Examining the glass transition region of hard sphere colloids by simulations

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Abstract

A recent analysis of experimental results for viscosity and diffusion coefficients as functions of the volume fraction in colloidal systems near the glass transition has uncovered a substantial discrepancy with the predictions of Mode Coupling Theory (MCT). Considering the degree of difficulty of the experiments, and in particular the difficulty in precisely determining the volume fraction for the systems under study, it hasn’t been clear to what degree the discrepancy comes from inaccurate experimental values and to what degree it comes from failure of Mode Coupling Theory. The goal of this project was to shed light on this question by using computer simulations. We have used molecular dynamics to simulate a binary hard sphere colloidal system consisting of 8000 particles interacting via a Weeks-Chandler-Andersen (WCA) pair potential. Our simulations covered temperatures of 0.1 and 0.01 in LJ units and volume fractions between 0.006 and 0.69. We found that as the volume fraction increased, there was a sharp decrease in the product of diffusion coefficient and viscosity. Our results are in qualitative agreement with the available experimental data, but differ significantly from the Mode Coupling Theory predictions. We suggest a possible interpretation of these results in that they provide evidence for the presence of dynamical heterogeneities - strong spatial fluctuations in the relaxation rate in glass forming liquids.
Chapter 1

Introduction

1.1 Overview

In the present project we study the properties of hard-sphere colloidal liquids from low densities to densities in the regime where the glass transition occurs. When a molecular liquid is cooled, the molecules may rearrange themselves to form an ordered structure; this process is called crystallization. During the crystallization process the sample changes phases from a liquid to a solid and this is shown by a discontinuous change in the volume.\(^1\) However, if the fluid is cooled too quickly for the molecules to arrange in an ordered structure, crystals do not have time to nucleate and grow thus causing the system to become a supercooled liquid. If the supercooled liquid is further cooled, the molecules eventually “freeze” into a disordered arrangement called a glass. The glass behaves like a solid on a laboratory time scale.\(^2\) The transformation from a supercooled liquid to a glass is called the “glass transition” and is not a phase transition. Unlike what happens in the formation of a crystal, the formation of a glass is associated with a continuous change in the properties such as specific heat and shear viscosity.\(^3\)

In some studies of the glass transition, colloids are used. A colloid consists of small,
solid particles suspended in a liquid. In one example of a glassy colloid, the particles are hard spheres made of polymethylmethacrylate (PMMA) suspended in poly-12-hydroxystearic acid. PMMA particles have hard cores surrounded by slightly compressible surface. PMMA are thus simulated as particles that have a hard sphere potential; they only interact when each of the PMMA particles physically touch each other.

One experimentally controllable variable is the volume fraction $\phi$ which is the ratio of the volume of the particles to the volume of the system. At certain volume fractions phase changes occur in the system. The freezing volume fraction $\phi_f$ is the point at which crystallization begins and the melting volume fraction $\phi_m$ indicates when crystals have
fully developed (see Figure 1.2). Between $\phi_f$ and $\phi_m$ crystals and fluid coexist. The phases just described are found if the system is in equilibrium. As in molecular liquids, crystallization can be avoided and the system can stay in the liquid state beyond the melting volume fraction. Eventually, as the volume fraction is further increased, this “supercooled liquid” undergoes a glass transition at a volume fraction $\phi_g$ and becomes an amorphous solid. By contrast to molecular liquids, in colloidal liquids the control parameter is the volume fraction and not the temperature. For a monodisperse hard sphere fluid, the freezing volume fraction is $\phi_f = 0.494$, and the melting volume fraction $\phi_m = 0.545$. The effect that different volume fractions can have on the crystallization is shown in Fig. 1.3.

## 1.2 Glass Transition Phenomenology

### 1.2.1 Relaxation

The self part of the intermediate scattering function (FSQ) is

$$F_s(q, \tau) = \frac{1}{N} \sum_{j=1}^{N} \cos(\vec{q} \cdot \Delta \vec{r}_{j}(\tau))$$

(1.1)

where $\vec{q}$ is the wave vector and $\Delta \vec{r}_j$ is the displacement of the $j^{th}$ particle from its initial position. The function $F_s(\vec{q}, \tau)$ starts at a value of 1 when observations begin ($\tau = 0$) and decays at a rate dependent on the type of system being examined. We see that if the particles stop moving (the system freezes and $\Delta \vec{r}$ remains constant) then the FSQ reaches a constant value. Also, if we probe the system at different times during the simulation, we produce different FSQ curves. These different times are called waiting times. The FSQ curves can be an indication of whether the system has reached an equilibrium state. A system is said to be in equilibrium if its properties are independent
Figure 1.3: From Ref. PMMA spheres suspended in a liquid of similar density as the spheres for a range of volume fractions. For volume fractions below $\phi_f$, crystals do not form. Between $\phi_f$ and $\phi_m$ crystals are in coexistence with the liquid and at $\phi_m$ the sample has crystallized. Note that at $\phi_f$ and $\phi_m$ the solution reaches an equilibrium state. The glass transition, which occurs for $\phi > \phi_g$, occurs when the spheres are not able to form crystals and thus have not reached an equilibrium state. Rows (a), (b), and (c) show the time evolution of the system.
of the initial conditions and preparation history, and only depend on the actual extended parameters, such as temperature, pressure, volume fraction, extended fields and others.\textsuperscript{6} If the system has reached equilibrium, then the curves of FSQ for the different waiting times will collapse, or will have the same value within statistical error (See Fig. 1.4). If the curves do not collapse, then the system is still changing in time during the time interval being examined. When this occurs, the system is said to be aging.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Figure1.4.png}
\caption{For a $\phi = 0.57$ system that was quenched to a temperature of 2.6, we see that the intermediate scattering function collapses for all of the waiting times. The $t_w$ lines refer to the different waiting times that were tested. For example, tw-50k means that 50000 simulation steps passed before the $F_s(q, t)$ for a waiting time of 50000 was measured.}
\end{figure}

From the FSQ we can obtain the relaxation time of the system. The relaxation time can be defined several ways but they all yield roughly the same quantity. Typically it is defined as the time at which the FSQ reaches some constant value where this constant value is typically chosen to be $\text{FSQ} = 1/e \approx 0.37$.

The way that a supercooled liquid relaxes is described by a two-step relaxation process (See Fig. 1.5). In Fig. 1.5, three regimes can be identified. The first regime repre-
sents fast relaxation where the particles are not “aware” that they are forming a glass and still exhibit Arrhenius behavior. In this early regime, the intermediate scattering function decays rapidly. In a second regime, named the \( \beta \) relaxation regime, the intermediate scattering function reaches a plateau value associated to each particle being limited in its displacement by a “cage” formed by its neighbors. At a much longer time scale, in the \( \alpha \) relaxation regime, particles eventually escape from this cage and diffuse around the system by moving from cage to cage. In the \( \alpha \) relaxation regime, the position of the particles loses all correlation with their initial values, and the intermediate scattering function decays to zero.

![Figure 1.5: From Ref. 1 Self part of the Intermediate Scattering Function plotted as a function of time, from a numerical simulation study. Two step relaxation is observed, for low enough temperatures.](image)

The mean squared displacement (MSD) describes the evolution of the position of the particle from its original position and its value is given by

\[
\Delta(t) = \frac{1}{N} \sum_{j=1}^{N} (\mathbf{r}_j(t) - \mathbf{r}_j(0))^2.
\]
1.2.2 Transport Coefficients

Transport coefficients describe bulk properties of a homogeneous system. Typical transport coefficients are the diffusion coefficient and viscosity. The diffusion coefficient \( D = \Delta(t)/6t \) describes the mass flow in response to a density gradient within the system. The shear viscosity \( \eta = \sigma/\dot{\gamma} \) relates the flow of the fluid to an applied shear stress. The calculations of these quantities with regards to simulations are discussed in Sec.1.4.4. These specific quantities are related through the Stokes-Einstein relation for homogeneous liquids

\[
D\eta/T = \text{constant.} \tag{1.3}
\]

where \( D \) is the diffusion coefficient and \( \eta \) is the viscosity.

1.2.3 Classification of Glass Forming Liquids

Glass forming liquids can be classified into strong and fragile liquids as proposed by Angell. One indication of the formation of a glass is the dramatic increase in the viscosity as the temperature is reduced by a factor of 2 or less. This relationship can be seen in Figure 1.6 where the natural log of viscosity is plotted against the ratio of the glass transition temperature \( T_g \) to the temperature of the system. Liquids that obey the Arrhenius relation

\[
\eta = A \exp[E/k_bT] \tag{1.4}
\]

are called “strong” liquids and are represented by the straight lines in the plot. In Eq. 1.4 \( E \) is a quantity with units of energy, \( k_b \) is the Boltzmann constant, and \( T \) is the temperature. However, note that not all of the liquids follow this relationship and that some show
a much stronger dependence on the temperature. These are called “fragile glasses” and their viscosities are sometimes fitted by the Vogel-Tammann-Fulcher (VTF) equation\textsuperscript{1,2} given by

\begin{equation}
\eta = A \exp[B/(T - T_o)]
\end{equation}

where $A$ and $B$ are constants.

Figure 1.6: From Ref.\textsuperscript{1} Comparison of strong and fragile glasses. Strong glasses follow an Arrhenius behavior, but fragile glasses display a much faster growth of the viscosity as the temperature is reduced.

1.2.4 Dynamical Heterogeneities

In the discussion about transport coefficients, we made the assumption that our system was homogeneous, i.e. a property like $D$ has the same value in one region as it does in another. However, in a supercooled liquid this does not occur, and there are localized regions whose transport coefficients differ from each other.\textsuperscript{9} This means that Eq.1.3 does not hold because when dynamical heterogeneities are present, $D$ and $\eta$ are
not representative of the bulk, but are instead the average over the different $D$ and $\eta$ of each of the dynamical heterogeneities.

### 1.3 Glass Transition Theories

There are many different theories that try to explain the glass transition. Some are based on the concept of excess entropy $\Delta S = S_{\text{liq}} - S_{\text{cryst}}$ which is the difference in entropy between the liquid and crystal phases. Entropy is usually lower in a crystal than the corresponding liquid, but at a low enough temperature any system will tend towards states that minimize the energy, thus favoring the crystal state. However, if the system does not crystallize, it stays in the metastable supercooled liquid state. The entropy of the supercooled liquid can be determined, and it turns out that if its values are extrapolated to low temperatures, they eventually fall below the entropy of the stable crystal. The temperature at which this happens is called the Kauzman temperature.\(^1\)\(^2\) Thus some theories attempt to explain the glass transition through describing how the entropy changes with temperature. One of the theories that attempts this is the Adams-Gibbs theory, where the transition is believed to occur because of a second order thermodynamic point of view to explain the glass transition.\(^2\)

Another idea is that the transition is a dynamical one. Essentially, this relies on the idea that as the liquid is cooled, ergodicity is broken and the molecules become physically arrested and are prevented from trying the different states that are thermodynamically available. This latter idea is encapsulated in Mode Coupling Theory which attributes this arrest to the formation of cages and the increase in time that the particles remain in the cages as a function of density and or temperature.
1.3.1 Adams-Gibbs Theory

The Adams-Gibbs Theory is based on the idea that a thermodynamic transition occurs near the glass transition. It is known that the excess entropy decreases as the glass transition temperature is approached. When the system is at a high temperature, there are many microstates that the system can be in. When the sample is cooled, the molecules are not able to sample as many configurations because they are less able to overcome the peaks and valleys of configuration space. This inability to sample configuration space leads to an increase in the relaxation time; the particles, even though they are disordered, are essentially stuck into a few configurations. The Adams-Gibbs theory relates the change in entropy and the increase in relaxation time $\tau_v$. The Adams-Gibbs equation is

$$\tau_v \propto \exp\left(\frac{B}{T S_c}\right),$$

(1.6)

where

$$B = \frac{E^{*}_a S^{*}_c}{R}.$$  

(1.7)

In the above equations $E^{*}_a$ is the activation energy of separate domains within the sample, $S^{*}_c$ is the configuration entropy per mol, $S_c$ is the configuration entropy of the real liquid, $T$ is the temperature, and $R$ is the gas constant. This equation indicates that the Arrhenius behavior is absent because of the increase in cooperactivity, which is connected to the drastic decrease in the number of microstates possible that the system can sample.
1.3.2 Mode Coupling Theory

Mode Coupling Theory (MCT) has had success in predicting the glass transition for hard-spheres. The idea is that as the density of the spheres increases, each sphere can become "trapped" in a "cage" formed by the neighboring spheres, and it can be prevented from moving for some time. As the density increases, the number of times that the trapped particle must collide with its neighbors before it can escape becomes larger. The system being bound is described by the $\beta$ regime of the two step relaxation. For mode coupling theory, the relaxation time goes like $\tau \propto (T - T_c)^{-\gamma}$ where $T_c$ is the temperature in which the glassy state is achieved. It is important to note that the transition to a glassy state is not governed by thermodynamics like in the Adam-Gibbs Theory but instead by the kinematics of the liquid. The following equation summarizes MCT but is a simplified version with only one wave number.

\[
0 = \frac{\partial^2 \psi}{\partial t^2} + \nu \frac{\partial}{\partial t} \psi + \Omega_0^2 \psi + \Omega_0^2 \int_0^t dt' m(t - t') \frac{\partial \psi(t')}{\partial t} \tag{1.8}
\]

where $\psi(q, t)$ is a time dependent density correlation function, $\nu$ is the viscous damping coefficient, $\Omega_0$ is the frequency of oscillation, and the 4th term is a memory integral that describes the dynamic glass transition.

1.4 Models and Simulations

1.4.1 Molecular Dynamics Simulations

The following discussion of methods is mostly based on Allen and Tildesley\textsuperscript{10}.

Molecular Dynamics is a numerical method which involves solving classical equations of motion for a many body system. The Hamiltonian includes the Kinetic and Potential energy terms and is represented by Equation 1.9 where $p$ and $q$ represent the
particle positions and momenta respectively.

\[ \mathcal{H}(\mathbf{q}, \mathbf{p}) = \mathcal{H}(\mathbf{p}) + \mathcal{V}(\mathbf{q}) \]  

(1.9)

The potential \( \mathcal{V} \) is the term that determines how all of the particles interact in the system. For instance, if the model includes a Coulomb potential, so that particles are interacting at long distances, we would need to calculate the effect that all of the particles have on each other. This is not an issue for small systems on the order of a few particles, but it becomes prohibitively time consuming for systems with more particles, because the computational cost goes as \( N^2 \), where \( N \) is the number of particles in the system. Thus in order to reduce computation time, approximations may be made to the potential term. In general terms, the potential can be expressed as

\[
\mathcal{V} = \sum_i v_1(\mathbf{r}_i) + \sum_i \sum_{j>i} v_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)
\]  

(1.10)

where \( v_1, v_2, \) and \( v_3 \) are respectively the one-body, two-body, and three-body potential contributions.

### 1.4.2 Model Potentials

The first term in Equation 1.10 describes how the particles interact with the boundaries of the system or with external fields. The rest of the terms describe how the particles interact with each other. In our simulations, we will only consider two-body contributions to the potential.

A typical pair potential contains a steep repulsive interaction at short distances and a weak attractive interaction at long distances. A pair potential of this general form that is
commonly used in computer simulations is called the Lennard-Jones potential (Fig. 1.8). It is given by

\[
v_{LJ}(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)
\]

where \(\epsilon\) specifies the depth of the potential well and \(\sigma\) specifies at what radius the hard spheres interact. This potential is mathematically less complex than more realistic potentials, but still gives a reasonable representation of pair interactions.\(^\text{10}\)

Sometimes potentials are reduced into simpler, more idealized forms. These include the hard sphere potential, where there is an infinite repulsive potential a certain distance from the center of the particle. This is an idealized approximation to hard spheres that are used in experiments. Typically, the colloidal particles used in experiments might have a small attraction due to static charge on their surfaces. Also since the hard-spheres are not perfectly rigid, the potential is not truly infinite. Soft sphere potentials differ from hard sphere potentials in that they have a more gradual increase to the infinite repulsive potential.

![Graphical representation of the hard sphere potential. At some cutoff, the potential becomes infinitely repulsive. Also note the lack of an attractive term as hard spheres ideally have no charge on them.](image)

A potential that combines the idea of the hard sphere and soft potential is the Weeks-
Figure 1.8: This plot shows the Lennard Jones and the Weeks-Chandler-Andersen (WCA) potentials. The Lennard Jones potential is representative of common pair potentials in that it contains a repulsive wall as the radius of the particle is approached and a long attractive tail. The WCA potential is similar to the LJ potential except that it does not contain the attractive tail.

The Weeks-Chandler-Andersen (WCA) potential (See Fig. 1.8). The WCA potential for hard spheres is essentially a shifted LJ potential with only the repulsive part. This potential can be used to simulate particles that have a softer repulsion than hard sphere, but no attraction. The form of the WCA potential is the following:

$$v^{WCA}(r) = \begin{cases} v^{LJ}(r) + \epsilon & \text{if } r < r_{min} \\ 0 & \text{if } r_{min} \leq r \end{cases}$$  \hspace{1cm} (1.12)

where $r_{min} = 2^{1/6}\sigma$ is the distance where the minimum of the Lennard Jones potential is located.
1.4.3 Representing System Dynamics

Newtonian

Newtonian dynamics involves solving the equations of motion without any correction terms and just takes into account interactions between different particles.

\[ \vec{F} = \sum m \frac{d\vec{v}}{dt} \]  (1.13)

Langevin

The effect of the solvent is not taken into account in Newtonian dynamics. To accomplish this one can add a damping term to the equations of motion\(^{11}\)

\[ m \frac{d^2x}{dt^2} = -6\pi \eta a \frac{dx}{dt} + \chi(t) \]  (1.14)

where \( \eta \) is the viscosity and \( \chi(t) \) represents a time varying fluctuating force term that accounts for collisions with individual solvent molecules.

Explicit Solvent

Another option is to model the solvent explicitly. To do this, a solvent could be modeled by adding much smaller particles (representing the solvent molecules) to simulations using Newtonian Dynamics (See Fig. 1.4.3).

1.4.4 Simulations

To make the algebra in computations easier, reduced Lennard Jones units are used. These units are dimensionless and allow the magnitude of the numbers being computed to be small and more easily managed. In order to make the units dimension less, we
change $r \rightarrow r\sigma$, $e \rightarrow e\epsilon$, and $t \rightarrow t\sqrt{m\sigma^2/\epsilon}$.\textsuperscript{7}

Periodic boundary conditions are used in molecular dynamics. The system is broken into periodic cubes based around a central cube, with the central cube being the simulation box used in simulations. When a particle leaves the central cube, it is replaced by a copy of the particle on the opposite side of the cube, but moving in the same direction (See Fig. 1.10. By representing the system this way, only the positions of the central cube need to be stored and the number density of the system remains conserved.

In numerical simulations, the system is described by the number of particles in the simulation (N), the volume of the system (V), the energy (E), the temperature (T), and the chemical potential ($\mu$). Using these quantities many of the properties of the system can be found. Some of the most important quantities are called transport coefficients and they relate microscopic information about atoms on the particle level, to properties that describe the entire system.\textsuperscript{10,7}
There are four main ways that the simulation can be set up and they revolve around what physical quantities of the system are held constant. These include the microcanonical ensemble (constant NVE), the canonical ensemble (constant NVT), the isothermal-isobaric ensemble (constant NPT), and the grand canonical (constant $\mu$VT). In fact most quantities that are pertinent to this project can be obtained using Newton’s equations and applying the equations to these ensembles. The idea is that all of the properties can be represented in phase space and that any property that we wish to know is a function of this phase space. For N particles in the system there are 6N dimensions to this phase space (each dimension corresponds to position and momentum values). The use of these ensembles requires that the system be at equilibrium as required by the derivations from statistical mechanics.
Computing Transport Coefficients in Equilibrium

Diffusion and viscosity are transport coefficients that are computed in this thesis. When the diffusion coefficient \(D\) is referred to through the rest of the paper, we are referring to the self diffusion coefficient given by

\[
2tD = \frac{1}{3} \frac{1}{N} \sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle
\]

where \(r_i\) is the position of the \(i_{th}\) molecule, \(N\) is the number of molecules, and \(t\) is time.

Viscosity

The viscosity \(\eta\) can be computed in equilibrium by

\[
2t\eta = \frac{V}{k_B T} \frac{1}{R} \sum_{i=1}^{N} \langle (\mathcal{D}_{\alpha\beta}(t) - \mathcal{D}_{\alpha\beta}(0))^2 \rangle
\]

where

\[
\mathcal{D}_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^{N} r_{i\alpha} p_{i\beta}.
\]

In Eqs. 1.16 and 1.17, \(\alpha\) and \(\beta\) represent cartesian coordinates (i.e. \(x\), \(y\), or \(z\)), \(t\) is the time, and \(p_i\) is the momentum of the \(i_{th}\) particle.

1.4.5 Non-Equilibrium Molecular Dynamics

The viscosity of the system, though it can be obtained by equilibrium dynamics, is originally defined as a quantity that is measured when the system is out of equilibrium. Essentially Non-Equilibrium Molecular Dynamics (NEMD) simulations are performed so that the transport coefficients can be better approximated. The problem with equilibrium dynamics simulations is that correlation functions may have large statistical fluctuations which translate in large statistical errors in the determination of the viscosity.
The difference in NEMD simulations is that we produce a small disturbance \(^*\) and look at the response the system has.

There are a number of ways that NEMD simulations can be performed. Essentially all of the ways involve adding an extra term in both the position and momentum through the relations\(^{10}\)

\[
\begin{align*}
\dot{q} &= p/m + \omega_p \cdot \mathcal{F}(t) \\
\dot{p} &= f - \omega_q \cdot \mathcal{F}(t)
\end{align*}
\]

These disturbances can be introduced through three main methods. One is to turn on the disturbance at some time and hold it constant. Another way is to apply a pulse to the system (essentially a delta function) and measure the response. The third is to introduce some oscillatory stimulus. Many of these methods are used in experiments to measure the same quantities. Care should be taken when dealing with NEMD simulations because periodic boundary conditions may not suitable.\(^{10}\)

**Measuring Viscosity**

In this paper we only use NEMD for measuring viscosity, which can measured a number ways. One of them is to create a non-orthogonal simulation box then deform it at a desired strain so as to create a shear profile (See Fig. 1.11). This would bring the system out of equilibrium and then the response to the perturbation would be observed.

Another way to determine the viscosity is to perform momentum swaps.\(^{13}\) Fig. 1.12 gives a visual representation of how this works. In this method the simulation box is divided into an odd number of layers and a target velocity is selected. In the first layer, the particles that had the velocity closest to the target velocity in the positive x-direction

\(^*\)The system is brought out of equilibrium enough so that the fluctuation is much larger than in the equilibrium situation. This can greatly reduce the signal to noise ratio.
Figure 1.11: The viscosity can be measured by creating a shear profile where shearing forces are applied to the boundaries of the box.

are selected. Particles in the middle layer with the velocity closest to the target velocity in the negative x-direction were selected. These velocities are swapped with each other and a velocity gradient develops. The slope of this gradient is related to the viscosity of the sample by

$$j_z(p_z) = \frac{\delta v_x}{\delta z} \eta$$

where $j_z(p_z)$ is the momentum flux, $\eta$ is the viscosity, and $\frac{\delta v_x}{\delta z}$ is the slope of the velocity profile.

1.5 This Work

The work was motivated by a very significant discrepancy between the available experimental data for the viscosity and the diffusion coefficient of colloidal liquids at volume fractions close to the glass transition volume fraction and the theoretical predic-
Figure 1.12: Momentum swap method for measuring viscosity. Atoms with a chosen velocity $v$ moving in the bottom layer (yellow) were swapped with particles moving in the opposite direction in the middle layer (blue). As more of these swaps were produced, a velocity profile is generated that is shown to the right of the simulation box. The slope of this profile ($\delta/v\delta y$), in conjunction with the total momentum swapped between the layer, is used to find the viscosity of the fluid.

tions based on Mode Coupling Theory. In Ref.\textsuperscript{14} Wilson Poon discussed the relationship between low shear viscosity experimental data from Ref.\textsuperscript{4} and diffusion coefficient experimental data from Ref.\textsuperscript{15}. The shear viscosity data was measured using PMMA hard-spheres; they covered a volume fraction range from $\phi \approx 0.30 - 0.60$. Diffusion data are available from two data sets, which together span volume fractions $\phi \approx 0 - 0.566$. In \textsuperscript{14}, these data sets were reanalyzed and compared to Mode Coupling Theory (MCT) predictions from Ref.\textsuperscript{16}. At volume fractions above 0.4, the MCT theory and the experimental data diverge by an order of magnitude (See Fig. 1.13).

Poon suggests three reasons for this discrepancy. The first is that both of the data sets are wrong which, as he admits, is not likely. The second is that one of the data sets is incorrect, which he guesses is probably the viscosity data because the actual experiment is hard to perform. The third option is that the relationship between viscosity and diffusion is not well understood.
Figure 1.13: The graph from Poon\textsuperscript{14} which shows how the experimental data (blue) diverge from predictions by MCT (pink) around a volume fraction of 0.4. The horizontal axis is the volume fraction and the vertical axis is the reduced Stokes-Einstein ratio (Eq. 3.4)

In this work we compute diffusion coefficients and shear viscosity in molecular dynamic simulations, and compare our results both to the experimental results and the the results of Mode Coupling Theory. Our goal is to shed light on the origin of the discrepancy between experiments and theory, and to try to determine if simple models of colloidal particles are sufficient to describe the glass transition regime.

This Thesis is organized as follows: in Chapter 1 we have presented an introduction to the problem, the models, and the methods used. In Chapter 2 we discuss simulation details. In Chapter 3 we present our results and discuss them. In Chapter 4 we give our conclusions and proposals for future work.
Chapter 2

Our Simulations

For this work we decided to use the LAMMPS molecular dynamics simulator. LAMMPS can simulate a wide variety of systems ranging from solids to gases and polymers to single particles. Because of this versatility, we were able to tailor LAMMPS to perform simulations that fit our needs. The system modeled was a binary Lenard-Jones system which consisted of 8000 particles interacting via a shifted LJ potential without the long distance attractive tail. This is also known as the Weeks-Chandler-Anderson (WCA) potential (Sec. 1.12).

It is important to understand how LAMMPS will solve the viscosity and diffusion values that we need. The program works by creating an input file which contains all of the instructions for the creation and testing of the system. For instance, particle positions and masses are read and a simulation box is created. The way that the particles interact (i.e. potential terms) and the size of the particles is then defined.

It is at this point that the characteristics of the experiment are implemented and the process resembles a classical experiment. For instance, we specify what initial temperature the system has and what temperature we will quench it to. We also determine how long the simulations are run for as well as what parameters we want to measure.
LAMMPS stores general information such as the particle’s position as well as its velocity. However, if a more complicated computation must be performed, usually a dedicated command is called. This is how the diffusion coefficient and the viscosity can be measured.

Using LAMMPS we were able to explore two different systems. The first system was governed by Newtonian Dynamics and was governed by an NVT, or canonical, ensemble. The Newtonian system was used for a number of reasons. The first was that it was a reasonable model to use for hard-spheres and it was easily implemented into LAMMPS. Also the simulation times were relatively fast. The major drawback for the system was that it did not model the solvent that is present in experiments. This meant that there was no explicit viscous damping force present. The particles only interacted with each other and were governed by the pair potentials that were specified in the input file of LAMMPS. There was also the issue that at low densities, the system exhibited ballistic motion; the system behaves like a gas due to the lack of this viscous damping force.

To address this, Langevin runs were performed under an NVE system. One drawback to this model is that the simulation run time was noticeably longer for Langevin simulations because of the additional viscous drag term. There was also a problem when measuring the viscosity which will be discussed below.

The diffusion coefficient and the viscosity were measured using LAMMPS. The diffusion coefficient was found from Eq. 1.15. In order to extract this value from the output of LAMMPS, the fix msd command is used which tells LAMMPS to compute the average mean squared displacement (MSD). From Eq. 1.15, we see that the Diffusion Coefficient is proportional to a constant times the MSD. Thus by plotting the MSD vs. time, from the slope we can determine D.

The problem with the latter method enters when using the Langevin equations of
motion. The Langevin system provides a damping force that is proportional to the velocity of the particle. This is unphysical for the method that was used to calculate the viscosity, because the drag force should be proportional to the velocity of the particle minus the velocity of the solvent. This is unimportant if there is no macroscopic flow in the system, but becomes important when such flow is expected to exist like in the momentum swap method (Sec. 1.4.5). Thus when we attempted to use this method in Langevin simulations, the method failed because the velocities were damped to almost zero.

One way to suppress this effect would be to have the particles damp to some velocity value other than zero. A choice that we attempted was to estimate the solvent velocity as the average velocity of the surrounding particles of the swapped atoms. However, for various technical reasons, this attempt failed, and thus we were not able to collect viscosity data in the Langevin runs.
Chapter 3

Results

To obtain the diffusion coefficient, we studied the behavior of the Mean Square Displacement (MSD) as a function of time. In a typical plot of MSD vs. time $t$, such as Fig. 3.1, we can recognize at least two regimes: a ballistic regime, where the MSD is proportional to $t^2$, and a diffusive regime, where the MSD is proportional to $t$. The ballistic regime corresponds to times short enough that most of the particles in the system have suffered no collisions and their individual displacements are proportional to the time interval. As a consequence the MSD, which is proportional to the square of the displacements, is proportional to $t^2$ when the system is in this regime. In the diffusive regime, the MSD is proportional to the time $t$. In a log-log plot of the MSD as a function of time, the two regimes correspond to straight sections of the plot, with slopes corresponding to the exponents, i.e. 2 for ballistic motion and 1 for diffusive motion (see Fig. 3.1). In all cases we determined the diffusion coefficient $D$ by fitting the MSD to Eq. 1.15 within a time interval completely included in the diffusive regime. For most of our systems this meant determining the slope of the MSD for times above 600 LJ time units.
3.1 Newtonian Simulations: Ideal Gas Limit

One check that we applied to our data was to compare the transport coefficients to the ones predicted by kinetic theory for the low density and high temperature (i.e. ideal gas) regime. From Reif [11] we have the kinetic theory viscosity prediction for a system of hard spheres of mass \( m \) and temperature \( T \):

\[
\eta = \frac{1}{3\sqrt{2}\sigma_o} \sqrt{\frac{8kT}{\pi m}}
\]  

(3.1)

where \( k \) is the Boltzmann constant, \( \sigma_o = 4\pi a^2 \), and \( a \) is the radius of a sphere. In Lennard Jones units, we can set \( m = 1 \) and \( k = 1 \). Making these substitutions we have

\[
\eta = \frac{1}{3\pi^{3/2}a^2} \sqrt{T}
\]  

(3.2)
For the diffusion coefficient, we have, in the same approximation:

\[ D = \frac{1}{6\pi^3/2 a^2} \frac{1}{n} \sqrt{T}. \quad (3.3) \]

Figs 3.2a and 3.2b show the ratios of the measured diffusion coefficient and viscosity to the corresponding kinetic theory values. For the lowest densities, the ratios are approximately independent of temperature, as expected. For higher densities, kinetic theory is no longer applicable, and the ratio becomes sharply temperature dependent, as is also expected.

### 3.2 Newtonian Simulations: Computing Transport Coefficients

#### 3.2.1 Diffusion Coefficient

We now consider the diffusion coefficient computed in NVT simulations without explicit drag forces. We study how it depends on the temperature and density of the system. In Fig 3.3 we see that the diffusion coefficient generally decreases as a function of density and increases as a function of temperature, or stays approximately constant as a function of temperature. This is consistent with physical intuition: as the temperature increases, the particles have more energy and it is easier for them to move around the system. Note that as the density increases, so does the number of neighbors that each of the particles interacts with, and it becomes harder for the particle to move around. Thus we expect the diffusion coefficient to be smaller for higher density systems.

In Fig. 3.3a we can notice, as could be noticed also in Fig 3.2b, that the proportionality of the diffusion coefficient with \( \sqrt{T} \) is only valid for very low densities, and this behavior is immediately suppressed as soon as the density is around 0.2 or larger. For larger
Figure 3.2: The ratio of our results to kinetic theory are shown for viscosity (a) and for diffusion (b). As expected, for low volume fractions high temperatures, we maintain a constant value. As the volume fraction increases, we find that there is a sharp divergence from the trend which is expected because the particles have stronger interactions with their neighbors.
Figure 3.3: Diffusion coefficient (a) as a function of temperature at constant density and (b) as a function of density at a constant temperature computed for the system with Newtonian dynamics.
densities, the diffusion coefficient stays approximately constant for changing temperature.

**Viscosity**

We performed NEMD simulations for the Newtonian system over the same temperature and density range as the equilibrium dynamics simulations. By performing NEMD simulations we were able to determine the viscosity (See Fig. 3.4). We see that as the volume fraction is increased, the viscosity also increases. The behavior as a function of temperature depends on the volume fraction: for low and moderate densities, the viscosity grows as a function temperature in qualitative agreement with kinetic theory. For higher densities and at low temperatures, the viscosity decreases as the temperature increases, reflecting the fact that a temperature increase moves the system further away from the glassy regime.

**3.3 Langevin Results**

The same density-temperature plane was sampled for the Langevin runs, but as mentioned in Ch.2, only the diffusion coefficient was measured. In Fig. 3.5 We see that as the volume fraction increases, the diffusion coefficient decreases, with a sharp decrease occurring for low temperatures. From Fig. 3.5b we see that the diffusion coefficient increases as the temperature is increased. Both of these conclusions are in qualitative agreement with the Newtonian results.
Figure 3.4: The effect that density and temperature have on the viscosity is shown in the figures for the Newtonian system.
Figure 3.5: Langevin diffusion coefficient (a) as a function of temperature at constant density and (b) as a function of density at a constant temperature for the Langevin model.
3.4 The Colloidal Glass Transition

Having discussed in general the behavior of our model for all temperatures, we now focus on the extremely low temperature regime $T \ll \epsilon$. In this regime, the potential becomes larger than several times $k_b T$ for any interparticle distance $r$ smaller than the range $2^{1/6} \sigma$ of the potential, unless $r$ is very close to the range. As $T/\epsilon \to 0$, our model behaves as a system of hard-spheres with radius $a$ given by half the range of the potential, i.e. $a = \frac{1}{2} \sigma 2^{1/6} = \sigma 2^{-5/6}$. We can thus address the discrepancy between the experimental results for viscosity and diffusion coefficient as reanalyzed by Poon\textsuperscript{14} and the Mode Coupling Theory results by Banchio et. al.\textsuperscript{16}

In Fig. 3.6 we plot the diffusion coefficient $D$ for very low temperatures ($T/\epsilon$) as a function of the volume fraction $\phi$ both for the model with explicit solvent drag force and for the model without explicit solvent drag force. In the system without explicit drag, we notice the large change of the diffusion coefficient with volume fraction at low volume fractions, as predicted by kinetic theory. In the system with explicit drag, kinetic theory is not directly applicable, and this large variation is absent.

At intermediate and high volume fractions, there are two important characteristics of the plots. The first is that there is a sharp decrease in $D$ as the density increases as qualitatively predicted by MCT. This is due to the slowing down of particle motion, associated with the particles becoming trapped in “cages” and with the emergence of two step relaxation (Sec. 1.2.1).

The next important observation is that as the volume fraction increases, the two curves for the same temperature (with and without explicit drag included) collapse with each other. This indicates that for large densities the liquid drag force becomes negligible compared to the interparticle forces. One possible explanation is that the particles are so densely packed that their velocities are essentially zero and the viscous damping
term in the Langevin equations of motion ceases to be important.

Figure 3.6: Shows how the diffusion coefficient depends on volume fraction and also on the type of forces being applied to the particles. We see that as the volume fraction is increased, the choice of system becomes less important.

Next we determine the viscosity. The viscosity is plotted as a function of volume fraction in Fig 3.7. This again indicates an expected behavior in which the viscosity grows very rapidly as the system becomes more dense, and this growth is more dramatic at lower temperature, (i.e. as the hard sphere limit is approached).

In order to compare the theory to experimental results, Poon\textsuperscript{14} used the quantity:

\[ f = \frac{D_{SL}(\phi)}{D_{free}} \times \frac{\eta_o}{\eta_s} \] 

(3.4)

where \( D_{free} \) is the single particle diffusion coefficient in a solvent of viscosity \( \eta_s \) and \( D_{SL}(\phi) \) and \( \eta_o \) are respectively the measured self-diffusion coefficient and viscosity of the colloidal liquid. Since we have obtained both the diffusion coefficient \( D \) and viscosity \( \eta \), we can multiply our values and obtain the Stokes Einstein ratio \( \tilde{f} \equiv D\eta / T \), which is equivalent to Poon’s \( f \), except for an unimportant constant factor. In Fig. 3.8 this ratio is plotted as a function of the volume fraction \( \phi \), at the lowest temperature \( T = \)
Figure 3.7: Plot for the viscosity of the Newtonian system for low temperatures. The important trend is the exponential increase in the viscosity as a function of volume fraction.

0.01, for the model without explicit solvent drag.

We find that our $f$ value decreases by around two orders of magnitude as $\phi$ is increased beyond $\phi \approx 0.55$, i.e. as the glass transition is approached. This is in qualitative agreement with the experimental results\textsuperscript{15} but in disagreement with the Mode Coupling Theory results\textsuperscript{16}. In Fig. 3.9 we compare $f$ computed using the diffusion coefficient obtained for the system with explicit solvent drag force and the viscosity obtained for the system without explicit solvent drag with $f$ computed fully without explicit solvent drag. As expected, the sharp decrease in $f$ for volume fractions near the glass transition is similar in the two cases.

It was mentioned before that at volume fraction larger that $\phi \approx 0.63$ the system does not equilibrate during the simulation time, and therefore this generates some uncertainty in the values of diffusion coefficient, viscosity and $f$. However, we have observed that the variations of the transport coefficients with the waiting time are of the order of 10-20%, which is much smaller that the order of magnitude changes that are observed as a function of volume fraction. This leads us to believe that the observed effects are not
Figure 3.8: Normalized Stokes Einstein ratio $f$ for data obtained from our simulations for the model without explicit solvent drag. Note that the trend of the decrease in $f$ as the volume fraction increases beyond $\phi \approx 0.55$. This trend is similar to the one seen in the experimental data\textsuperscript{17}, though not in the MCT results from Banchio.\textsuperscript{16} The data are shown for different waiting times $t_w$, and at the biggest volume fraction, a slight dependence on $t_w$ is observed, because the system is relaxing so slowly that it doesn’t equilibrate during the timespan of the simulations.

Figure 3.9: Comparison between Langevin diffusion and Newtonian diffusion. The important aspect of the graph is that the curves collapse for the lower densities. This was assumed to be a reasonable comparison because we concluded that at high densities, it was Newtonian and Langevin systems give similar results. This importance is that $f$ decreases as the volume fraction increases.
artifacts of this lack of equilibration and that they would still be present if the simulation times were increased dramatically up to the point where the system equilibrates.
Chapter 4

Conclusions

The project was motivated initially by an observation by Wilson Poon\textsuperscript{14} about discrepancies between experimental and theoretical results. There was discussion on experimental results for the self-diffusion coefficient from van Megen\textsuperscript{15} and viscosity data from Chaikin.\textsuperscript{4} These experimental results were compared to theoretical results (the “Generalized Einstein Relation”) that were obtained by Banchio et. al. by applying Mode Coupling Theory to the problem.\textsuperscript{16} The discrepancy between the experimental and theoretical results revolved around the data for high volume fractions near the glass transition. Thus the goal of this project was to compute viscosities and diffusion coefficients in simulations of a model of a glassy liquid and to attempt to shed some light on the discrepancy between the theory and Poon’s re-analysis of the data. One crucial difference between the models we simulated and the systems studied in the experiments and in Mode Coupling Theory is that those systems were either monodisperse or very close to monodisperse, but by contrast we simulated a 50:50 binary mixture of two kinds of particles.

The LAMMPS molecular dynamics simulation software aided this exploration. Systems were chosen that consisted of 8000 particles of a binary colloid interacting via
WCA potential. The particle potential was chosen so that they behaved like soft spheres with a hard repulsive core at temperatures of the order of the energy scale of the potential, and as hard spheres at temperatures much lower than that. Separate simulations using Newtonian and Langevin equations of motion were performed. The Langevin system differed from the Newtonian by the addition of a viscous damping term, representing the drag force exerted by the solvent on the colloid particles.

To check the validity of the model we studied the low density and high temperature regimes so that we could compare the results to kinetic theory. We observed the expected trends of a decrease in the diffusion coefficient as the density increased and the temperature was lowered. The viscosity decreased as the temperature was lowered and the density lowered. When the ratio was taken between the expected kinetic theory value and the value from simulations, this ratio was found to be approximately constant at low densities. The Stokes Einstein ratio was computed for the Newtonian system so that the calculation of the viscosity and the diffusion coefficient could be compared. For low temperatures and intermediate densities, this ratio was constant at constant temperature.

Runs at low temperature were also completed. From the diffusion versus volume fraction plot, we determined that once the volume fraction reached a high enough value, it did not matter whether the Newtonian or Langevin equations of motion were used. We speculated that this can be attributed to the high density restricting movement of the particles, thus effectively eliminating the effect of the viscous damping term in the Langevin system.

We used the normalized Stokes Einstein ratio \( \tilde{f} = D\eta/T \) to combine the diffusion data and viscosity data from our runs and compare them to the trends seen in the experiments and the theory. We found that our simulation results follow a qualitatively similar trend to those in experiments but deviate drastically from the predictions by Mode Coupling Theory.
In his notes\textsuperscript{14}, Poon suggests that there are three possibilities to explain the discrepancy between the experimental and theoretical values. One is that both experimental data sets are wrong, which Poon find possible but very unlikely. The second is that one of the data sets is incorrect and the one that is most likely to be incorrect is the viscosity data set because of the difficulty in performing the experiment. The third possibility is that there is something completely misunderstood in the relationship between the diffusion coefficient and the viscosity for hard spheres. Our results, although not directly applicable to Poon’s problem because they were obtained for binary systems, suggest that the last of the three possibilities is the one that holds.

Future work could include completing more runs for higher densities at the lowest temperatures. To improve the statistical errors of the results, longer run times for higher densities and lower temperatures could be completed. This would allow us to probe deeper into the area of interest, while still being able to equilibrate the system. The current runs were completed in density increments of 0.1 and an improvement would be to generate results for more closely spaced densities. This would allow the fitting of the results to various possible analytic expressions, thus helping to address an important open question in the physics of colloidal suspensions, namely whether the viscosity and the diffusion coefficient have any singularities as a function of the volume fraction, and if so, what is the form of these singularities. An explicit solvent could also be used to model the system. This might provide a more accurate model for the system in the experiments, but would admittedly take a significantly longer time to simulate.
Bibliography


