Norwegian University of
Science and Technology

DEPARTMENT OF PHYSICS

SPECIALIZATION PROJECT

Characterization of ordered and disordered systems using molecular dynamics

Author:
Amund Berthueussen

Supervisor:
Raffaela Cabriolu

December, 2021

Abstract

Studying glass and glass transitions is important for many real world applications. In this report characterization of a solid, liquid and a glassy state of a binary colloidal Yukawa system have been performed using Molecular dynamics simulations with the Lammps software. In particular, the self-diffusion coefficient and the structure of the three states were obtained at different temperatures and successfully compared with a similar study previously published. A shearing experiment was also performed on the glassy-system to study the self-diffusion coefficient in the steady state regime. This analysis shows how this potential model is able to reproduce a non-newtonian behavior for the glassy-system in perfect agreement with the previous study. Furthermore, the stress-strain curve during shearing is in good agreement with previous results, however the height of the overshoot does not perfectly coincide with previous results. This mismatch is believed to be caused by a very limited statistic compared to the one presented in the paper, and it will be the subject of further investigations.

Contents

Chapter 1

Introduction

The distinction between a material in a solid state and a liquid state can be summarized by the difference in amount of internal energy contained by the system. This is because the phase transition, or melting point, that marks the border between a solid and liquid state is determined by the energy of the system. Although this distinction seems simple, the difference in behavior of the two states are both significant and important. A field of attracting forces between the particles that forms the material induces a gain by ordering the particles in specific patterns. Because of this, a low energy state would be locked into one of these energy minima. This is exactly what defines a solid state. The forces opposed on each particle by the interaction potentials are high compared to the internal energy of the particles, making them only vibrate around a fixed point. This is why solids surrounding us every day are rigid and mostly non-compressible. When heating up a solid, the internal energy increase and the vibrations grow, forcing the solid to expand.

By increasing the internal energy of the system even further, you eventually reach the point where the energy of some particles is sufficient to break free from the interaction forces keeping the system ordered. This breakdown denotes the phase transition to liquid, and the particles are now subject to more freedom and are able to flow. Only short-range order is now present in the system, but, unlike a gaseous state, this system is nearly incompressible for most cases. The particles ability to move around give rise to a phenomenon called diffusion. For an equilibrated state, this diffusion is only driven by random motion of the particles and thereby called self-diffusion. This property of liquids is one of the measurements that could be used to distinct liquids from solids, where no diffusion of particles is present.

An interesting system occurs if the liquefied system undergoes a rapid cool-down, also known as quenching. Because of the short timespan of the quenching process, the energy suddenly decrease and most of the particles will not be able to order themselves in the most energy efficient states. This results in a system with only short-range ordering of the particles. And because the particles have low internal energy, they are locked into this fixed position which they can vibrate

around with no diffusion present. The end result is a state that shares properties with both solid and liquid materials. This is known as a glassy system and because of its structure it is referred to as being an amorphous solid [1]. Previously this state was often called a supercooled liquid because its structure was similar to a liquid state, but the particles seemed to be frozen in this unordered configuration.

To investigate and characterize the different three states, i.e., a solid, liquid and a glassy state, a Yukawa binary colloidal model was studied using molecular dynamics simulations. Colloidal systems are essential to life and are extremely useful in many commercial and industrial situations as well. They function in every body cell and are also essential in food, agriculture, concrete, horticulture and the floral industry, but also in the mining and cosmetics field. A colloid is a mixture composed of particles immersed in a dispersing medium. A colloid is defined by the size of the particles involved. If the particles or molecules in a mixture are around 1 nanometer scale in their diameter, the mixture is defined as a solution. If the particles are larger than 1,000 nanometers, it is a suspension. Anything in between those limits is considered a colloid. The unique characteristics of colloids are due to this intermediate size of the dispersed particles.

In this report, a colloidal system made of two different particles sizes was modelled using the Yukawa potential. The initial configuration of the system in a bcc crystal phase was equilibrated to represent the solid state. After characterizing the state using different tools, the system was heated up until the order of the system broke down and the melting temperature was surpassed. This liquified state was also investigated and analysed before it was rapidly cooled down again to a temperature below the freezing point and a glassy state was present. This system was then characterized and compared to the previous states. Figure 1.1 illustrates the progression of the thought experiment that takes a material from the solid state to the glassy state. The diffusion of the colloidal system in this study was further investigated by calculating the diffusion coefficients for several states equilibrated at different temperatures. A similar experiment for diffusion for the binary colloidal system with a Yukawa potential was conducted by J Zausch et al [2], and the findings from this study will be compared to their results.
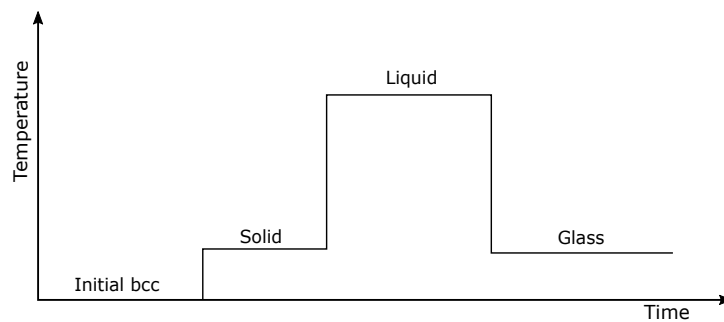

Figure 1.1: Timeline for the characterization of the different states.

An important behavior is known to occur for the colloidal system using a Yukawa potential. For the glassy state, non-Newtonian behaviors have been reported. Non-Newtonian behaviors is characterized by a changing viscosity for variations in some parameters, e.g. strain. These systems are surrounding us every day in foods, cosmetics etc., but are still not fully understood. A good amount of recent studies have been conducted in this field, as summarized in Bonn et al [3].

At the end, some experiments with shearing of the binary colloidal system were also conducted. The effect that the shearing had on the self-diffusion of particles in the system was analysed and plotted. This is where shear thinning behavior of the colloidal system was expected to occur, as the glassy state with a Yukawa potential is known to have a reduced viscosity when shear is applied. This is reflected in the diffusion of the particles which increases during the steady state after shearing, compared to the corresponding equilibrium case at the same temperature. In addition, the well-known overshoot of the stress in the stress-strain curve was obtained and compared with results from [2].

Chapter 2

Methods

In this chapter the method for preparing and simulating the different systems investigated in this project is presented. The radial distribution function and the diffusion coefficients were the main methods used to characterize the systems and are also introduced in this chapter.

2.1 Molecular Dynamics simulations

Molecular dynamics (MD) is a numerical simulation method used to analyze the structure and movement of particles in systems with sizes ranging from only a few particles to billions of particles. With an initial configuration of one or several different kinds of particles, the energy of the system is calculated by evaluating the forcefield over the system. This is obtained by looking at the potentials working between the particles and external potentials that may affect the system. After that, the following classical Newtons laws of motion

$$F_i = m_i \times \frac{d\vec{u}_i}{dt},$$
$$i = (1, 2, ..., N) \qquad (2.1)$$
$$\vec{u}_i = \frac{d\vec{r}_i}{dt},$$

are used to calculate the new velocities and positions of each particle [4]. This numerical integration is repeated for a sufficient number of steps, until the dynamics to be studied have occurred.

A canonical ensemble was used in this study to ensure a system environment with a controlled temperature. This means that the number of particles, N, the volume, V, and temperature, T, of the system was conserved during a whole simulation run. A simulation like this is usually referred to as an NVT simulation because of the constraints set on three of its parameters. A micro canonical ensemble, NVE, could also have been chosen for this study, but NVT-simulations controls the sample's temperature making it comparable with real experiments situation. To ensure the constant temperature, the system was coupled to a thermostat. The thermostat exchange energy with the system to, among other things, prevent viscous heat to change the environment of the simulations.

A software called LAMMPS [5] was used to do the MD simulations in this project. LAMMPS stands for Large-scale Atomic/Molecular Massively Parallel Simulator and is designed to run efficiently on parallel computers. Its possibility to customize the simulation system with specific atom types, force fields and boundary conditions, made it easy to incorporate the colloidal system to be studied in this project. An example of the input files used in the software is shown in Appendix A for the initial configuration of the system running at a temperature of $T = 0.14$.

2.1.1 The system

The specific system used in this study was a binary colloidal system containing a 50:50 mixture with a total of $2N_A = 2N_B = N_{tot} = 2000$ particles of kind A and B. The diameters of the colloids are given as $d \equiv d_{AA} = 1.0$, $d_{AB} = 1.1d$ and $d_{BB} = 1.2d$, and their masses are given as $m = m_A = m_B = 1.0$. Hence the only difference between the two particles-kind is their diameter. The particles are arranged into a cubic sample of density $\rho = 0.675 m_A/d^3$. This density allowed no crystallization or phase separation occur in the temperature range under consideration [2].

For the force field, a potential called the Yukawa potential was used to model the interactions between the particles. The Yukawa potential is named after the physicist Hideki Yukawa and is a pairwise potential used to simulate the interactions in systems consisting of attracting or repelling particles. The potential is given by

$$u_{\alpha\beta}(r) = \epsilon_{\alpha\beta} d_{\alpha\beta} \frac{exp(-\kappa_{\alpha\beta}(r - d_{\alpha\beta}))}{r}, \qquad (2.2)$$

with $\alpha, \beta = A, B$. The energy parameters $\epsilon_{\alpha\beta}$ was set to $\epsilon \equiv \epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.4\epsilon$ and $\epsilon_{BB} = 2.0\epsilon$, and the screening parameters $\kappa_{\alpha\beta}$ was set equal with a value of $\kappa_{AA} = \kappa_{AB} = \kappa_{BB} = 6/d$. A plot of the potential with the specific values are shown in figure 2.1. From this plot and equation (2.2), one can see that the potential is strictly positive and that the particles contained in the system are always repelling each other.
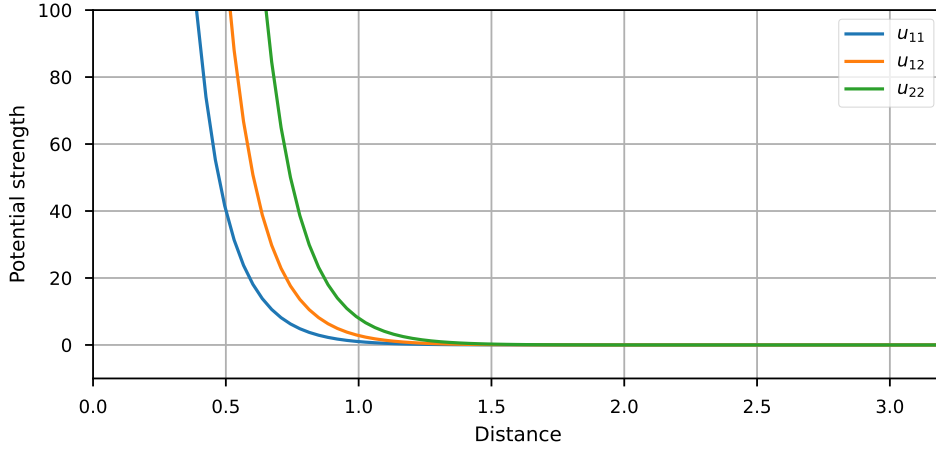
Figure 2.1: A plot of the specific Yukawa potential used in the simulations.

The potential is often referred to as the screened Coulomb potential as it can be reduced to the Coulomb potential simply by letting the screening parameters be zero. A predefined module for the Yukawa potential was used in the Lammps simulation software.

In this study, the so called Dissipative Particle Dynamics (DPD) thermostat was coupled to the system [6]. The DPD thermostat can be formulated by the equations of motion given as

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}, \qquad \dot{\vec{p}}_i = \vec{F}_i + \vec{F}_i^D + \vec{F}_i^R, \qquad (2.3)$$

where $\vec{r}_i$ is the position and $\vec{p}_i$ is the momentum of particle i. $\vec{F}_i$ is the conservative force given by the gradient of the Yukawa potential formulated in (2.2) for the particle i. The thermostat works by adding a dissipative force, $\vec{F}_i^D = \sum_{j\neq i} \vec{F}_{ij}^D$, and a random force, $\vec{F}_i^R = \sum_{j\neq i} \vec{F}_{ij}^R$, to the equation of motion.

The dissipative force is defined as

$$\vec{F}_{ij}^D = -\zeta\omega^d(r_{ij})(\hat{r}_{ij}\vec{v}_{ij})\hat{r}_{ij}, \qquad (2.4)$$

where $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$ is the relative velocity between particle i and j. $\hat{r}_{ij}$ is the unit vector in the interatomic axis $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. ω^D denotes a weight function which vanishes for $r \geqslant r_c = 1.25d$. The friction constant ζ was set to a value of $\zeta = 12$ to give the system microscopic properties close to that of pure Newtonian dynamics, $\zeta = 0$. This means that the term $\vec{F}^D$ describes the frictional forces in the system due to interactions between the particles and the use of relative velocities ensures that the momentum is locally conserved. The random force is given in a similar way by

$$\vec{F}_{ij}^R = \sigma\omega^R(r_{ij})\theta_{ij}\hat{r}_{ij}, \qquad (2.5)$$

with σ as the noise strength, which was set equal to $\sigma = \sqrt{2k_b T \zeta}$ by using the fluctuation-dissipation theorem. θ_{ij} is a Gaussian white noise variable and ω^R is another weight function simply given as $[\omega^R(r)]^2 = \omega^D(r)$. The described thermostat was implemented using an internal LAMMPS command, which can be seen in appendix A.

2.1.2 Radial distribution function

To evaluate the degree of order in each of the simulated states, the radial distribution function (RDF) was calculated. In molecular dynamics the radial distribution function, denoted as $g(r)$, is commonly evaluated by determining the number of particles in a distance between r and $r + dr$ from a reference particle. Dividing by the volume of the shell, a measure of the local density is given. By dividing again by the bulk density, ρ, the RDF is estimated and can be summarized by

$$g(r) = \frac{dn_r}{4\pi r^2 \rho dr}. \tag{2.6}$$

Here dn_r is the number of particles in a shell of thickness dr at a distance r from the reference particle.

The RDF can be interpreted as the probability of finding a particle at a given distance, r, from a reference particle, relative to that of a uniform distribution of particles. For an ordered homogeneous structure, like a crystal, the RDF will have distinct peaks at distances given by the lattice parameters. For a nonzero temperature the particles in a solid will vibrate, resulting in wider and less distinct peaks. At even higher temperatures and when the system has gone through a phase transition, the order of the system breaks down. The distinct peaks in the RDF will be largely reduced respect to the ones relative to the solid state, and, only a portion of the short-range order will remain. For the gaseous state, no distinct peaks will be present. Because of this high dependence on the structure order, the radial distribution function has an important part in the characterization of the different states simulated in this project. The RDF for the solid, liquid, and the glassy state was evaluated by using equation (2.6) for all 2000 colloids, and then averaging. The algorithm for calculating the radial distribution function utilized a k-dimensional tree to partition the spatial data of the system. Results from the self-written algorithm was tested and compared against results from the visualization software OVITO [7] to verify the validity of the codes.

2.1.3 Diffusion

Diffusivity is another property that can be used to differentiate between systems of crystal, liquid and glass. There are three different diffusion coefficients, Fick, collective and self-diffusion. Fick and collective refers to gradient of chemical potential and particles and are commonly connected to a flux. In this project, only equilibrium states were investigated and therefore the measured diffusion was

not gradient driven, but a so-called self-diffusion. Self-diffusion is the result of Brownian motion in the system and is highly connected to its temperature. By measuring the mean-squared displacement of the particles in the system, $\langle r^2(\tau) \rangle$, the self-diffusion coefficient, D, can be estimated using the Einstein relation:

$$\langle r^2(\tau) \rangle = 2dD\tau, \tag{2.7}$$

where d is the system dimension. Here d was set to three. By plotting the mean-squared displacement, the diffusion coefficient was estimated by linear regression of the data and equation (2.7). With an initial change of the temperature in a colloidal system, the particles will take some time to equilibrate with the change in conditions. This induces gradient driven diffusion of the particles, a time period referred to as the ballistic regime. To ensure that only self-diffusion of the system was measured, the regression line was calculated without including the first datapoints that clearly was not a part of the linear regime.

In a system with a crystal structure, the particles are locked in specific positions. This prevents a single particle to migrate, and no self-diffusion will be present, indicated by a self-diffusion coefficient equal to zero. The same conclusion applies to the glassy structure. However, for the liquid systems the particles are free to move. In addition to a higher temperature, this results in a net displacement for a single particle. The liquid systems will accordingly have a nonzero self-diffusion coefficient.

2.2   Initialization of the system

To initialize the system, the particles was placed into a body-centered cubic (bcc) configuration. The unit cell of the bcc structure holds two particle's kind, this makes it an inherent binary system if the two particles are differentiated. In this case one was given a diameter of d_{AA} and the other was given a diameter of d_{BB}. The lattice parameter was set to give the desired density and the resulting colloidal system is visualized in figure 2.2.
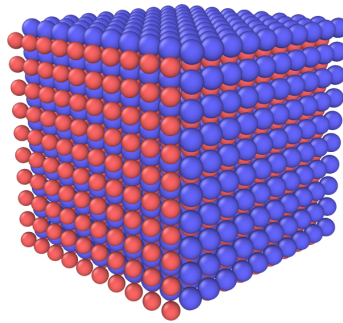

Figure 2.2: Visualization of the initial body-centered cubic configuration of the binary colloidal system

The Yukawa potential used in this study easily forms a disordered or glass-like state if the initial configuration of the particles is not well ordered, even without the usually required quenching process. The bcc structure was therefore a good choice for the initial configuration for this study because it gives a high ordering, which can be confirmed by the distinct peaks of the RDF given in figure 2.3.
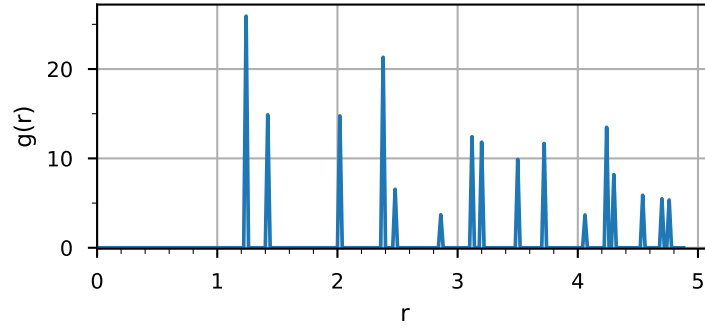

Figure 2.3: Radial distribution function of initial bcc structure.
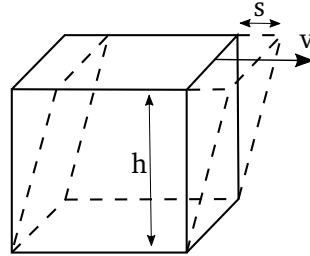
2.3 Shearing by simulation

2.3.1 Strain rate

Figure 2.4: Shear strain on a cubic box.

During a shearing simulation, the shear strain, γ, is defined as the deflection path, s, divided by the shear gap, h, see figure 2.4. This gives a dimensionless measure of the shearing and in the field of rheology this is often represented as a percentage. For a Controlled Shear Rate (CSR) experiment, the deflection speed, v, is constant and the simulation can be described through the shear rate,

$$\dot{\gamma} = \frac{\partial \gamma}{\partial t} = \frac{v}{h}.$$ (2.8)

The software tool used for the simulations had an embedded command for running a shearing experiment. In these simulations, a constant shear rate was set in the xy-direction on systems initiated with different temperatures. All systems

were initially equilibrated to the desired temperature by doing an adequate number of steps without any shearing, and, after that, the shearing protocol was applied. The diffusion coefficient was estimated once the system under shear reached the so called "steady-state" regime. During this stage the state variables are unchanging in time, but the system is still not at the equilibrium because it is under shear. In addition, the stresses in the system were investigated and plotted as a function of shear along all the simulation time. This was done by evaluating the xy-component of the stress tensor.

2.3.2 Shear stress

When shearing is applied to a colloidal system you will get opposing forces on two of its boundaries. This will induce stresses in the system. For molecular dynamics simulations of homogeneous systems, it is common to use the viral stress as a measure of the mechanical stress in the system. The volume averaged viral stress for the xy-direction, $\langle \sigma_{xy} \rangle$, is given by

$$\langle \sigma_{xy} \rangle = \frac{1}{L^3} \Big\langle \sum_i \Big[-m_i(u_{i,x} - \bar{u}_x)(u_{i,y} - \bar{u}_y) + \sum_{j>i} r_{ij,x} F_{ij,y} \Big] \Big\rangle, \qquad (2.9)$$

where L is the side of the cubic system, L^3 is the volume of the system and $u_{i,x}$ is the velocity of particle i in the x direction. $r_{ij,x}$ is the x-component of the distance between particle i and j, while $F_{ij,y}$ is the y-component of the interaction force between particle i and j. Because the shear stress is a collective quantity, it requires a lot of simulation to get an accurate averaging result, unlike the RDF and MSD measurements where each simulation gives an average over all the particles in the system. When the shear stresses was measured in this study, an internal command for calculating the stresses was used in the software and an average over ten simulations was calculated. In addition, a simple moving average was applied by letting each data-point be an average of its ten neighbouring data-points. This removed noise from the stress-strain curve.

Chapter 3

Results And Discussion

The solid state of the binary colloidal system was obtained by heating up the initial configuration described in section 2.2 to a temperature of $T = 0.14$, and then let it equilibrate for 500k steps. The radial distribution function for both the type-A and type-B particles of this state is visualized as the blue lines in figure 3.1. The plot shows several distinct peaks corresponding to the same location as the peaks shown in the RDF for the initial bcc-structure, figure 2.3. A high order in both short range and long range is clearly visible. The difference is that the peaks are now wider, which indicate that the particles representing each peak are not frozen but vibrate around a fixed position. This is expected for a heated solid when the energy is not enough to overcome the interaction potentials. To further confirm the fact that the particles only vibrate in a fixed structure, one can look at the mean squared displacement of the system showed as the blue line in figure 2.7. No net movement of the particles was detected for the given state and together with the high structural order, the lack of self-diffusion in the system is enough to characterize this system as a solid state.
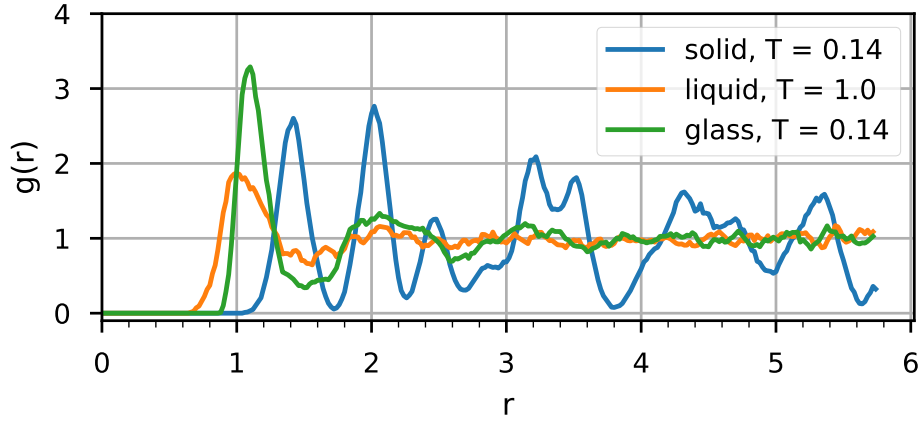
(a) Type-A particles
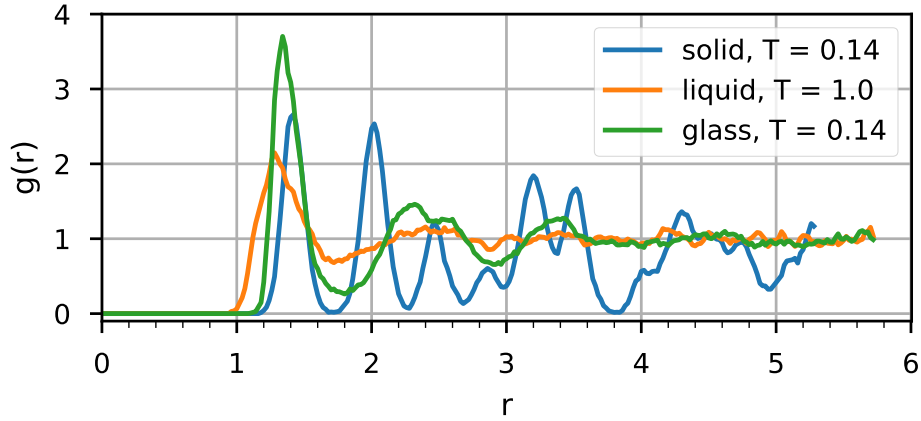
(b) Type-B particles

Figure 3.1: Radial distribution function for all the three different simulated states of the binary colloidal system. All states was equilibrated for 500k steps at their given temperatures.

The next state that was characterized occurred when the solid state at $T = 0.14$ was heated up further. At $T = 1.0$ the system was equilibrated for 500k steps, giving the new state. The radial distribution function for both kind of particles in this system is visualized as the orange lines in figure 3.1. In this system the distinct structure that previously was present, has dissolved. The only obvious peaks occur at the radius r_{AA} for the type-A particles and r_{BB} for the type-B particles, but no long-range order is evident. This is typical for a liquid state as the energy of the particles are high enough to make them flow in the system. The peaks given by the colloidal radii shows that the particles are colliding into each other with high frequency. The freedom of the particles is clearly visualized in the mean squared

displacement showed by the orange line in figure 3.2, indicating that self-diffusion is present in the system. This concludes a liquefied state of the binary colloidal system.
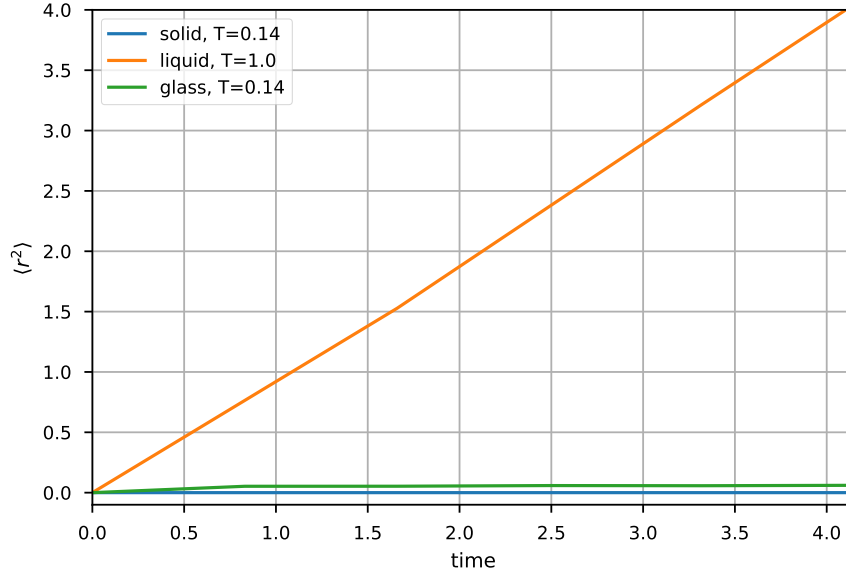

Figure 3.2: Mean squared displacement for type-A particles in all three different simulated states of the binary colloidal system. Type-B particles is not plotted as they would give the exact same dynamics.

At last, the system with a temperature of $T = 1.0$ was quenched by suddenly changing the temperature back to $T = 0.14$ which resulted in a new state. The radial distribution for both kind of particles in this new state is visualized as green lines in figure 2.6. Here one can see a distribution similar to the liquefied state, as only a short-range order of the structure is detectable. The long-range order is not present, something that should indicate that the system has not settled into a distinct structure, and one could guess that the particles are not fixed around a given position, but flowing like in the liquid state. The plot of the mean squared displacement however tells a different story, as can be seen by the green line in figure 3.2. Like the solid state, the particles do not have a net movement, concluding that no self-diffusion is present. Only a small increase of $\langle r^2 \rangle$ at the start of the measurement can be seen. This is likely due to presence of residual kinetic energy in the system. The residual energy is a result of the rapid cool-down of the liquid, but as can be seen, it dissipates quickly. Low order in the structure and no consistent increase in displacement of the particles in this state, indicates that the particles are frozen into a high energy state similar to the structure of a liquid. This is a glassy state previously described in the introduction. These results clarifies that this amorphous solid of the binary colloidal system really have

characteristics from both a solid and a liquid state.

The further investigation of the colloidal system was done by measuring diffusion for different temperatures, namely from $T = 0.1$ to $T = 1.0$. This was done using the linear regression of the mean squared displacement. Figure 3.3 shows the mean squared displacement measurements for both type-A and type-B particles for the colloidal system at the particular temperature of $T = 0.2$. Note that when calculating the coefficients, data from 400k timesteps was used to avoid the inherent randomness in self-diffusion to impact the results. However, the figure illustrates the ballistic regime taking place in the beginning of the simulations. This data was avoided in the calculation of the coefficients and the final self-diffusion coefficients was taken by the slope of the linear regime shown in the graph by dotted lines.
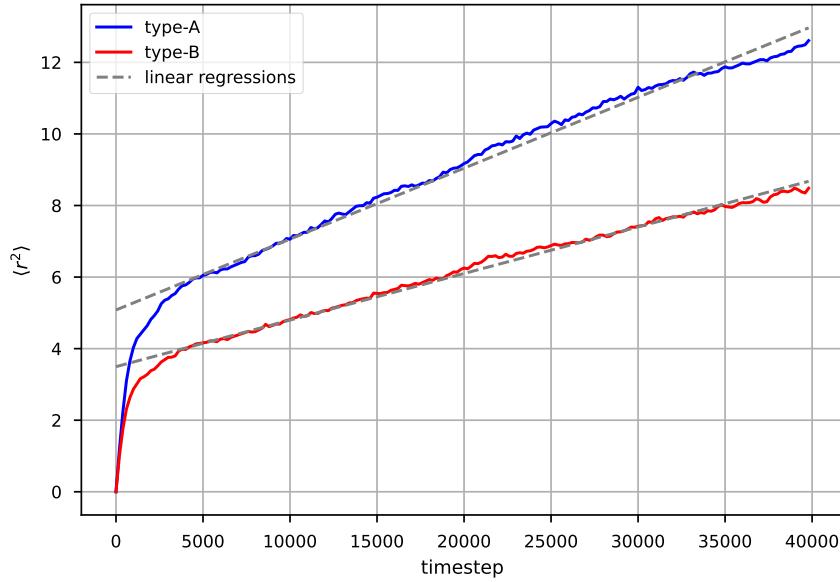

Figure 3.3: Mean squared displacement for type-A and type-B particles of the binary colloidal system at a temperature of $T = 0.2$. The dashed lines represent a linear regression where data from the ballistic zone was not included.

All the diffusion coefficients that were calculated using equation (2.7) for both type-A and type-B particles are plotted against inverse temperature and visualized in figure 3.4. The results obtain by J Zausch et al [2] for type-B particles are also presented in the figure (red dashed line). As expected, the diffusion of the system decreases exponentially down to zero as the temperature is lowered towards the critical temperature of $T = 0.14$ and the system transitions into the solid state and/or glassy state. At lower temperatures, the diffusion is practically zero. The self-diffusion coefficients calculated for the type-B particles coincide with the res-
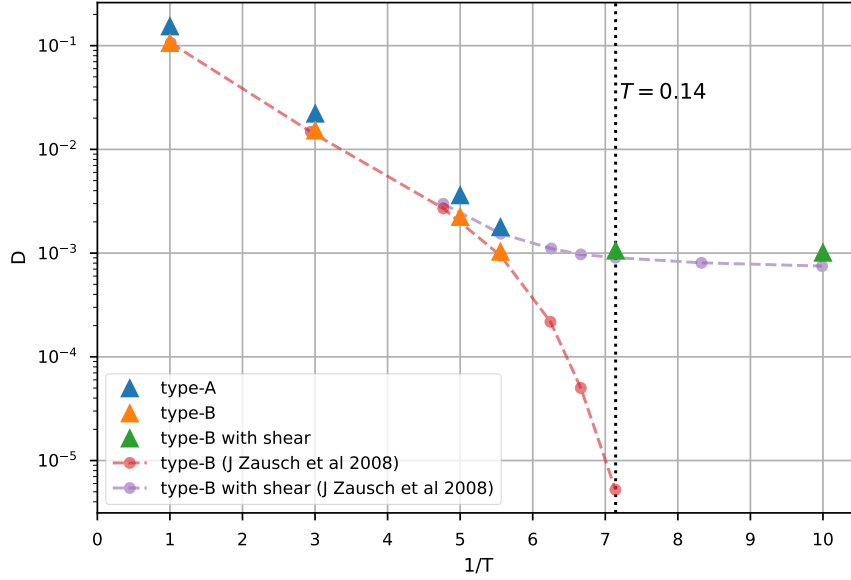
Figure 3.4: Self-diffusion coefficients for both type-A and type-B particles simulated at different temperatures. In addition, the self-diffusion coefficient for type-B was measured when a sharing was applied at low temperatures. The coefficients are compared to the results obtained by J Zausch et al [2], visualized by the red and purple lines.

ults given by J Zausch et al. Both the type-A and type-B particles show the exact same dynamics, but it can be noted that type-A particles consistently measure a higher diffusion constant. The higher rate of diffusion can simply be explained by the lower radius of the type-A particles. This gives them a higher grade of mobility in a dense volume of particles, where the bigger type-B particles will have a higher chance of colliding into other particles when moving in a given direction.

Next, shearing of the glassy state system was tested and analyzed. With a shear rate of $\dot{\gamma} = 3 \times 10^{-3}$, the diffusion coefficient for type-B particles was plotted in fig 3.4 for temperatures below the transition temperature. As showed earlier, the equilibrated glassy state should not have any consistent increase of mean squared displacement and thus a zero value for the diffusion coefficient. However, when a shearing is present in the system, a nonzero diffusion coefficient is calculated with a value of $D \approx 10^{-3}$ for the given shear rate $\dot{\gamma}$. This is an interesting result and shows that the glassy state simulated by the binary colloidal system has non-Newtonian properties. The shear thinning behavior observed here, means that the stresses induced by the shearing lowers the viscosity of the glassy state, allowing for self-diffusion of particles.

It is obvious that shearing can change the dynamics of the system in noticeable ways. To understand the effect from shearing better, the relationship

between stresses in the system and the applied shear was established by plotting the stresses $\langle \sigma_{xy} \rangle$ against strain $\gamma = \dot{\gamma} t$. Figure 3.5 shows this stress-strain curve for the colloidal system initially equilibrated at a temperature of $T = 0.14$ and sheared with a strain rate of $\dot{\gamma} = 3 \times 10^{-3}$. Ten simulations were run, all with slightly different equilibration time to differ the initial configuration. The blue line shows the mean value and the grey area illustrates the associated standard deviation. The resulting stress-strain relation are compared to results from equivalent simulations done by J Zausch et al [2], visualized by red dots. These results are however obtained by an average from 250 individual simulation runs.
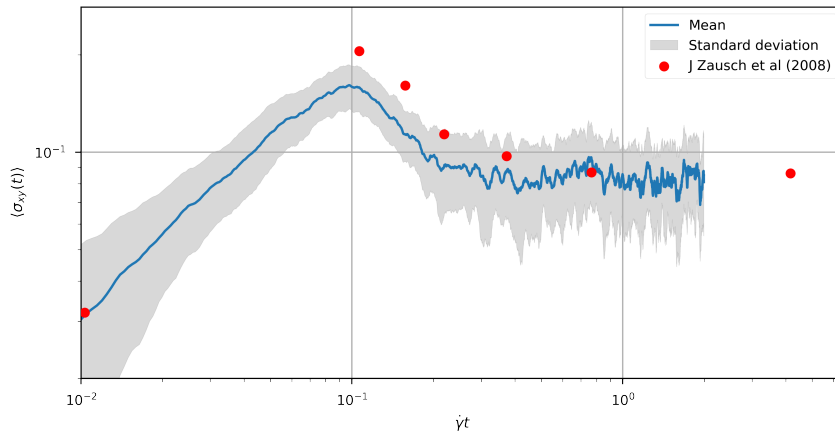

Figure 3.5: The relationship between stresses in the system and the applied stain plotted in a log-log scale. A shear rate of $\dot{\gamma} = 3 \times 10^{-3}$ was applied at an equilibrated glassy system with a temperature of $T = 0.14$. Blue line represent the mean of ten simulations and the grey area illustrates its standard deviation. The curve is compared to the equivalent results obtained by J Zausch et al [2], visualized by the red dots.

As one can see, the stresses increase linearly for small strain values. This region is called the elastic zone and here the shearing is reversible. With an increasing strain the stresses will eventually reach a peak value. This is where the system breaks down and the stresses start to decrease until it reaches a lower steady state level. The overshoot of the stresses is a well-known phenomenon and can be measured in many real-world materials today.

One thing to notice is that the peak value for the results from this study is lower than what was obtained by the comparable results. The reason for this mismatch is yet to be discovered, but as one can see, the stress-strain curve looks to be correct for the low strain values. It also looks to equilibrate at the correct steady-state level for high strain values. The peak value for a specific system is shown to be dependant of the initial configuration of the particles. Because of this, the mismatch is expected to be an averaging problem. It is reason to believe that a slight difference in equilibration time is not enough to differ the initial configuration

enough to get credible calculations. In addition to including more simulations in the averaging, the results could be improved by using different random seeds in the equilibration process for the initialization configurations used in the shearing experiments. This way, you would be sure that the systems sheared upon had not fallen into similar energy states. This is something that should be investigated deeper in a later study with more focus on the stress-strain relation.

Chapter 4

Conclusion

Simulations of the solid, liquid and glassy state of the binary colloidal system showed expected results for both the radial distribution functions and the evolution of the mean squared displacements. The analysis showed that these two rheological tools were enough to differentiate between the simulated states and to characterize them. This also clarified how the glassy state could relate to both the solid and the liquid states. The calculated self-diffusion coefficients illustrated how the diffusive behavior of the solid state was related to the temperature of the system, which also coincided with results from previous work. In addition, a non-zero self-diffusion coefficient was found for the glassy system when shearing was applied. This proved non-Newtonian behaviour for the glassy state where the sharing forces lowered the viscosity of the system. Shear thinning behaviour like this is important and should be investigated further using the Yukawa potential.

The stress-strain relation showed the expected overshoot when the system broke down, but did not coincide with comparable results from earlier papers. This mismatch was believed be a result of poor averaging of simulations with too small differences in the initial configurations. A further investigation of this relation and the shear thinning behaviours of the colloidal system in this study is to be studied deeper in a later study as it has big importance in real-world applications.

Bibliography

[1] T. G. Mezger, *Applied Rheology: With Joe Flow on Rheology Road*. Austria: Anton Paar GmbH, 2015.

[2] J. Zausch, J. Horbach, M. Laurati, S. U. Egelhaaf, J. M. Brader, T. Voigtmann and M. Fuchs, 'From equilibrium to steady state: The transient dynamics of colloidal liquids under shear,' *Journal of Physics: Condensed Matter*, vol. 20, no. 40, p. 404 210, Sep. 2008. DOI: `10.1088/0953-8984/20/40/404210`. [Online]. Available: `https://doi.org/10.1088/0953-8984/20/40/404210`.

[3] D. Bonn, M. M. Denn, L. Berthier, T. Divoux and S. Manneville, 'Yield stress materials in soft condensed matter,' *Rev. Mod. Phys.*, vol. 89, p. 035 005, 3 Aug. 2017. DOI: `10.1103/RevModPhys.89.035005`. [Online]. Available: `https://link.aps.org/doi/10.1103/RevModPhys.89.035005`.

[4] T. J. Vlugt, J. P. van der Eerden, M. Dijkstra, B. Smit and D. Frenkel, *Introduction to Molecular Simulation and Statistical Thermodynamics*. Delft, The Netherlands, 2008, ISBN: 978-90-9024432-7. [Online]. Available: `http://www.phys.uu.nl/%E2%88%BCvlugt/imsst`.

[5] A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott and S. J. Plimpton, 'LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales,' *Comp. Phys. Comm.*, vol. 271, p. 108 171, 2022. DOI: `10.1016/j.cpc.2021.108171`.

[6] T. Soddemann, B. Dünweg and K. Kremer, 'Dissipative particle dynamics: A useful thermostat for equilibrium and nonequilibrium molecular dynamics simulations,' *Phys. Rev. E*, vol. 68, p. 046 702, 4 Oct. 2003. DOI: `10.1103/PhysRevE.68.046702`. [Online]. Available: `https://link.aps.org/doi/10.1103/PhysRevE.68.046702`.

[7] A. Stukowski, 'Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool,' *MODELLING AND SIMULATION IN MATERIALS SCIENCE AND ENGINEERING*, vol. 18, no. 1, Jan 2010, ISSN: 0965-0393. DOI: `{10.1088/0965-0393/18/1/015012}`.

Appendix A

Lammps Input File

The input file described in code listing A.1 was run using the LAMMPS software to simulate the binary colloidal system described in this project. The initial.config file was either the initial configuration described in 2.2 or one of the output files from an earlier simulation.

Code listing A.1: Lammps input file used for simulations of the binary colloidal system. Temperature was set to $T = 0.14$

```
units           lj        # Use Lennard-Jones units
atom_style      sphere    # Use Colloids
dimension       3

# Import initial configuration or previous configuration:
read_data       initial.config

# Define system parameters:
set             type 1 mass 1.0
set             type 2 mass 1.0

set             type 1 diameter 1.0
set             type 2 diameter 1.2

variable        t equal step

# Multi neighbor and comm for efficiency

neighbor        1 multi
neigh_modify    delay 0
comm_modify     mode multi
comm_modify     vel yes

# Colloid potential (Yukawa) and thermostat
pair_style      hybrid/overlay yukawa 6.0 2.5 dpd/tstat 0.14 &
                0.14 1.25 34387
# The hybrid command allows to combine the yukawa potential
# and the dpd thermostat for the temperature.

pair_coeff      1 1  yukawa  403.4588  3.4784   # Yukawa parameters for type 1 1
pair_coeff      1 2  yukawa 1132.0466  3.3253   # Yukawa parameters for type 1 2
pair_coeff      2 2  yukawa 3214.6338  3.1984   # Yukawa parameters for type 2 2
```

```
# dpd parameters:
pair_coeff      1 1  dpd/tstat 12 1.25
pair_coeff      1 2  dpd/tstat 12 1.25
pair_coeff      2 2  dpd/tstat 12 1.25


change_box      all triclinic


fix             1 all nve

# Apply shearing in the xy-direction:
#fix                        2 all deform 1 xy erate 0.003

# Simulate and output files:
dump            1 all custom 100 dump.colloid_014K  id type xu yu zu


thermo_style    multi
thermo_style    custom step time temp etotal press vol pxx pxy xy
thermo          20


#thermo_style   custom time temp pxx pyy pzz pxy pxz pyz
#thermo         100


timestep        0.0083


run             100000 every 10000 'write_data data_014K_bcc_glass_$t.colloid'
```