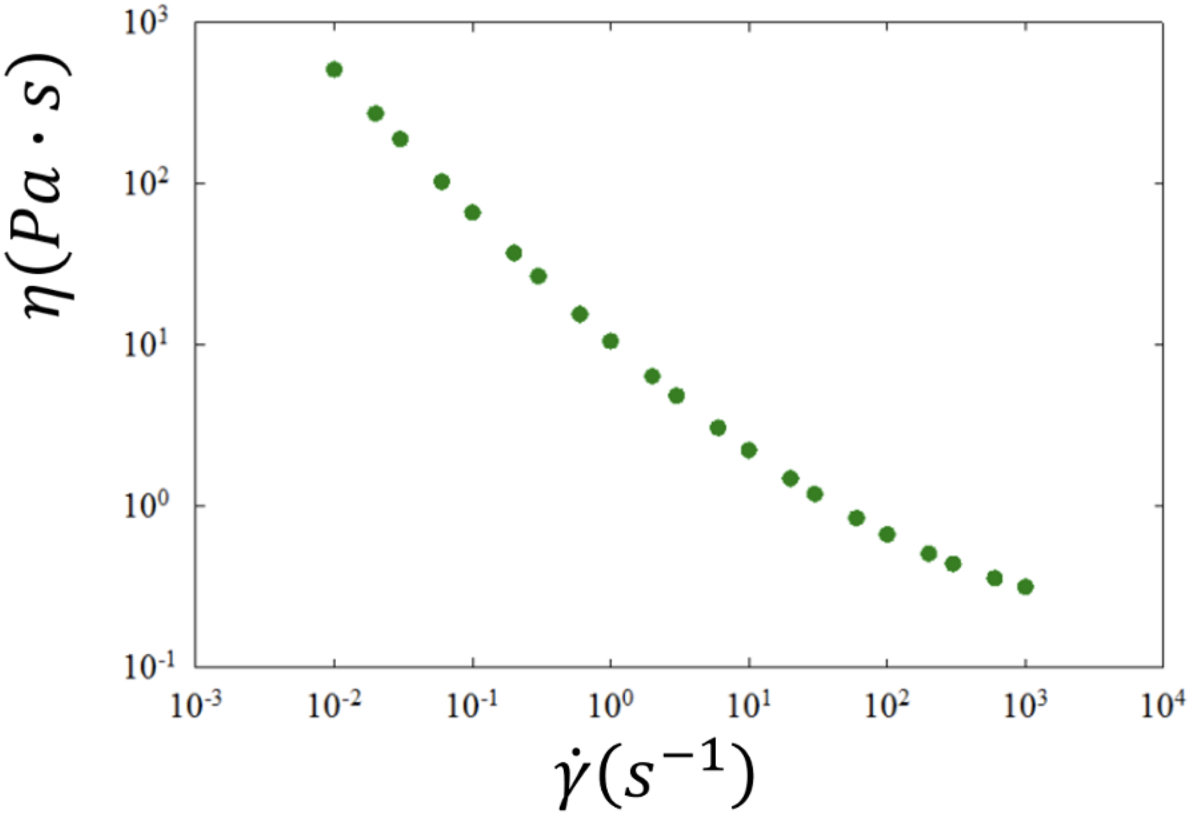

Figure 8: Viscosity vs Shear Rate from Oak Ridge Experiment

The experimental parameters were a density of 0.85, screening parameter (zk) of 3.20 and coupling parameter (A) of 3.12 under shears of 0.5, 5.0, 15.0, and 20.0 so our own study simulated a system under the same parameters. The simulation showed very similar results upon qualitative observations. Figure 9 reflects how the simulated system also experienced shear thinning tendencies since the viscosity decreased as the shear increased.

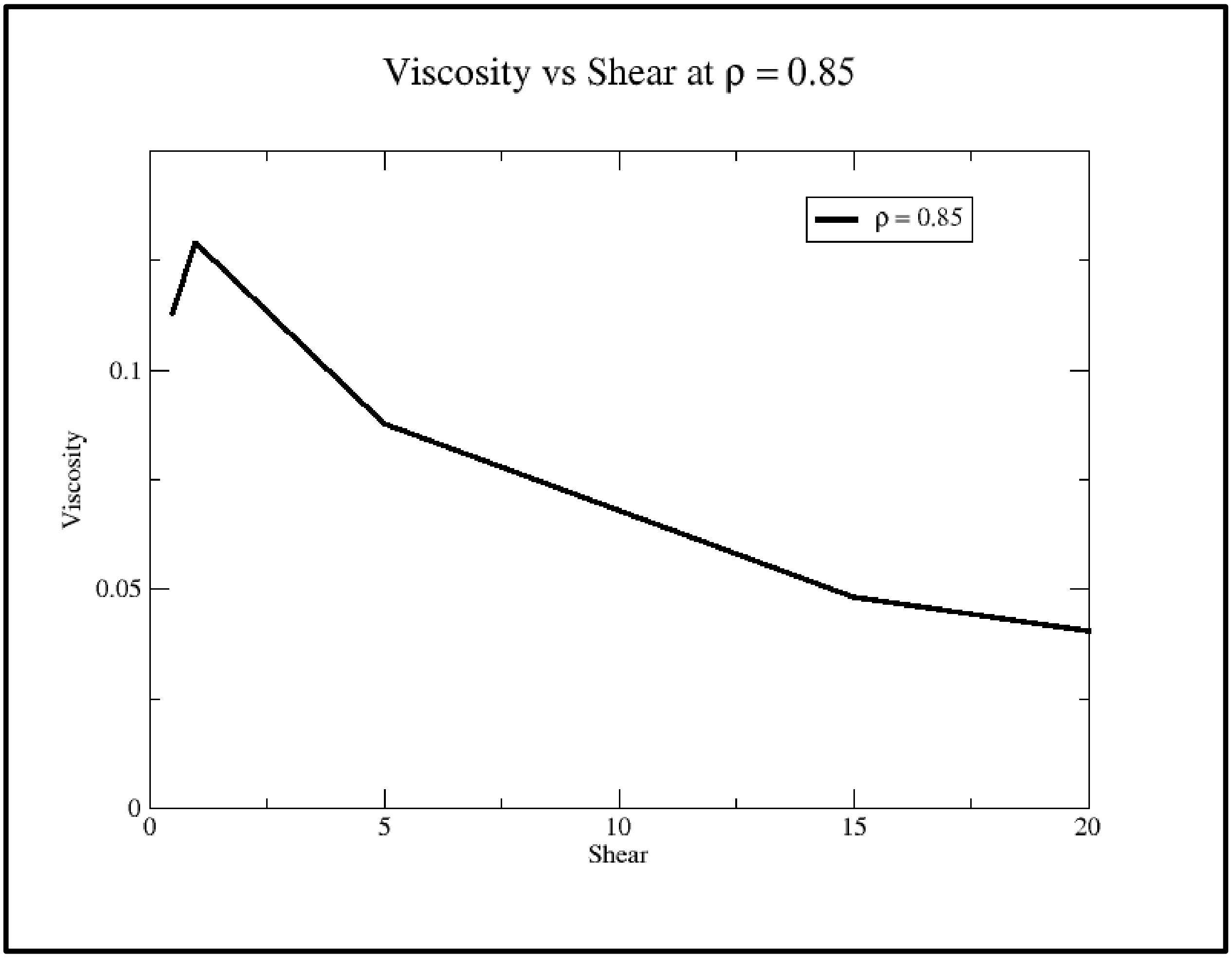

Figure 9: Simulated Viscosity vs Shear Data Under Oak Ridge Experiment Parameters

From the simulation, radial distribution data was also collected. Figure 10 reflects these data and it describes the system's transition to a liquid state. The smooth curves reveal that, under the aforementioned parameters, the system has a smooth transition to the liquid state. By smooth meaning that the actual curves on the figure do not have many peaks breaking up the lines which can be seen in later radial distribution graphs in this study and that after a $r/\sigma$of 2, there is not much variation in the G(r). If the curves were less smooth, then the transition could experience more abrupt changes during the process. From this figure, it can also be noted that as the shear on the system increases, there is a better flow in the transition to the liquid phase since the y values trend less away from 1.

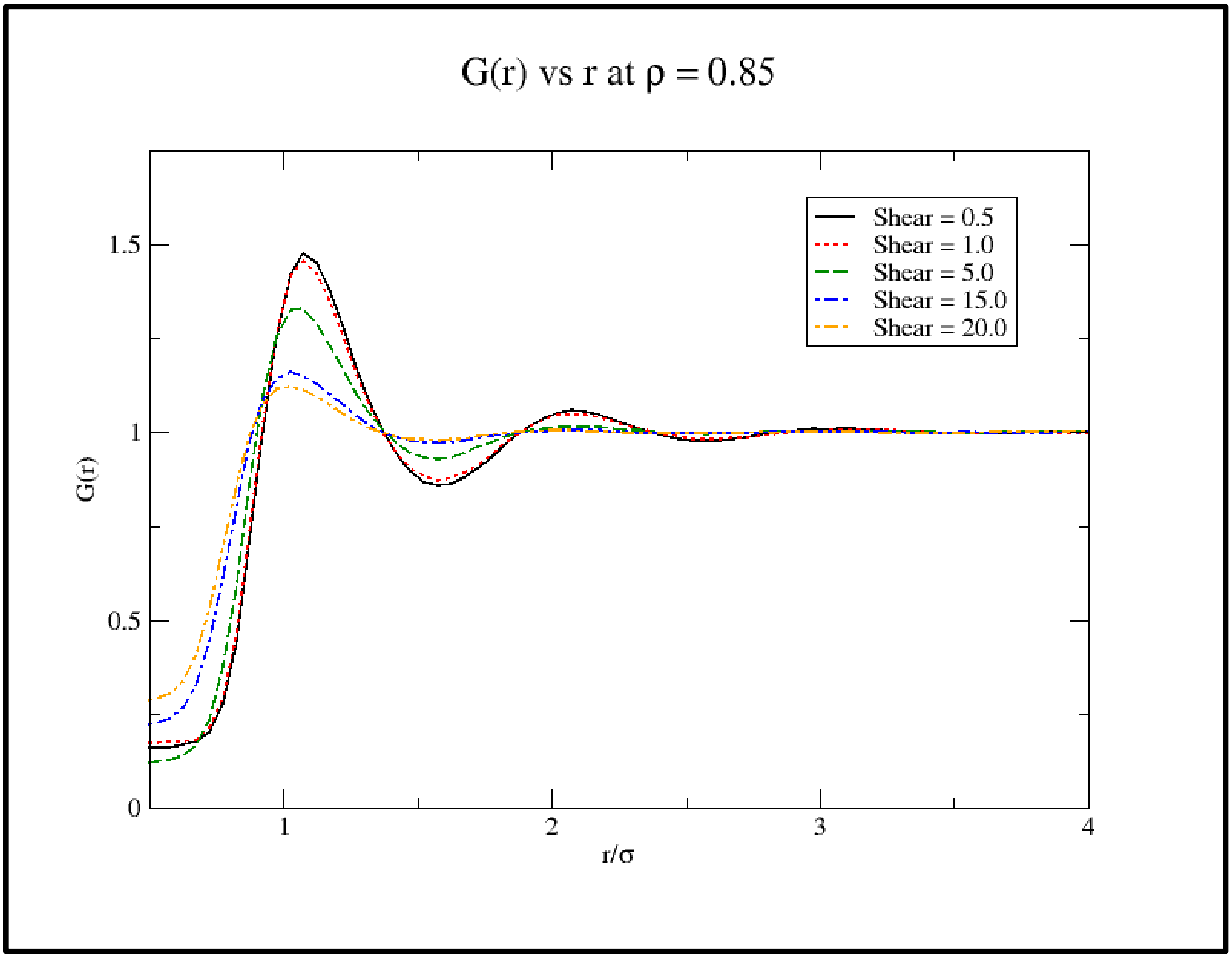

Figure 10: Simulated Radial Distribution Data Under Oak Ridge Experiment Parameters

Between the simulation results from the Viscosity vs Shear graph and the results from the radial distribution graph, both suggest that the code created was able to successfully simulate data similar to laboratory experiments.

3.2 Radial Distribution Results

After testing the code to determine if it could adequately simulate experimental data, the system was considered under other parameters to further investigate shear thinning behavior in simulated systems. The new set of parameters that the system was simulated under was with a screening parameter (zk) of 8.00, coupling parameter (A) of 1.00×10^2 at densities of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 under shears of 0.0, 0.5, 1.0, 5.0, 15.0, and 20.0.

The first part of the data acquired from these simulations was in the form of radial distribution data. Figures 11-16 express the radial distribution data for the system under different shears at differing densities. Similar to the radial distribution figure for the simulated under experimental parameters, all of these figures also show the trend of better flow into the liquid state as the shear is increased within the system. However, at each density there is no set proportion between how much better the transition into the liquid state becomes as shear is increasing. For example, the first curves at the density of 0.1 at the five different shears is much shallower than the first curves at the density of 0.6. These figures also reflect that the smooth transition to the liquid state becomes less fluid as the density increases as seen most prominently in Figure 14, 15, and 16. In these cases, the system will not become a liquid, but instead crystallize. When double peaks emerge at the second and third peak of each of the figures, it indicates a transition to a crystalline form. Such trends are reasonable since the increased density of the system would hinder the ease of movement of the particles to a liquid state and more likely to form crystal structures.

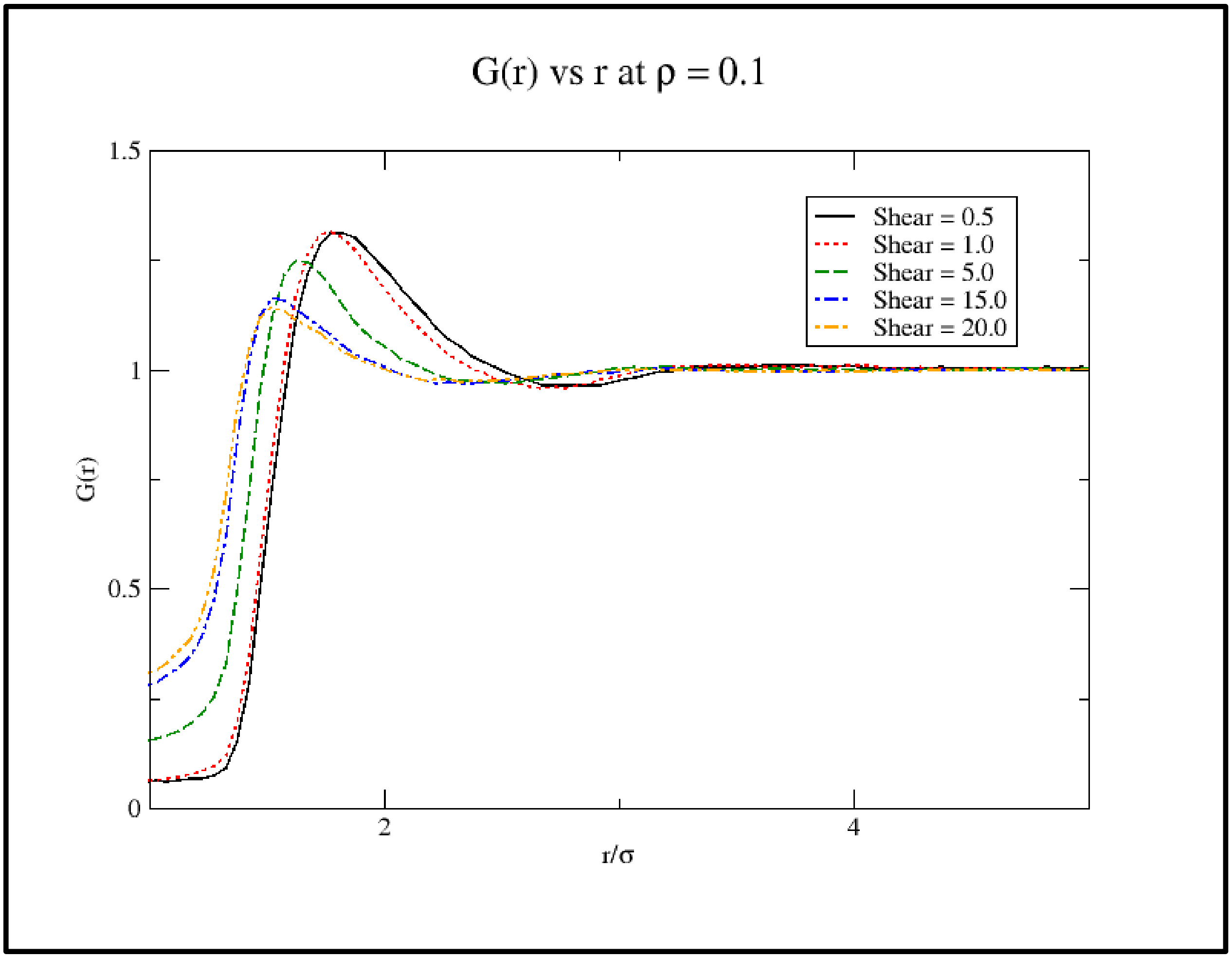

Figure 11: Radial Distribution at Density 0.1

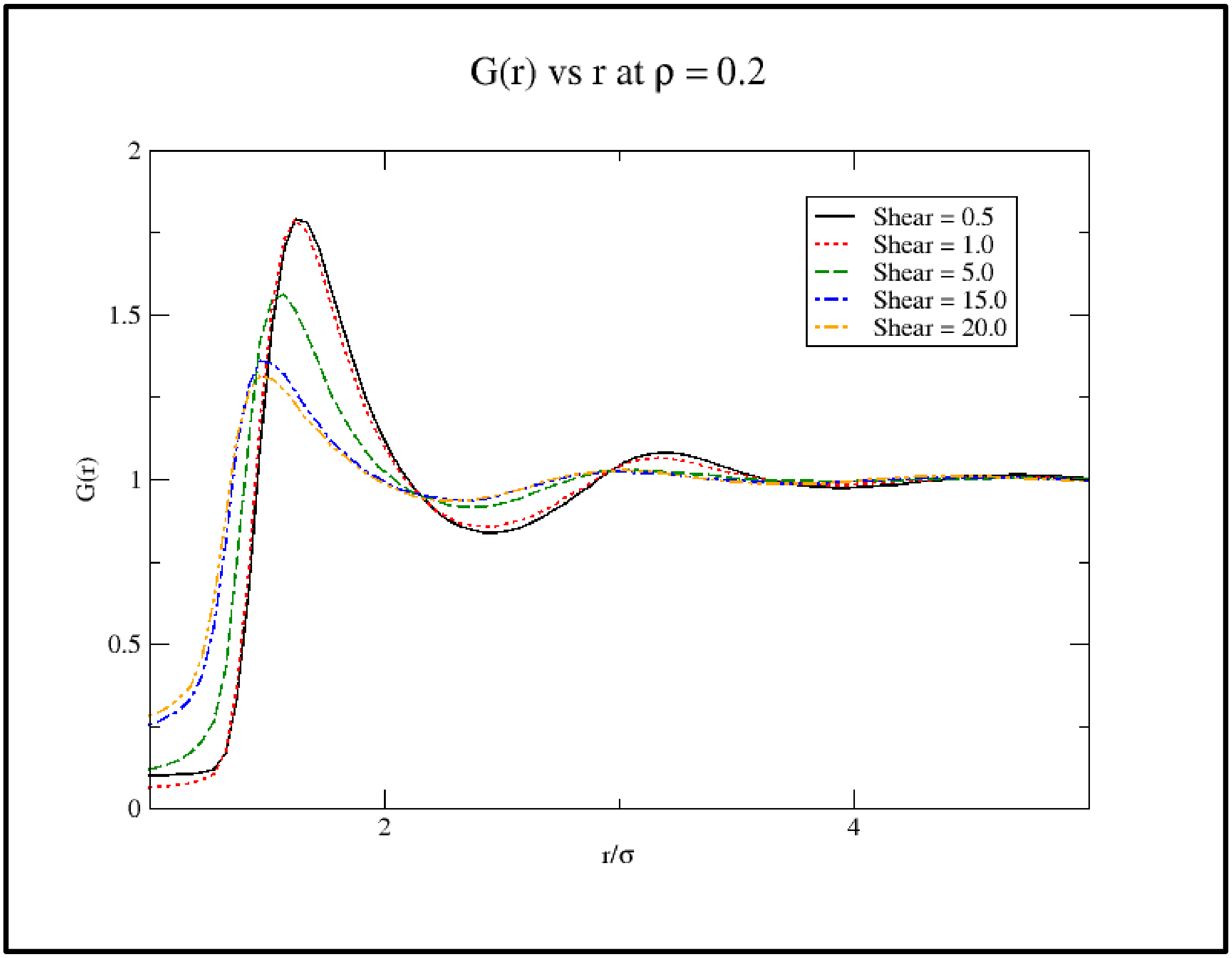

Figure 12: Radial Distribution at Density 0.2

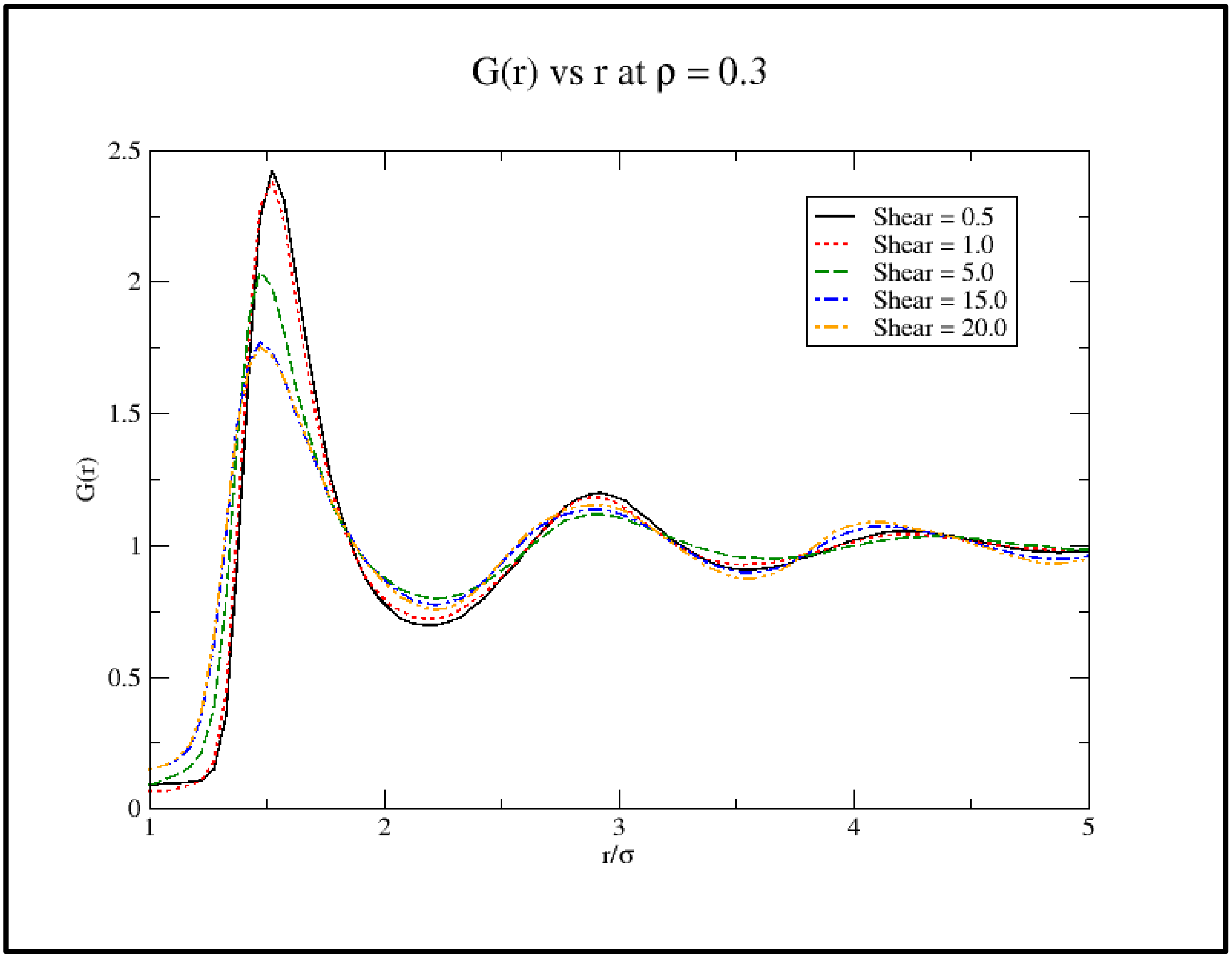

Figure 13: Radial Distribution at Density 0.3

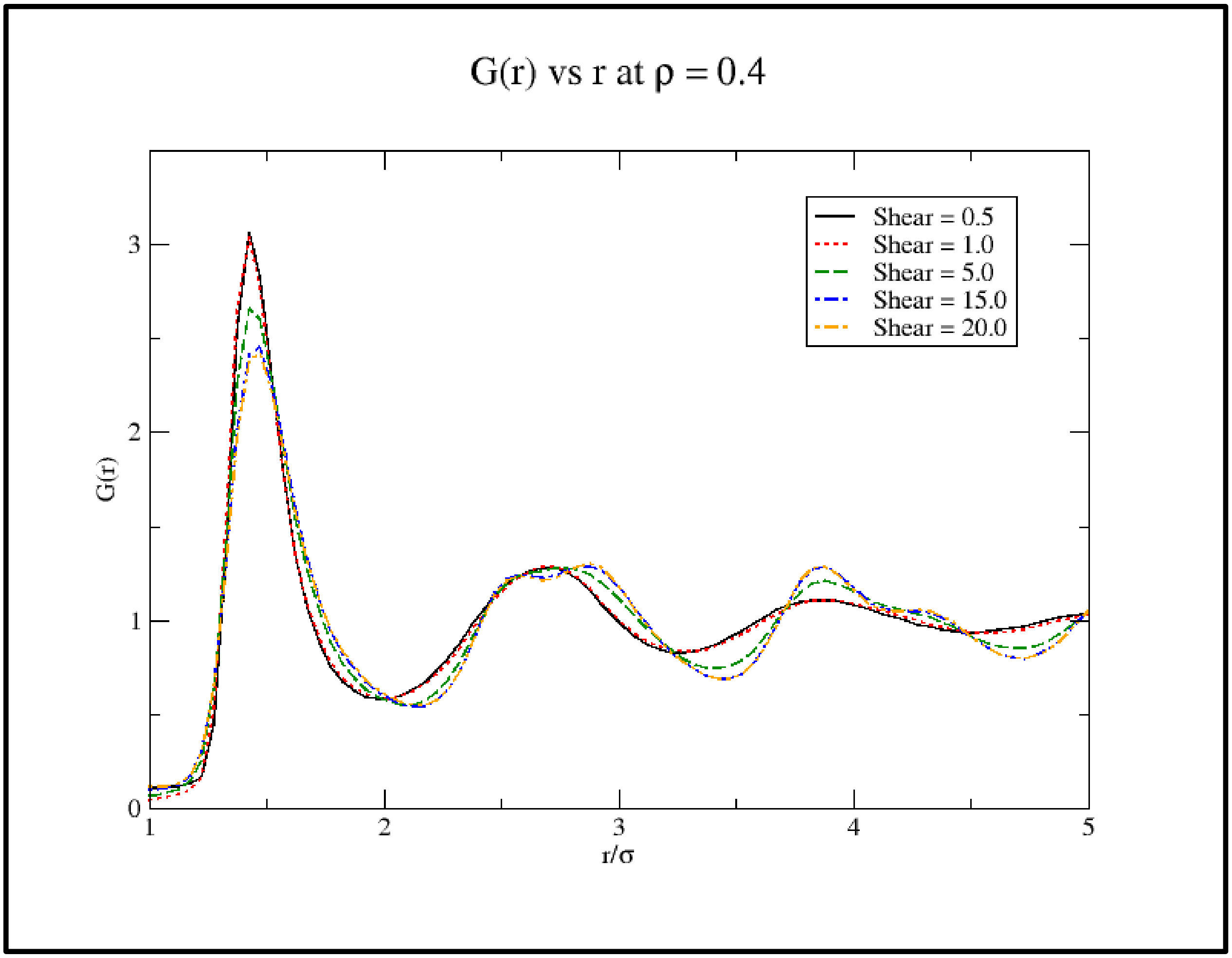

Figure 14: Radial Distribution at Density 0.4

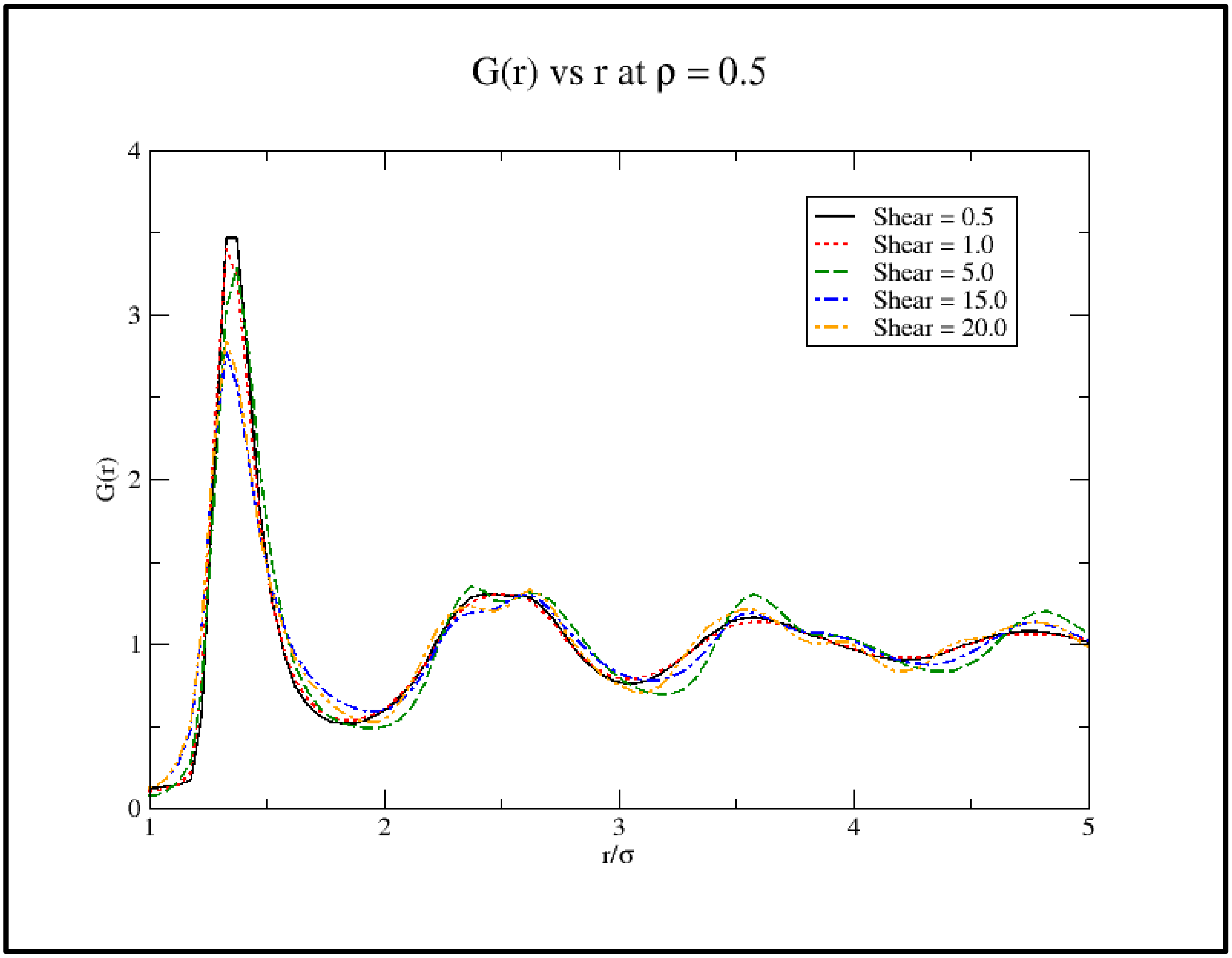

Figure 15: Radial Distribution at Density 0.5

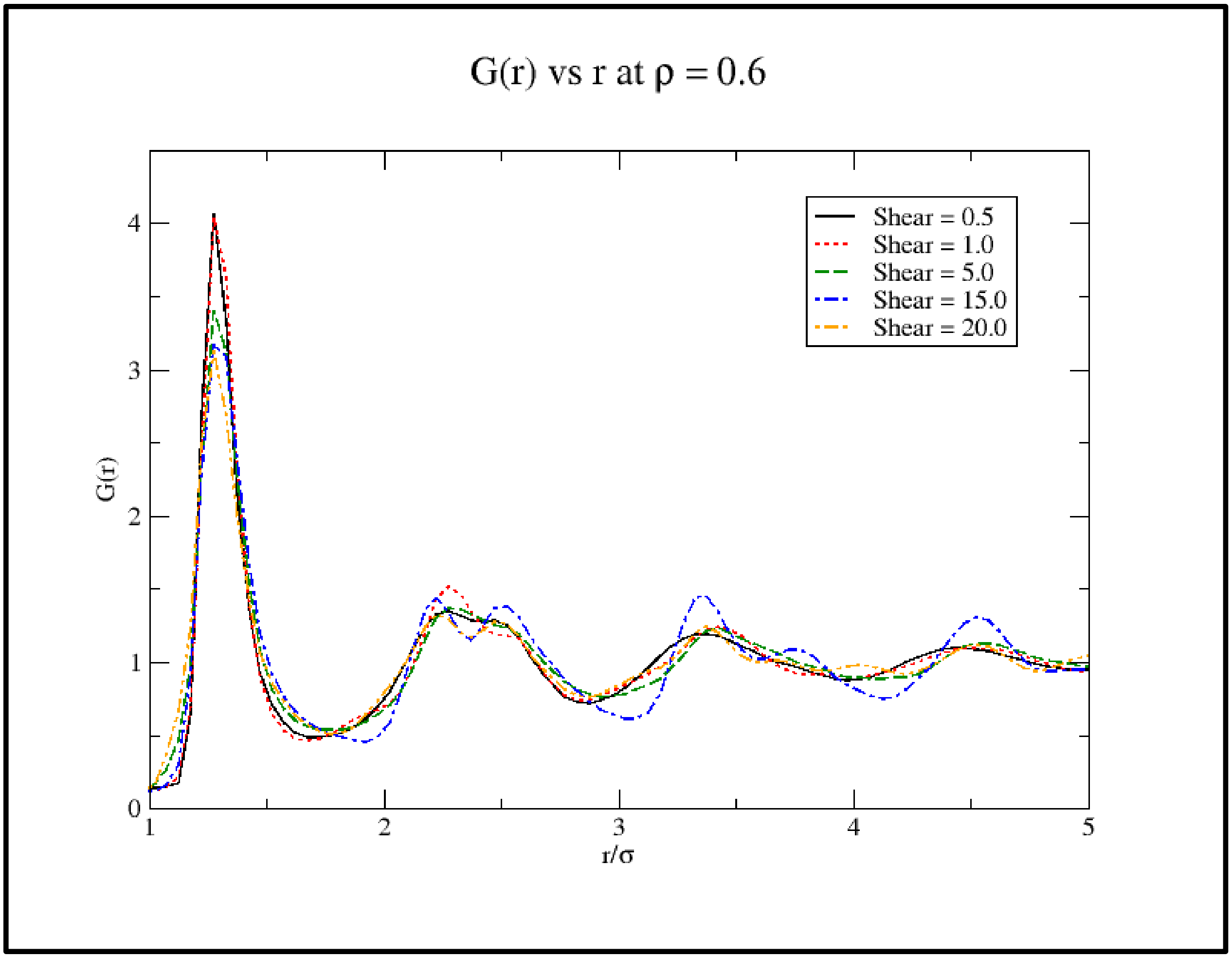

Figure 16: Radial Distribution at Density 0.6

3.3 Viscosity vs Shear Results

After considering the radial distribution data, the viscosities of the various simulations were collected and analyzed where viscosity is a function of shear. This system simulated another substance that would be considered having shear thinning behavior at densities 0.1, 0.2, and 0.3 since decreasing viscosities are seen as shears increase as seen in Figure 17. The figure also reveals that the degree of viscosity decreases is not uniform across all densities. At higher densities, the system will still exhibit lower viscosity as the shear increases, but it will be at a much slower decrease than the lower density counterparts. Such behavior is reasonable since the increasing density would minimize the free space in the system available for movement.

Figure 17 also reveals conflicting information about the system at densities 0.4, 0.5 and 0.6 from the analysis of their radial distribution data. From Figures 14- 16 the graphs indicate that the system is transitioning to a crystalline state so their viscosities should be increasing as the shears are increasing; however, Figure 17 shows densities 0.4, 0.5 and 0.6 to have decreasing viscosities in response to the increasing shears. This conflict may be partially due to the missing hydrodynamic term in the systems code, which was not a primary focus in this study [3,19].

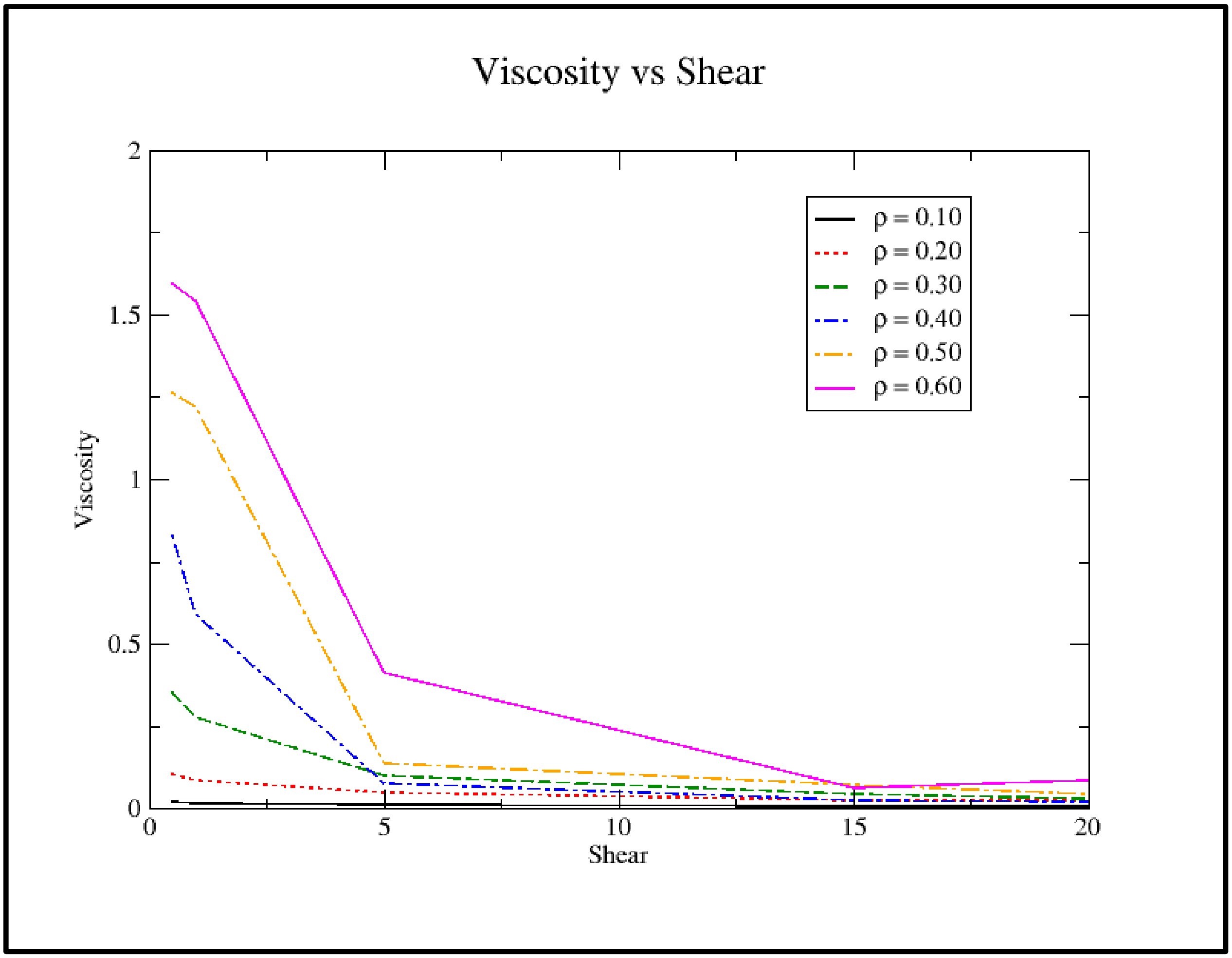

Figure 17: Viscosity vs Shear of Varying Densities

3.4 Elasticity vs Plasticity Results

The last information gathered from these simulations were the positions of the particles after each simulation was run for the purposes of studying elasticity and plasticity within the system. This study is based on the concept of applying what is known about elasticity and plasticity in solids to fluids. If the system returns to its initial configuration after shear is removed then it exhibits elastic behavior. If the system does not return to its initial configuration then it is exhibiting plastic behavior. Finding the conditions under which a system moves from elastic behavior to plastic can lend better insight to the limits of substances.

In Figure 18, the system was run at density of 0.5 and a maximum shear of 20.0. The system appears to be in an ordered state as seen in the layer formations.

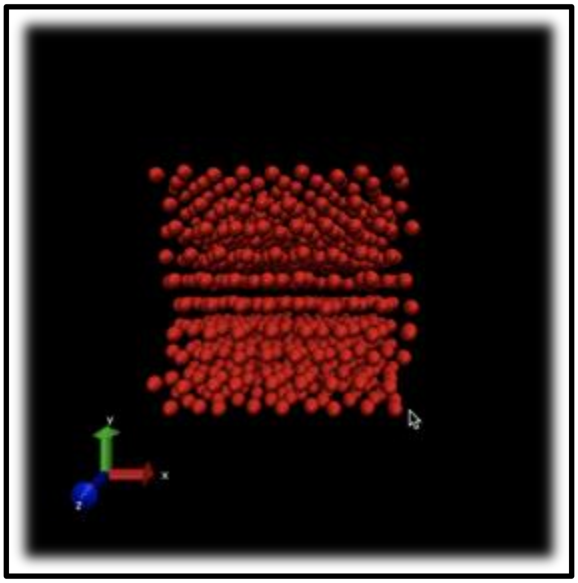

Figure 18: System at Density 0.5 and Shear 20.0

Figure 19 reveals the system at a density of 0.5 with shear removed. The system appears to still be in an ordered state, evident by the persistent layering, which would suggest that the system is exhibiting plastic behavior since there was no change in the particle configuration with shear and after shear was removed. This determination is a qualitative one meaning that there were no set measurements or calculations involved in determining the level of orderliness or disorderliness.

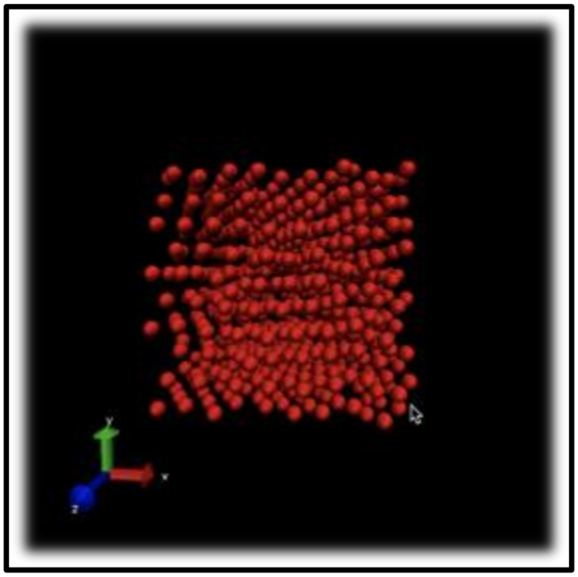

Figure 19: System at Density 0.5 and Shear 0.0

The same process was conducted when considering the system at a density of 0.4 as seen in Figures 20 and 21. Figure 20 shows the system at a density of 0.3 under a maximum shear of 20.0. The particles at the end of the simulation show a relatively ordered state since some layer formation is seen.

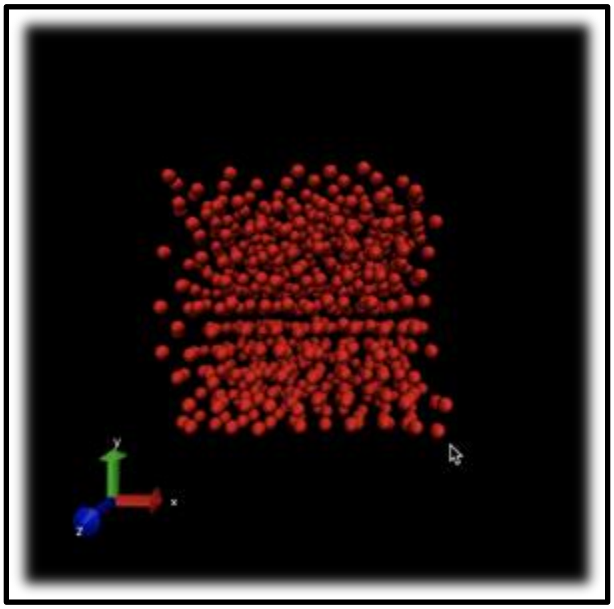

Figure 20: System at Density 0.3 and Shear 20.0

Figure 21 shows the particles in the system after the shear had been removed. However, unlike Figure 20, in Figure 21 a relatively disordered state is observed which would suggest that the system had begun to exhibit elastic behavior since the particles were resuming the random configuration they had prior to any shearing.

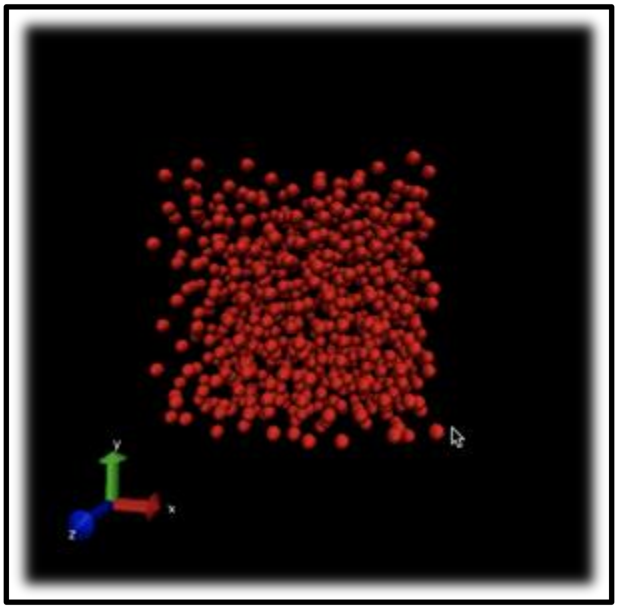

Figure 21: System at Density 0.3 and Shear 20.0

In all substances, there is a point at which the force exerted on it is so great that the substance can no longer resume its original configuration. This threshold can vary depending on density, temperature, number of particles etc. This study specifically looked at varying density.

Conclusion

The purpose of this study was to develop a program that could sufficiently simulate results comparable to experimental data with the intent of a studying shear thinning colloid. This study was successful in developing such a program and compared simulated results to experimental results from an experiment on silica [3]. The data compared was a qualitative inspection of viscosity as a function of shear. Figure 11 compared to the experimental data from Figure 10 confirmed the system was exhibiting shear thinning behavior.

The second portion of this study continued to observe shear thinning behavior under different parameters. These parameters showed that the system was still presenting shear thinning behavior at the densities of 0.1, 0.2, and 0.3. This portion of the study also observed the radial distribution results at various densities. The results displayed transitions to a crystalline phase in the systems with the densities of 0.4, 0.5, and 0.6 which reveals that increasing density of the system causes a shift to a crystalline form.

The last phenomenon investigated was the elasticity and plasticity of the system under shear. Similar to the viscosity analysis, the elasticity and plasticity study was a qualitative one based on the arrangement of particles in the box. This portion of the study revealed the system at a density of 0.3 to exhibit elastic behavior and the system at a density of 0.5 to exhibit plastic behavior.

Investigating shear thinning behavior from the perspective of radial distributions, viscosity as a function of shear, plasticity, and elasticity in the form of simulations is beneficial. Simulations may serve as alternatives to other rheological studies or as a supplementary tool. Simulations may also be used to study other behaviors of colloids such as shear thickening rather than the shear thinning. Rheological simulations present a less costly option for studying colloids. Simulated studies such as this are just the beginning and hold numerous possibilities for future studies such as considering the system under different parameters; altering temperature, number of particles, and/ or volume; or even more studies of elasticity and plasticity at different densities.

Supporting Materials: The Code

```
program boundary

implicit real (A-H,O-Z)

integer it, Iseed,ISEED1,ISEED2,np,n,i
Dimension CX(10000,10000), CY(10000,10000),CZ(10000,10000), strain(10000)
Common /pos1/  x(10000),y(10000),z(10000)
Common /pos2/  xr(10000),yr(10000),zr(10000)
Common /forces/  fx(10000),fy(10000),fz(10000)
Common /consitanits/  zk,A,dens,np,xl,delrx
common/semillas/iseed3,iseed2,iseed1
!assigned vaxlue]]
!do it=1,3
!prinit*, rand()
!time to run simulation
NTR=3000000
!time to start save configuration
NS=100000



NSTEPS=500
dt=0.000001
np=800       !number of particles
dens=0.85    !we change density and measure the change in energy, pressure
pe=5.0   !Shear
zk=3.2      !a constant
A=3.12
pres=0       !starting pressure
energy=0     !starting energy
VAR=SQRT(2.D0*DT)
tau=0                 !starting stress
xl=(REAL(np)/dens)**(1./3.)  !dimensions of box
vol=xl**3                    !volume of box




print*, xl, vol
iseed=3568
```

```
ISEED1=34564
ISEED2=46665
ISEED3=46448
!!!!!!!!Initial Configuration!!!!!!
print*,'im here'


     DO 10 I=1,NP
2      R=zran(iseed)-0.5d0

       S=zran(iseed)-0.5D0

      T=zran(iseed)-0.5D0

      X(I)=R*XL

      Y(I)=S*XL

      Z(I)=T*XL

      XR(I)=X(I)

      YR(I)=Y(I)

      ZR(I)=Z(I)

        DO 9 J=1,I-1

        xij=X(I)-X(J)

        yij=Y(I)-Y(J)

        zij=Z(I)-Z(J)

        RO=(xij)**2+(yij)**2+(zij)**2

        IF (RO.LE.1.D0) THEN
           WRITE(*,*)'traslapess',I,J
        GO TO 2
```

```
      ENDIF

9      CONTINUE

10     CONTINUE
print*,'I am still alive'


it=1
 ks=0
 delrx=0
 Call force(it,en,vr,stress)

 nn=0
print*,'almost there'
open (10, file= 'positionxyz1rho0.85sh5.0CHECKdat', status= 'unknown')    !we view the
positionxyz1.dat in VMD
  open (20, file= 'pressureandenergyrho0.85sh5.0CHECKdat', status= 'unknown')
 write (10,*)np
 write (10,400)
 Do it= 1,ntr

  Do n=1,np

  call AZARG(ISEED, ax)
  call AZARG(ISEED, ay)
  call AZARG(ISEED, az)

x(n)= x(n) + fx(n)*dt+ax*var + 6.*Pe*y(n)*dt
y(n)= y(n) + fy(n)*dt+ay*var
z(n)= z(n) + fz(n)*dt+az*var

xr(n)= xr(n) + fx(n)*dt+ax*var+6.*Pe*yr(n)*dt !Add equation from sheet
yr(n)= yr(n) + fy(n)*dt+ay*var
zr(n)= zr(n) + fz(n)*dt+az*var

!Modified Boundary Condition
CORY= ANINT(y(n)/ xl)
x(n)= x(n)-CORY* DELRX
x(n)= x(n)-ANINT(x(n)/xl)*xl
```

```
y(n)= y(n)-CORY*xl
z(n)= z(n)-ANINT(z(n)/xl)*xl

!x(n)= x(n)-xl*anint(x(n)/xl)
!y(n)= y(n)-xl*anint(y(n)/xl)
!z(n)= z(n)-xl*anint(z(n)/xl)

end do ! PARTICLES

nn=nn+1
delrx=pe*dt*real(nn)

if(delrx>1.)nn=0

xmod=mod(it,nsteps)
if(xmod.eq.0.0.and. it.gt.Ns) then

 if(it.LE.Ntr)then

ks=ks+1

print*,'i am still here', ks
 un=en/real(np)
 p=1.+vr/(3.*vol)/dens
 tau=tau+stress/(2.*vol)                    !These are what print the averages at the end of running the
program
 pres=pres+p
 energy=energy+un

 strain(ks)=delrx
 Do i=1,np

 cx(i,ks)=xr(i)
 cy(i,ks)=yr(i)
 cz(i,ks)=zr(i)
 write (10,401) x(i),y(i),z(i)
 end do


 400 format ('Configuration snapshot-XYZ format')
```

```
 401 format ('O',2x, 3(1x, g18.12))
403 format (2x, 3(1x, g18.12))
!
end if
end if
 call force(it,en,vr,stress)

   end do !TIME

 presure=pres/real(ks)        !!ks is the number of configurations
 einternal=energy/real(ks)
 tauxy=-tau/real(ks)
 viscosity=tauxy/pe

 print*, 'pressure=',presure, 'energy=',einternal, 'stress=', tauxy, 'viscosity', viscosity
 write(20,*)dens,presure, einternal, viscosity

 call GTRT(CX,cy,cz,Ks, strain)

end program

FUNCtION ZRAN(ISEED)




      implicit real*4 (a-h,o-z)

      common/semillas/iseed3,iseed2,iseed1


      mzran=iseed3-iseed1

      if(mzran.lt.0) mzran=mzran+2147483579

      iseed3=iseed2

      iseed2=iseed1

      iseed1=mzran
```

```
iseed=ishft(3533*ishft(iseed,-16)+iand(iseed,65535),16) +3533*iand(iseed,65535)

mzran=mzran+iseed

zran=.5+.2328306d-9*mzran

return

end



SUBROUtINE AZARG( ISEED,X )


IMPlICIt REAl (A-H,O-Z)

external zran

common/semillas/iseed3,iseed2,iseed1
pi=4.0*atan(1.0)

R=zran(iseed)

S=zran(iseed)

X=SQRt(-2.0*lOG(R))*COS(2.0*PI*S)

REtURN

END



    SUBROUtINE force(it,en,vr, stress)
    implicit real (A-H,O-Z)
    Common /pos1/  x(10000),y(10000),z(10000)
    Common /forces/  fx(10000),fy(10000),fz(10000)
    Common /consitanits/  zk,A,dens,np,xl,delrx
```

```
          en=0
          vr=0
          stress=0   !starting stress
          rc2=xl/2.
          do i=1,np
          fx(i)=0
          fy(i)=0
          fz(i)=0
          end do

          do i=1, np-1
          fxi=fx(i)
          fyi=fy(i)
          fzi=fz(i)
          do j=i+1, np

          xr=x(i)-x(j)
          yr=y(i)-y(j)
          zr=z(i)-z(j)

!Modified Boundary Condition
CORY= ANINT (yr/ xl)
xr= xr- CORY* DELRX
xr= xr- ANINT(xr/ xl) *xl
yr= yr- CORY* xl
zr= zr- ANINT(zr/ xl) *xl


          !xr=xr-xl*anint(xr/xl)
          !yr=yr-xl*anint(yr/xl)
          !zr=zr-xl*anint(zr/xl)





          r=sqrt(xr**2+yr**2+zr**2)

          if ((r.lt.rc2)) then
```

```
                        u=(A*exp(-zk*(r-1.)))/r


                        !f=derivaitive of u(r)

                        ff=((A*exp(-zk*(r-1.)))/r**3)*(zk*r+1.)
            W=A*(exp(-ZK*(R-1.)))*(ZK*R+1.)/r

                        !Pressure equation

                            fxi=fxi+ff*xr
                            fyi=fyi+ff*yr
                            fzi=fzi+ff*zr

                            fx(j)=fx(j)-ff*xr
                            fy(j)=fy(j)-ff*yr
                            fz(j)=fz(j)-ff*zr

                            en=en+u
                        !!!     STRESS !!!
                            stress= stress+ ff*(xr*yr)  !ex of summation

                            vr=vr+w

               !This is the pressure for each particle

                    end if
                    end do

                    fx(i)=fxi
                    fy(i)=fyi
                    fz(i)=fzi
                    end do
                    !write(20,*)it, en, w
                    return
                    end
  SUBROUTINE GTRT(CX,cy,cz,Ks, strain)  !strain returns the box to the original position so
that it doesn't shift when a force is applied
```

```
        IMPLICIT real (A-H,O-Z)
        PARAMETER(NN3=4500)

       INTEGER NHIST(NN3)
Dimension CX(10000,10000), CY(10000,10000), CZ(10000,10000), strain(10000)
Common /consitanits/  zk,A,dens,np,xl, delrx

       DO 5 I=1,NN3

       NHIST(I)=0

5     CONTINUE

!C        DELTA R,
       DELTAR=0.050

!C        MAXIMO VAlue histogram
       MAXBIN=AINT(XL/2.0/DELTAR)

       PI=4.D0*ATAN(1.0)

!C        Number of  configurations
       NTMAX=Ks
       print*, maxbin, ks, xl

       DO 20 L=1,NP-1

       DO 25 M=L+1,NP

!C        time
       DO 40 J=1,NTMAX


       XL0=CX(L,J)

       XLT=CX(M,J)

       XL0T=XL0-XLT
```

```
      YL0=CY(L,J)

      YLT=CY(M,J)

      YL0T=YL0-YLT


      ZL0=CZ(L,J)

      ZLT=CZ(M,J)

      ZL0T=ZL0-ZLT


!Modify below with book one
              CORY= ANINT(YL0T/ XL)
              XL0T= XL0T- CORY* strain(j)
              XL0T= XL0T- ANINT(XL0T/XL)*XL
              YL0T= YL0T- CORY* XL
              ZL0T= ZL0T- ANINT(ZL0T/XL)* XL

!     XL0T=XL0T-XL*ANINT(XL0T/XL)
!     YL0T=YL0T-XL*ANINT(YL0T/XL)
!     ZL0T=ZL0T-XL*aNINT(ZL0T/XL)

      R0T=SQRT(XL0T**2+YL0T**2+ZL0T**2)

      NBIN=INT(R0T/DELTAR)+1

        IF(NBIN.LE.MAXBIN)THEN

        NHIST(NBIN)=NHIST(NBIN)+2

        ENDIF

40    CONTINUE

25    CONTINUE

20    CONTINUE
```

```
!C      gr

       vol=xl**3



       C1=4.00*PI*(dens)/3.00


!save gr
      OPEN(50,FILE='grrho0.85sh5.0CHECKdat',STATUS='UNKNOWN')

!C


      DO 30 NBIN=1,MAXBIN

        RL=REAL(NBIN-1)*DELTAR

        RU=RL+DELTAR

        RT=RL+DELTAR/2.D0

        C2=C1*(RU**3-RL**3)

        GDRTA=REAL(NHIST(NBIN))/REAL(NTMAX)/REAL(NP)/C2

        WRITE(50,*)SNGL(RT),SNGL(GDRTA)

30      CONTINUE


      CLOSE (50)
!
!
      RETURN
!
       END
!
```

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