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Characterization of solid, liquid, and glassy state using molecular dynamics simulation

Bachelor's thesis in Physics
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DEPARTMENT OF PHYSICS

TFY4561 PROJECT

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Author:

Benjamin Trønnes

Supervisor:

Raffaella Cabriolu

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Abstract

Glassy and amorphous materials have existed for a large part of human history yet are not fully understood. However, glass and glass transitions are extremely important for many real-world applications. In this report, a binary colloidal system forming a glass under certain conditions has been modeled using the Yukawa potential and the molecular dynamics simulator, LAMMPS. The implemented system was prepared according to a standard protocol to characterize its solid, liquid, and glassy state. To distinguish the three states, diffusion and structure of them have been obtained by simulations and it has been found that they are in good agreement with previous simulation studies.

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Chapter 1

Introduction

Glass is one of the oldest materials in human history that is still used on a large scale today. It's widely used in construction, science, and arts, but despite its long history and many uses it's a quite complex material we don't fully understand. Even though a lot of research has been done on it with one definition of glassy materials being set in 1962 [1]. There's still a lot that's unknown or uncertain. There are some important differences between glassy, solids, and liquid states. Solids are characterized by a short and long order. The particles in a solid state are vibrating around their equilibrium positions and in this state, the system is occupying an energy minimum. This ordered and rigid structure is a characterizing feature of the solid state with the only movement being the vibration of the particles that's linked to the temperature. In general, a crystal state persists up to a certain temperature range.

Increasing the temperature of the solid over the so-called melting temperature or T_m the particles can reach a high enough energy that allows the particles to move over their equilibrium positions, at this point the system assumes a liquid state. In the liquid state, the system will be generally disordered with only a short-range order. In this situation, the particles can move more freely and their diffusion around the samples becomes important. In an equilibrium state, this diffusion is only driven by random motion, also known as Brownian motion, and it is called the self-diffusion. This self-diffusion phenomenon is negligible in perfect crystals or solids. The liquid state persists at temperatures higher than T_m .

Certain systems exhibit the glassy state when they are cooled down very quickly from the liquid state to a temperature $T_g < T_m$ that is also called "glass-transition temperature". In those materials, the cooling quench is so fast that the particles are not able to settle into the order states or to crystallize. This state is known as a glassy or amorphous state. In the glassy state, the particles do not have enough energy to diffuse and the ordering of the previous liquid state persists. The quenching speed is important in determining the properties of the glass, and if the system is cooled down slowly enough it will crystallize instead of becoming a glass[2]. A visual difference between crystal and glass on the atomic scale is shown in figure 1.1.

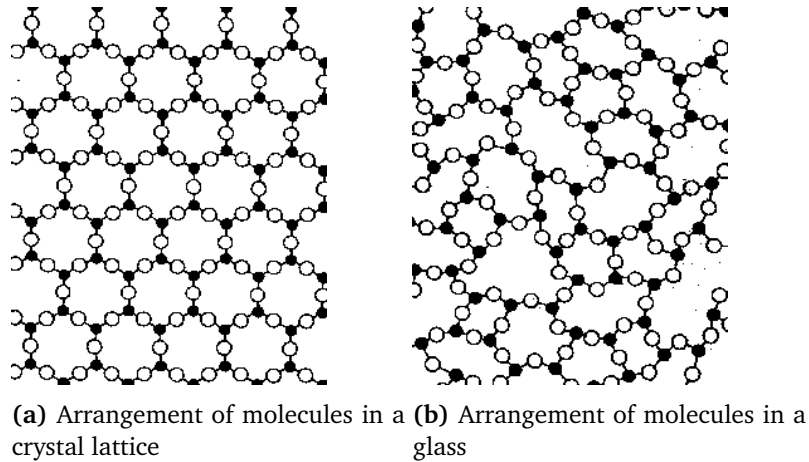


Figure 1.1: Visualization of the difference between a crystal and an amorphous solid [2]

A colloid is a mixture consisting of particles and a dispersing medium with the size of the particles being defined by the type of colloid. If the size of the particles in the mixture is less than 4 nm it's considered a solution, if they are larger than 1000 nm it's considered a suspension, and if they're between the two it's a colloid. In addition to the glassy state, certain colloidal systems assume also a non-Newtonian behavior. A non-Newtonian material changes viscosity in response to external stress. A common example of such a system is the mixture of water and cornstarch. It behaves like a normal fluid under certain deformations, but under certain stress, it thickens making it possible to walk on it as on a solid.

In this project, a binary colloidal system was modeled with a Yukawa potential and simulated with a molecular dynamics engine known as LAMMPS. I have created an initial configuration of the system with a bcc crystal structure consisting of two particles kind with different sizes. This initial configuration was equilibrated at Temperatures typical of its solid state. Afterward, the system was heated up to obtain a liquid and then cooled down in separate steps to obtain a glassy state. These three states were studied using different methods allowing characterization of the different states. The diffusivity for the three states and at different temperatures was obtained and compared to the values found by J. Horbach et al. [3].

Chapter 2

Methods

2.1 Molecular Dynamics

To simulate the evolution and properties of a system of particles a Molecular Dynamics (MD) simulation program was used. The MD technique can be applied to study samples containing up to billions of particles [4]. A molecular dynamics algorithm works by taking the positions and velocities of the particles and calculating the new positions and velocities from Newton's laws of motion [5]:

$$F_i = m_i \times \frac{d\vec{v}_i}{dt} \quad (2.1)$$

$$\vec{v}_i = \frac{d\vec{r}_i}{dt} \quad (2.2)$$

so that the velocities and positions of the particles are updated using numerical integration over several time steps. Here F_i is the force on particle i . Whilst m_i is the mass, v_i is the velocity, and r_i is the position of particle i . The force on each particle is found by the gradient of the interaction potential between the particles, the velocities are found by integrating the forces, and finally, the positions are found by the velocities. In conclusion, positions and velocities are updated based on the potential that is describing at every time step the interaction between the particles. The MD technique can provide different values and properties from the system.

When working with numerical simulations or calculations it's common to use dimensionless variables. In this project, the Lennard-Jones units will be used meaning that the temperature used in this project is the reduced temperature defined as:

$$T^* = \frac{k_B T}{\epsilon} \quad (2.3)$$

Here T^* is the reduced temperature used in this project while k_B is the Boltzmann constant. The variable T is the real temperature measured in Kelvin and ϵ is the energy parameter of the potential. In this context, when the temperature in the simulation is the reduced temperature.

The system was modeled to be in the Canonical ensemble. This means that the number of particles N , the volume of the system V , and the temperature of the system T are conserved for the entire simulation which is why it is sometimes referred to as a NVT simulation. Though it could have been possible to use the Micro Canonical ensemble or NVE simulation, using the NVT allows us to control the temperature much like one would in a physical experiment. Thus it's more appropriate for this project. To have a constant temperature the system is coupled to a thermostat. The thermostat exchanges heat with the system allowing a change of internal energy within the system and changing the environment of the system.

The particular MD simulation software used in this project was LAMMPS [6], or Large-scale Atomic/Molecular Massively Parallel Simulator. LAMMPS works well for large-scale molecular dynamics simulations as it's capable of running parallel simulations on computers with different hardware or operating systems whilst still getting the same results. It's also capable of using customized setups of atom styles, potentials and external temperatures or forces. This makes it well suited for the study of our binary colloidal system.

2.1.1 System parameters

The system we are studying is a binary colloidal system consisting of two types of particles with diameters $d \equiv d_{AA} = 1.0$ and $d_{BB} = 1.2d$ respectively. The system consists of a 50:50 mixture of these particles A and B so that the total number of particles is $2N_A = 2N_B = 1600$. The initial system was built with a density of $0.675m_A/d_{AA}^3$ with the two particle types having mass equal unity, i.e. $m = m_a = m_b = 1.0$.

The interaction between particles was modeled with the Yukawa potential. This potential can be used for systems with attractive or repelling particles and is given by [3]

$$u_{ab} = \epsilon_{ab} d_{ab} \frac{\exp(-\kappa_{ab}(r - d_{ab}))}{r} \quad (2.4)$$

where we use $\alpha, \beta = A, B$. The energy parameters are then set to be $\epsilon \equiv \epsilon_{AA} = 1.0$, $\epsilon_{BB} = 2.0\epsilon$ and $\epsilon_{AB} = 1.4\epsilon$, and the screening parameter used is $\kappa_{AA} = \kappa_{BB} = \kappa_{AB} = 6/d$. This potential is always repulsive and it is sometimes called the screened Coulomb potential because when the screening parameter is set to 0 the formula reduces to the Coulomb potential.

When the potential is implemented in LAMMPS the expression used for the Yukawa pair style is instead,

$$E = A \frac{\exp(-\kappa r)}{r} \quad (2.5)$$

where A is an energy-distance parameter. If these two expressions are expected to give the same values then A can be calculated as

$$A = \epsilon_{ab} d_{ab} \exp(\kappa_{ab} d_{ab}) \quad (2.6)$$

The calculated parameters from this equation as well as the cut-off distances are seen within the code excerpt in the appendix A.1

To control the temperature of the system a thermostat that uses the Dissipative Particle Dynamics (DPD) was chosen. The DPD thermostat can be expressed by the equation:

$$\dot{\vec{r}}_i = \frac{\vec{P}_i}{m_i} = \vec{F}_i + \vec{F}_i^D + \vec{F}_i^R \quad (2.7)$$

where \vec{F}_i is the gradient of the Yukawa potential giving a conservative force, while the dissipative force $\vec{F}_i^D = \sum_{i \neq j} F_{ij}^D$ and the random force $\vec{F}_i^R = \sum_{i \neq j} F_{ij}^R$ are introduced by the DPD to function as a thermostat. The dissipative force is given by

$$F_{ij}^D = -\zeta \omega^2(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \vec{\mathbf{v}}_{ij})\hat{\mathbf{r}}_{ij} \quad (2.8)$$

where $\hat{\mathbf{r}}_{ij}$ is the unit vector of $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and r_{ij} is the distance between the particles i and j . $\vec{\mathbf{v}}_{ij} = \vec{\mathbf{v}}_i - \vec{\mathbf{v}}_j$ is the difference in velocity between the particles. The function $\omega(r_{ij}) = \sqrt{1 - r_{ij}/r_c}$ is a weight function that vanishes whenever the distance between the particle reaches the critical distance $r_c = 1.25d$. And $\zeta = 12$ is the friction coefficient. Its value is set so that the microscopic properties are close to those of purely Newtonian dynamics with $\zeta = 0$ [3]. The dissipative force \vec{F}^D then describes a frictional force between particles. Similarly, the random force is given by

$$F_{ij}^R = \sigma \omega(r)\theta_{ij}\hat{\mathbf{r}}_{ij} \quad (2.9)$$

Here $\sigma = \sqrt{2k_B T \zeta}$ is the noise strength mainly responsible for the change of internal energy in the system as T is the temperature of the thermostat. θ_{ij} is a Gaussian white noise variable and ω is the same weight function as in the dissipative force equation. This thermostat is implemented through an internal LAMMPS command as shown in the code excerpt A.1

2.1.2 Diffusivity

One of the ways to characterize the different states of a material is the diffusivity. Quantitatively, the diffusivity is studied using three types of process; Flick, Collective, and Self-Diffusion. Flick and Collective refer to the gradients of chemical potential and particles which is commonly connected to the flux. However, as only equilibrium states are being considered in this project only the self-diffusion is used. Self-diffusion is caused by the Brownian motion of particles in the system and is thus linked to the temperature of the system. The self-diffusivity can be found using the Mean-squared-displacement (MSD) given by,

$$MSD = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = \frac{1}{N} \sum_{i=1}^N |\mathbf{r}^{(i)}(t) - \mathbf{r}^{(i)}(0)|^2 \quad (2.10)$$

Here $\mathbf{r}^{(i)}(t)$ is the position of particle i at time t , $\mathbf{r}^{(i)}(0)$ is the position of particle i at the start of the run and N is the total number of particles. Beyond just being a useful way of measuring the movement of particles within the system it's also possible to use it to calculate the self-diffusivity of the system. This is estimated using the Einstein relations:

$$MSD = 2nDt \quad (2.11)$$

where n is the number of dimensions, t is the time and D is the self-diffusivity. Due to the linear form of this equation, it's possible to approximate the self-diffusivity using a linear regression of the MSD and equation 2.11. For the linear regression the first bulk of time steps is ignored due to the rapid growth there clearly not being part of the linear regime. For this project it will be important as it can be used as a measure to show when the particles stop moving or when they "freeze". This is because for solids or crystals there will be no possible movement and thus no self-diffusivity, this is also what we see in a glassy state. Whilst for liquid states there will always be some movement and in turn a non-zero self-diffusivity.

2.1.3 Radial Distribution function

A different way to measure the level of order within a system is through the use of the Radial Distribution function (RDF). The RDF calculates the amount of particles around a particle in a spherical shell of thickness dr and distance r from the particle. By dividing the found particles by the volume of the shell and the bulk density ρ the RDF is found as:

$$g(r) = \frac{n_r}{4\pi r^2 \rho dr} \quad (2.12)$$

Here n_r is the amount of particles in the shell with thickness dr at a distance r from the particle.

The RDF can be considered to be the probability of finding a particle in a distance r around a reference particle. For ordered systems such as crystals the RDF will then give distinct peaks relative to the lattice parameter as seen in 2.2. Since for all nonzero temperatures there will be some vibrations in the particles the peak start to widen and become less distinct as the temperature increases. When the system reaches sufficiently high temperatures and goes through a phase transition the order breaks down and only a portion of the short range peaks remain as the RDF becomes more continuous. Should the system reach a gaseous phase there will be no distinct peaks at all. Due to it's dependence on the structure's order the RDF is well suited to characterize the different states of the system. The RDF is computed both through an internal function in LAMMPS and through the use of OVITO [7]. In both programs the RDF is calculated for each pair of particle types A-A, A-B, and B-B separately. For LAMMPS the RDF is calculated both at the start of the equilibration and at the end, whilst OVITO calculates the RDF using the positional data gathered at equilibrium.

2.2 Initialization of system

The system is initialized by creating a body centered cubic (bcc) system consisting of the two different particles A and B. This system is an inherent binary system as the two particles are differentiated by their size, with particle A having the diameter d_{AA} and particle B having the diameter d_{BB} . The lattice parameter was chosen to achieve the wanted density giving the resulting colloidal system in fig 2.1.

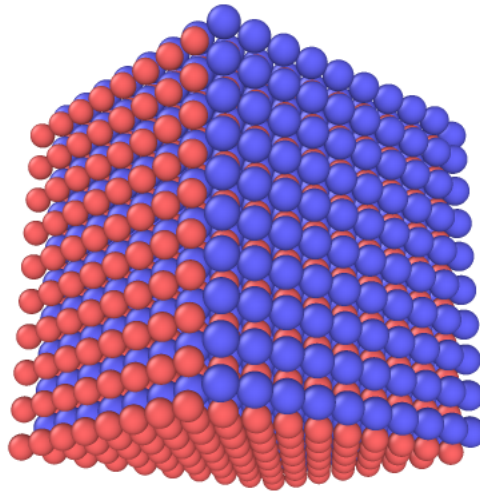


Figure 2.1: Initial configuration of the system in the form of a body centered cubic crystal

The high ordering of the bcc system makes it well suited for this experiment as the yukawa potential is capable of making a disordered or glass like structure even without the quenching step if the initial configuration of the system isn't well ordered. The high order of the bcc crystal can be confirmed by the RDF plot in figure 2.2

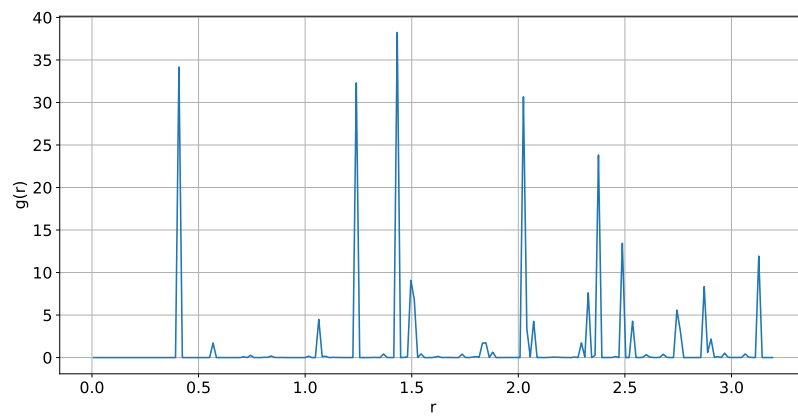
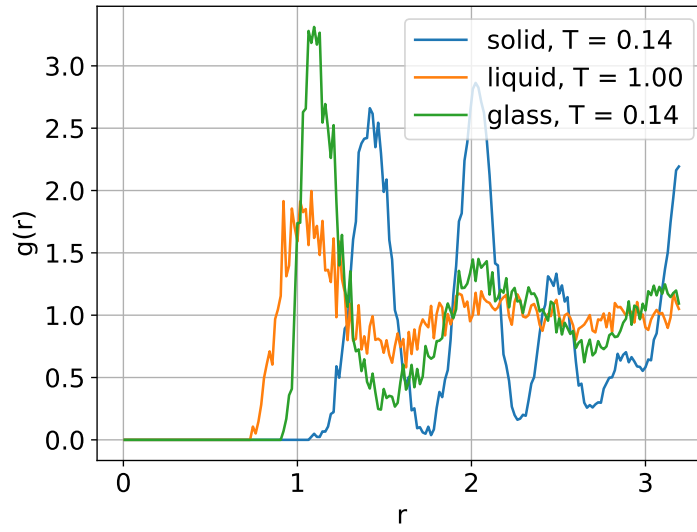


Figure 2.2: Radial Distribution of the initial crystal structure

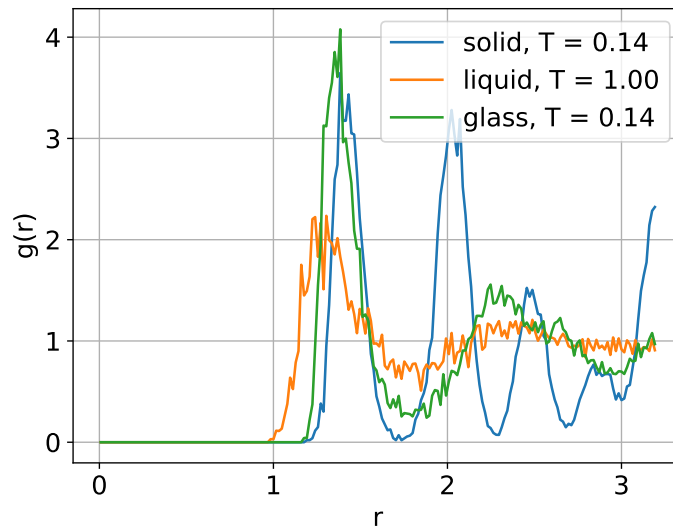
Chapter 3

Results And Discussion

First, the initial configuration was heated to a temperature of $T = 0.14$ to get a solid state. We wanted to follow the article specification of the system. However, 1600 particles in a bcc configuration inside a cubic cell and with the described density made it difficult to study the equilibrium solid configuration because not all the positions could be occupied by a particle. To have a realistic fully occupied solid structure we consider several particles equal to $N = 2N_A = 2N_B = 2000$. The blue lines in figure 3.1 show the radial distributions in the solid for particles A, (a) sub-figure, and particles B, (b) sub-figure. When compared with figure 2.2 it's clear that in the solid state, the particles are still bound by the potential but they're able to vibrate giving the radial distribution wider and lower peaks around the same positions as in the bcc crystal. Looking at the MSD in figure 3.2 it's also clear that there is negligible movement of the particles as expected for a solid material.



(a) RDF for particle A



(b) RDF for particle B

Figure 3.1: Radial Distribution functions for the A-A pairs and B-B pairs at temperatures $T = 1.00$ and $T = 0.14$

The 1600 particle configuration was then heated to the temperature $T = 1.00$ at which a liquid state was expected. I have built the RDF for this temperature that is represented by the orange lines in the figure 3.1. The radial distribution for particles A and B are plotted as the orange lines in figure 3.1. With the only peaks present in the plots around the diameters d_{AA} and d_{BB} of the particles in

their respective plots. The graphs show a lack of any order in the long range that is typical for the liquid state. The measure of movement for the particles can be studied with the mean square displacement of the particles shown by the orange line in figure 3.2. The orange line shows a very high diffusion in the system as expected for the liquid state.

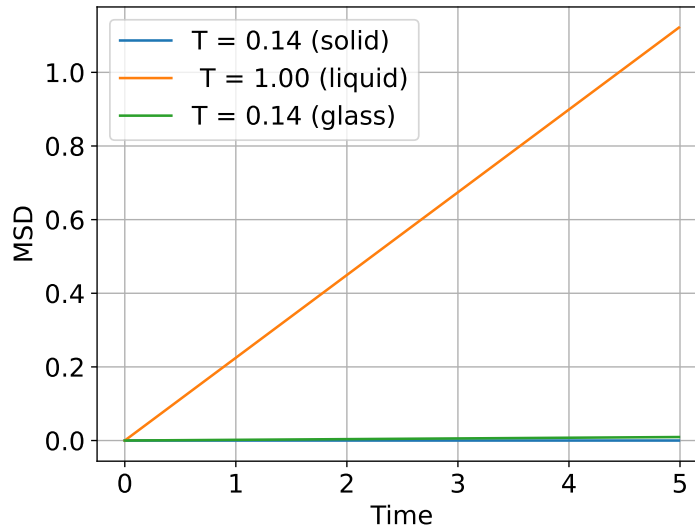


Figure 3.2: The linear regression of the mean square displacement for type A particles in the three characterized states of the system. Particles of type B would have the same dynamics and are therefore not plotted.

After this, the system was quenched from the temperature $T = 1.00$ down to $T = 0.14$ allowing a new state to form. The radial distribution is visualized by the green lines in figure 3.1. Much like in the liquid state, there's only a distinct peak in the short range and no clear order in the long range. Thus one could assume that the particles haven't settled into any specific structure and that they're still moving around. But by looking at the self-diffusivity it's clear that this isn't necessarily the case. The self-diffusivity is shown by the green line in figure 3.2. Indeed, diffusion of the system is close to zero indicating that there is little to no movement of particles. This is typical of a glassy state. The glassy state has no long-range order like the liquid state, but it also has low self-diffusivity like the solid state.

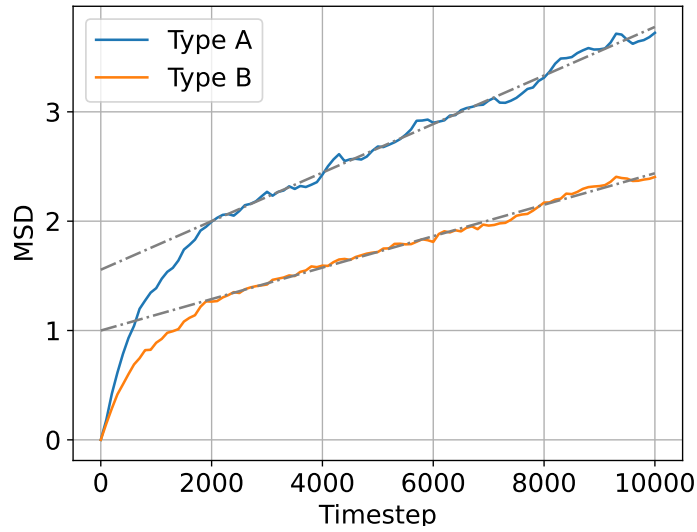


Figure 3.3: The mean squared displacement of both particle types in the binary colloidal system at temperature $T = 0.28$. The linear regression is displayed as the gray dashed lines.

Once the general characterization of the different states had been done for the liquid and glassy states the self-diffusion coefficients were calculated for different temperatures. These were reached by cooling down the liquid state from $T = 1.00$ to several temperatures. At each temperature, the MSD was calculated, and from it, the self-diffusion coefficients were obtained using the equation 2.11. An example of one of these MSD measurements along with the linear regression is plotted in figure 3.3. The found coefficients are plotted against the inverse temperature in figure 3.4 along the equilibrium coefficients found by J. Horbach et al. [3].

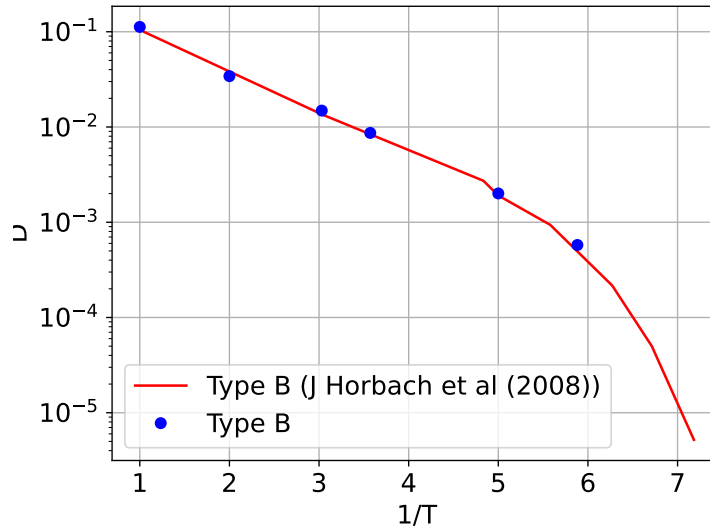


Figure 3.4: Self-diffusion coefficients of type B particles for different temperatures. The blue circles are values measured by the MSD and Einstein relation. Whilst the red line are the values found by J. Horbach et al. [3]

The values found from the simulations are quite close to those found by J. Horbach et al. [3]. However, the value at $T = 0.14$ is not included as reaching the expected self-diffusion coefficient would take far too long. The lower the temperature of the system, the higher the viscosity becomes and the longer it takes for the sample to reach equilibrium. Only particles of type B were plotted for comparison reasons, but the dynamics are the same for type A. However for type A the diffusivity will be slightly higher as the particles are smaller and thus more likely to be able to move through a dense volume. My simulation data, red points in Fig. 3.4, are in very good agreement with the data extracted from the publication of J. Horbach et al. [3].

Chapter 4

Conclusion

The simulation of the binary colloidal system and the three states observed; solid, liquid and glassy gave the expected results for the radial distribution and calculation of the self-diffusion coefficients. Using these two methods it's possible to characterize and differentiate between the different states as well as showing the similarities between the glass state and the two others. By calculating the self-diffusion coefficient for the different temperatures it's clear how temperature dependent the diffusivity is.

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Appendix A

Lammps Input File

The following input file was run using the LAMMPS software in order to simulate the binary colloidal system. The input file was either the initial configuration file *pos1_1600.dat* or an output file of the form *T_x_1600.data* from a previous.

Code listing A.1: Lammps input file used for the simulations. Temperature is easy to change through the *T* variable.

```
units lj
dimension      3
boundary       p p p
atom_style     sphere
read_data      T_1_1600.data #pos1_1600.dat #T_x_1600.data

set           type 1 mass          1.0
set           type 2 mass          1.0
set           type 1 diameter     1.0
set           type 2 diameter     1.2

group 1 type 1 #Creates group in order to compute for the specific types
group 2 type 2

#Current temperature
variable T equal 0.01 #Target temperature for the dpd

#Potential
pair_style     hybrid/overlay yukawa 6.0 2.5 dpd/tstat $T &
               $T 1.25 34387

#Yukawa Potential
pair_coeff     1 1 yukawa 403.429 3.47858
pair_coeff     2 2 yukawa 3214.63 3.80935
pair_coeff     1 2 yukawa 1132.05 3.64285
#DPD thermostat
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

neighbor       2.0 bin
neigh_modify  delay 20 check yes one 10000
comm_modify   vel yes
```

```
#Self-diffusion coefficient
compute msd_1 1 msd #
compute msd_2 2 msd #
compute myRDF all rdf 50 1 2

#Data for self calculation

timestep      0.0083

#Graphing of variables
thermo 100
thermo_style custom step time temp vol density lx ly lz c_msd_1[1] c_msd_2[1]
#Dump to file
#dump      1 all atom 100 T=${T}.lammprj

fix      msd 1 ave/time 1 1 100 c_msd_1[1] c_msd_2[1] file msd_T=${T}.txt
#Writes msd to file in a structured way

fix      rdf all ave/time 1 1 10000 c_myRDF[*] file rdf_T=${T}.txt mode vector
#Writes rdf to file in a structured way

#Gif creation
dump      4 all movie 100 T=${T}.gif type type size 640 640 #view 90 0
#Fun, but ultimately pointless
dump_modify 4 adiam 2 1 adiam 1 0.5 acolor 1 gray acolor 2 green

#NVE run
fix      4 all nve
run      10000

write_data T_${T}.data
```




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