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POLYTECHNIC UNIVERSITY
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Department of Applied Physics

Final Year Project Report

Project Title

Glassy Dynamics in Colloidal System

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Abstract

The Glassy Dynamic problem has long been an open question facing fierce debate in recent decades. Though many studies have been done and various models have been raised to understand the mystery of the dynamic arrest of glass problem, there is no consensus reached in the academia.

With the help of optical microscopic imaging, long time video recording of polydispersive colloid system with different densities is performed. The video images of individual particle resolution provides us valuable data to analyze frame by frame the dynamic of colloidal glass and gain insights on the origin of the sudden drop of glass dynamical rates when approaching the critical packing density, analogous to the glass transition temperature T_g . The analysis is carried out mainly in the MATLAB programming language. The model chosen to cross-validate our results is the Distinguished Particle Lattice Model (DPLM) of glass.

We observe predominantly ‘hopping’ motions in the dynamics. By analyzing the particle Mean Square Displacement (MSD), we are able to show the dominance of the Hopping Events’ contribution in the MSD of the system, which controls the dynamical property of glass system. We also define the subsequent motion of the hopping particles to be returning and escaping. By analyzing long time after the particle hops, we show the dominance of the returning events over escaping event in high density cases. This implies that majority of the hopping event is followed by returning events which, we believe, is sufficient to cause the dynamic arrest.



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Special thanks to Mr. Wong King Ping who has kindly offered his great insight into handling defocused data as well as his preliminary data processing functions. He also did a lot in the early stages of the data management.

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Table of Contents

Abstract	III
Acknowledgment	III
Table of Contents	IV
CHAPTER 1 INTRODUCTION	1
1.1 GLASSY DYNAMIC PROBLEM	1
1.2 MOTIVATION	1
1.3 OBJECTIVE	2
1.4 METHODS	2
1.5 ORGANIZATION	3
CHAPTER 2 LITERATURE REVIEW	5
2.1 REVIEW ON VARIOUS THEORIES AND MODELS	5
2.2 REVIEW ON EXPERIMENTAL ANALYSIS ON COLLOIDAL GLASS	5
CHAPTER 3 DATA PROCESSING TECHNIC AND ALGORITHMS	6
3.1 PRELIMINARY DATA PROCESSING	6
3.2 HIGH-PRECISION DENSITY MEASUREMENT	8
3.3 SYSTEM NOISE AND MICROSCOPIC MOVEMENT SUBTRACTION	11
CHAPTER 4 HOPPING EVENTS IN GLASS DYNAMICS	18
4.1 HOPPING AND CREEPING	18
4.2 MSD ANALYSIS FOR HOPPING AND CREEPING	21
4.3 RATIO FOR MSD HOPPING	23
CHAPTER 5 RETURN AND ESCAPE EVENTS	26
5.1 RETURN AND DYNAMIC SLOW DOWN OF THE GLASS SYSTEM	26



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5.2 DEFINITION FOR RETURN AND ESCAPE EVENTS.....	26
5.3 RETURN AND ESCAPE PROBABILITY	29
CHAPTER 6 CONCLUSION AND FUTURE RECOMMENDATIONS	31
6.1 CONCLUSIONS	31
6.2 FUTURE RECOMMENDATIONS.....	32
References.....	35



Chapter 1 Introduction

1.1 Glassy Dynamic Problem

The Glassy dynamics has long been one of the unsolved puzzle confusing physicists despite decades of intensive studies[1-3]. Glass, which is amorphous structure, can be obtained by a fast cooling of a liquid to its glass temperature, T_g . Strictly speaking, glass is neither liquid nor in form of standard solid. When the temperature T decreases and approaches T_g , the dramatic drop, usually in 14 orders of magnitude, in the dynamics of the system still remains an open debate in the academia. The physical origin of structural dynamics responsible for this slowdown, which is also well-known as the kinetic arrest, is yet an open question.

1.2 Motivation

Through years of investigation, various models and theories have been raised including Adam-Gibbs theory, dynamic facilitation (DF), random first-order transition (RFOT), mode-coupling theory and so on. Although there are many experiments conducted to validate any one of those theories, seldom did the experiment gave strong enough evidence to prove the correctness of the theory. This project is to fill in the gap for strong experimental evidence for validating the existing theory.

More specifically, in this project, experimental data is analyzed based on the model of Distinguishable-particle lattice model (DPLM) founded by Dr. Chi-hang Lam and Mr. Linghan Zhang.

1.3 Objectives

Using experimental data analysis to give more insights into the glassy dynamic problem, using the DPLM model.



- (1) Visualize the trajectories of the particles using various time steps and investigate the effect of averaging on particle trajectory graphs
- (2) Measure the density of the system with high precision
- (3) Investigate the Subsequent motion of the particle hop (Whether it returns to the previous hopping position or escape to other positions)
- (4) Compute the Hopping Return and Escape probability of the particle and compare different density experimental results
- (5) Divide the motion of the particles into hopping motion and creeping motion in the mean square displacement and analyze their contribution to the total dynamic of the system
- (6) See the particle displacement graph to justify the hopping and returning event

1.4 Methods

Colloidal Glass, which is composed of micro-size particles, have similar physical properties of atomic glass. However, the dynamic of the Colloidal Glass is strongly-concentration dependent instead of strongly-temperature dependent. Therefore, experiments can be done in a room-temperature setting using confocal microscopes to measure individual particles with high precision. Experiments are done using bi-dispersive plastic spheres with a radius ratio of 1.22. The small sphere diameter is around 3.77 micrometer with a Gaussian distribution and the larger sphere is around 4.59 micrometer. The system is immersed in the room-temperature water matrix and placed under the Microscope for long time filming. The environment temperature is kept constant or at minimum fluctuation so that the dynamic of the colloid system is mainly controlled by the density.

For the data analysis part, MATLAB is used mainly for computing large matrix



computations and minor python programs are also used. Programs are either modified or written to achieve the above-mentioned objectives. The sample of the filmed particles is shown as follows. Typically, the length of the experiment varies sample by sample as the criteria for making reliable and credible data analysis are systems that have a Mean Square Displacement larger than 1 unit length after fully relaxed. Usually, the separation between frames is 4 seconds per frame and long data sets can have more than 250,000 frames, which is around 1,000,000 seconds. The long length of the filming makes it possible to observe the microscopic picture of the glassy colloid and analyze its dynamic property in great details.

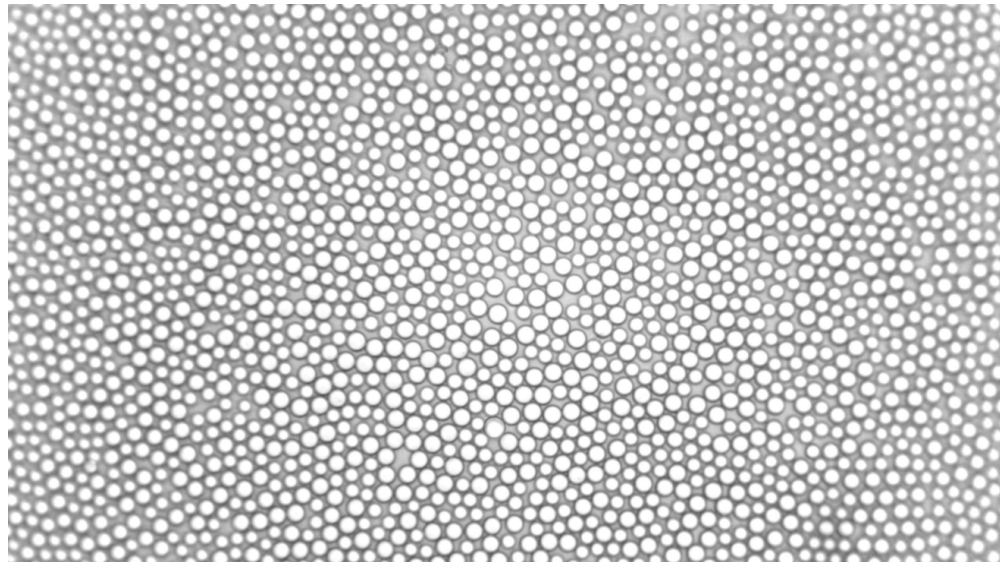


Fig 1.1 Typical experimental data frame

1.5 Organization

This glassy dynamic research project is mainly focusing on the data analysis of the experimental data filmed by microscope provided by Dr. Yip. Therefore, the organization of this report would be slightly different from an ordinary one. Main Chapters are separated by the main analysis problem solved and major work being done. The discussion and the conclusion of some of the minor chapters are within those



specific chapters and only major discoveries and findings would be raised to discuss and conclude at the end of this report.



Chapter 2 Literature Review

2.1 Various Theories and Models

In order to simulate and investigate the glassy system and the kinetic arrest problem, various models have been raised. Back in 1980s to 1990s, Kob and Kremer has shown that the dramatic slowdown of dynamic property can be achieved and simulated by molecular dynamics (MD) [4-5]. At the same time, the random first-order phase transition (RFOT) model was raised and became one of the leading theories for the mystery. Another model which was popular and promising was the kinetically constrained theory [6]

Despite the various model established, none of them gives a full microscopic justification of the facilitation rules. In 2017, Distinguished Particle Lattice Model (DPLM) was raised. It is characterized by particle distinguishability and site-particle-dependent random nearest-neighbor particle interactions [7]. Based on the model, a deeper theory called Local random configuration-tree theory was established based on the transport of voids by micro-string motions[8].

According to DPLM simulation results [7], the return probability become close to 1 at extremely low temperature which means that nearly all the hopping events are followed by returning event. The Particle hopping becomes extremely repetitive.

2.2 Experimental Analysis

Theory would be not sufficient and convincing without the help of experiments. Experiments were conducted to support or disapprove the above-mentioned various models. Using also confocal microscopy, Heckendorf et.al founded the Size-dependent localization in Polydisperse Colloidal Glass [9]. The system Heckendorf used was highly dispersive with large particles 3 times the size of the small particles. The experiment was conducted in the time scale of within 1000s.

One other interesting experimental data published on Science was done by Eric



R. Weeks [10]. The fastest particle, cluster size, structure and dynamic were captured using confocal microscopy during similar time scale ($\sim 10^5$ s). The focus was on the cluster effect in 3-d system colloidal glass and supercooled liquid. The experiment also shown the typical trajectory for particle hopping events as well as the vibrational motion.



Chapter 3 Data processing techniques and algorithms

3.1 Preliminary data processing procedure

3.1.1 Image-video conversion

The raw data comes in either the form of video clips or thousands of frames being labeled from 1 to the number of the frames in total by time sequence. Since the length of a typical data set would be in the order of 100,000 seconds, the video clips are usually few G in size.

In order to get useful numbers to do the data analysis, the videos are first cut into frames using ‘ffmpeg’ program, which is completely open sourced in the community. The specific command used is: `‘nohup ffmpeg -i <your-video-file> -r <max-frame-per-second> -f image2 %05d.jpg &’`.

After all the frame files are prepared, they are often grouped by time sequence with a usual group size of 10,000 frames. This is to limit the frame number to be processed each time due to RAM limitations. The grouping process is done by a python script which is faster than MATLAB.

One thing subtle but important is that frames are only temporal by-products of the data analysis. Since the video encoding can save up to 70% of the storage memory compared with using single frames, frames are converted back to the long videos after the calculation. It is the reverse version of the cutting by ‘ffmpeg’ tool. The specific command used is: `‘ffmpeg -r <frame-per-second> -f image2 -start_number <start_number> -I %0<padding_number_of_0>d.jpg -vcodec libx264 -crf 15 -pix_fmt yuv420p <videoname>’`



3.1.2 Image to 0.dat conversion

To investigate the dynamical properties of the system, the information we need from the raw data are as follows: All particle size and position at all time. The system is 2-D so the position is divided into X-axis and Y-axis values. The particles are identified in every individual frames by MATLAB built-in program 'imfindcircle.m'. A particle label is being tagged to each particle in the frame founded and the frame ID that found that particle as well. The data structure after the process of finding particles is:

X	Y	Mass (Area)	Radius	Frame-ID	Particle-ID
---	---	-------------	--------	----------	-------------

Table 3.1 The basic structure of the data

Afterward, a track program is utilized to keep the particle labels in different frame consistent, i.e. connect the separated frames by locating the closest particles in subsequent frames. Therefore, the 0.dat file would take the structure below, all the information acquired from the experiment result would be contained in this large matrix, which was extensively analyzed throughout the whole project using different datasets.

X	Y	Mass (Area)	Radius	Frame-ID	Particle-ID
X00	Y00	Mass 0	Radius 0	0	0
X01	Y01	Mass 0	Radius 0	1	0
...	...	...	...	...	...
X0,nf	X00	Mass 0	Radius 0	#frames	0
X10	Y10	Mass 1	Radius 1	0	1
X11	Y11	Mass 1	Radius 1	1	1



...	...	...	...	...	...
X _{n,nf}	Y _{n,nf}	Mass n	Radius n	#frames	#particle

Table 3.2 The sequence of frame and particle in data files

3.2 High-Precision Density Calculation

3.2.1 Density measurement problem

The glassy dynamic problem lies in the dynamic arrest of the glass when the Temperature is around T_g . Since colloidal glass's dynamical arrest problem is highly dependent on the density of the system, having a clear and high-precision density calculation algorithm is crucial as it lays the foundation for this research.

Due to its great importance and significance to the analysis of the dynamics of the glassy colloid, solid research and trails have been done in the pursuit of a reliable algorithm to calculate the system density. MATLAB built-in function 'imfindcircle.m' was chosen to locate the position and the radius of the particles. However, as Fig. 3.3 shows, the particle radius identified by the function is smaller than its actual radius due to optical limitations. Since the blurred boundaries can hardly be resolved, the only way to get the precise radius is to add up the particle radius

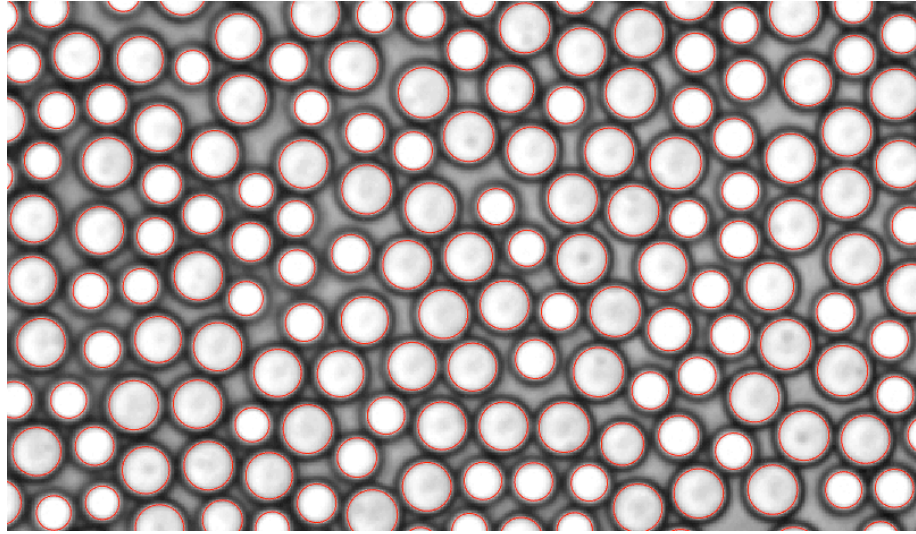


Fig 3.3 Detailed plot of the particle radius before the algorithm

3.2.2 Nearest-neighbor algorithm

The nearest neighbor algorithm is the algorithm that we ultimately chose to solve the density measurement problem. It is based on the assumption that the particles are touching each other in the majority of cases except for the extra-low density datasets. The algorithm first identifies the nearest-neighbors of every particle and then add up their radius by a small step if they do not touch with any of its neighbors.

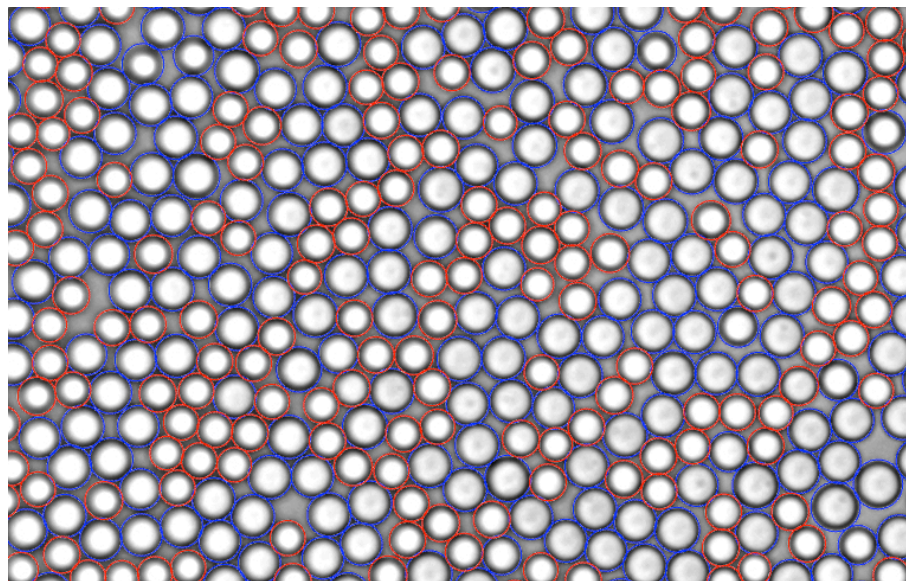




Fig 3.4 Detailed plot of the particle radius after the algorithm

Meantime, the accuracy of the algorithm is not only justified by visual comparison but from the radius distribution of the system. The experimental sample provided by the manufacturer states that the bi-system is having a radius ratio of 1.22. After fitting the histogram of the particle radius, the ratio of the big particle and small particle radius lies within the range of 1.222 – 1.227, which is very close to the manufacturer parameter. The fitted histogram is shown in Fig. 3.5

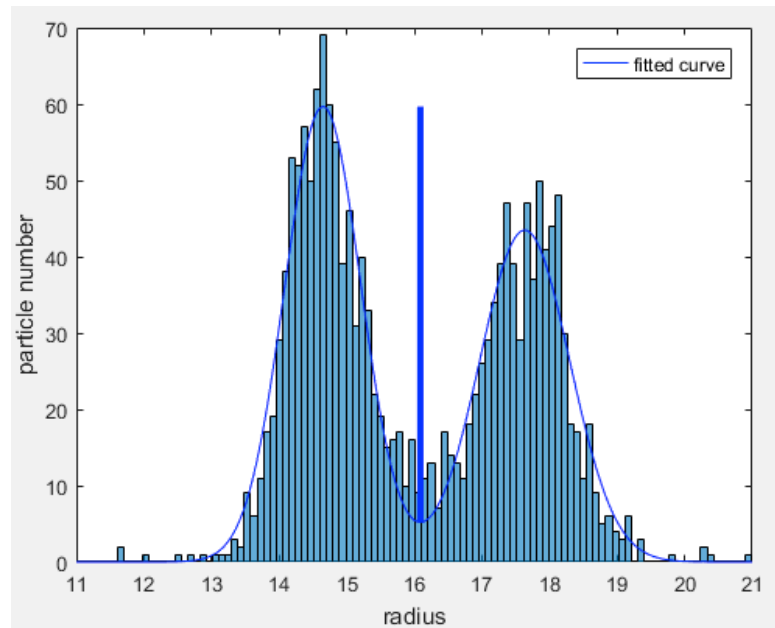


Fig. 3.5 Radius distribution of the bi-system with the bi-gaussian curve fitted

3.3 System noise and Microscopic movement subtraction

3.3.1 System noise problem

The experimental data is acquired by long-time microscopic confocal filming.



The typical filming time is so long that the gravitational pull of the microscope would defocus, which lead to a very blurred image. Although the microscope is checked regularly and hand-adjusted back to the focusing point once in a while, there is still part of the frames being filled with noise. The sample of the blurred frame is shown in the Fig. 3.6 below. As the red circle labels the noise in this particular frame, it is even hard to identify the particle visually whether there is a particle or not, longer data sets would tend to have more problems like this.

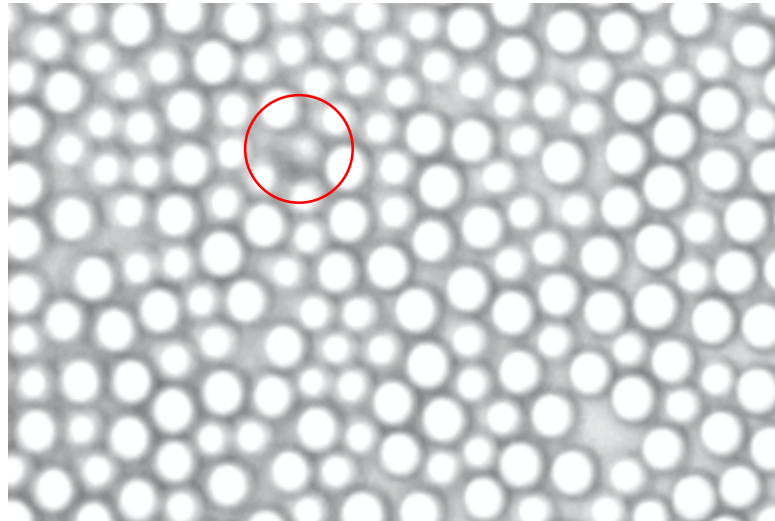


Fig. 3.6 Noisy particle that can not be detected

For the trajectory graphs, the missing particle would be a huge problem introducing lots of black points and also have a negative impact on other calculations like mean square displacement (MSD) and hopping return rate. Therefore, it is crucial to do some correction to the data so that the noise is suppressed and the main feature of the system is captured. To illustrate the severeness of the problem if no noise control is done, Fig. 3.7 is provided for reference of an unfiltered data trajectory. There are lots of black points indicating missing particles and also edge would have more noise to



suppress.

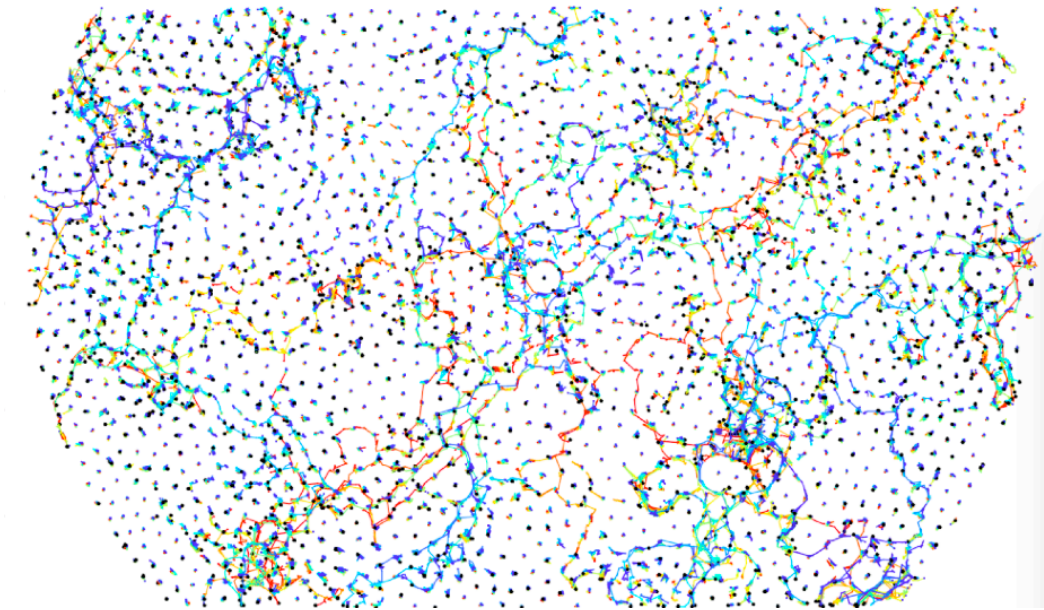


Fig. 3.7 Unfiltered data trajectory graph

3.3.2 Filter and fill-in algorithm for noise suppression

The filtering and fill-in algorithm is used to process the noisy data. It first layout the histogram of the particle appearing in different frames. Typical data would have large amount of the particles found in the majority of the frames and some of those missing due to defocus. The histogram Fig. 3.8. shows that this data is relatively well focused, having the absolute majority of the particles at the maximum frame number and some small noise at 20000 frames. The first step to do is to cut the particles that are appearing too little frames, which would be the left part of the red line shown.

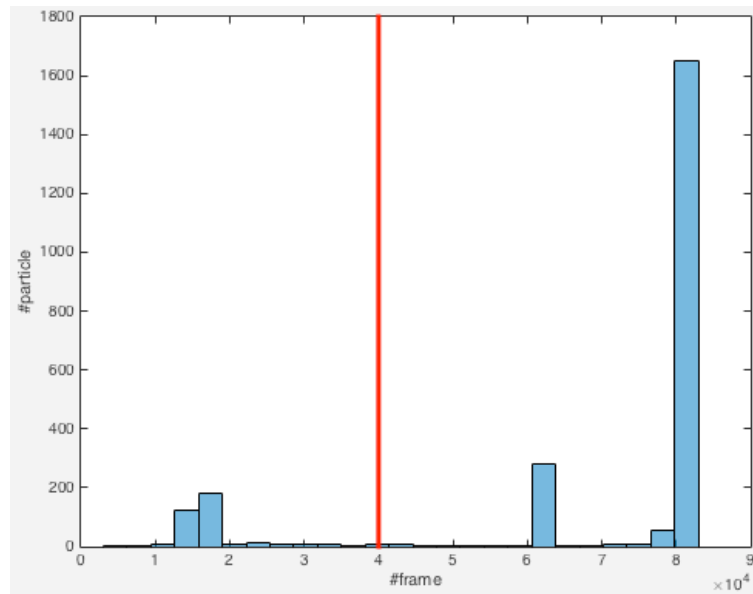


Fig. 3.8 Histogram of particles frequency in a typical game containing 2100 particles

Afterwards, the algorithm would fill in the position of the particles by postulation based on their position before or after it is missing. There are three possibilities for noise data: (1) Missing from the beginning (2) missing from the end (3) missing in the middle part. These three cases are not mutually exclusive, i.e. they can happen for the same particle if the frame is very blurred. For the (1) and (3) case, the algorithm has no idea where are that particle went afterward or beforehand, therefore the only reasonable thing to do is to fill in the particle position that last detected and let the particles remain in those positions. For the case (2), the middle positions of the particle can be postulated at the transition state between the two known state. The position will be having the same separation for all the middle-missing part. Meanwhile, if the particle detects one other particle having the similar position but not overlapping through the entire length of the experiment, it would connect the two ‘half-appearing’ particles and make them the same particle as in case (2). The result of the noise reduction is shown in the Fig. 3.9. Not only did it remove the black points but also



connected particles that are separated by the noise.

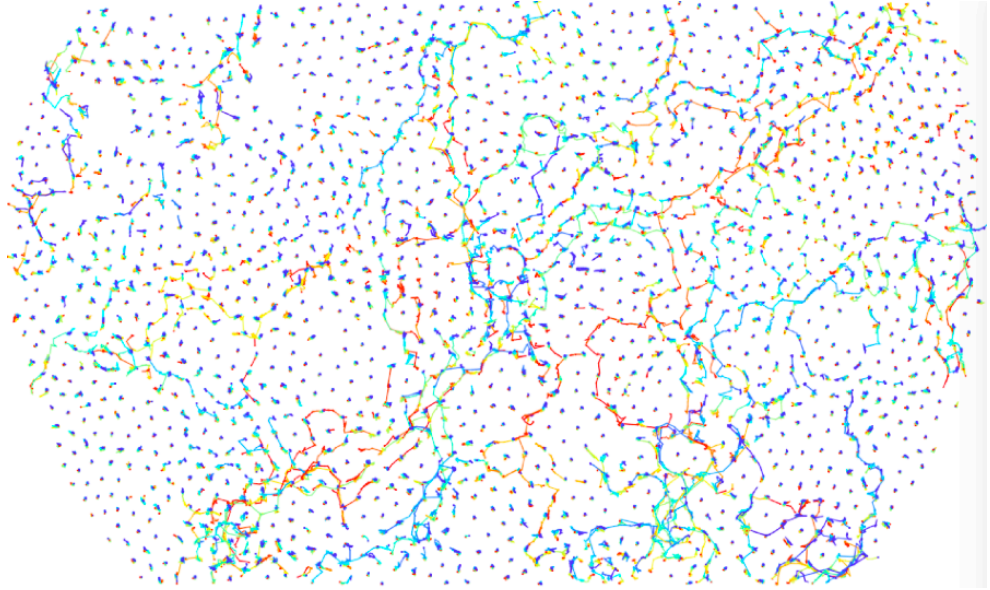


Fig. 3.9 Filtered data trajectory path

3.3.3 Microscopic movement reduction Problem

Despite the experiment were carried out with extreme care, the microscope unavoidably would experience some force during the long experiment time. Though the shake of the microscope can be undetectable for human beings, the effect is devastating for data analysis since all the particles would be shifting from one position to the other position with its own vibrational motion. The Fig. 3.10 illustrates one of the examples that the microscope is moving.

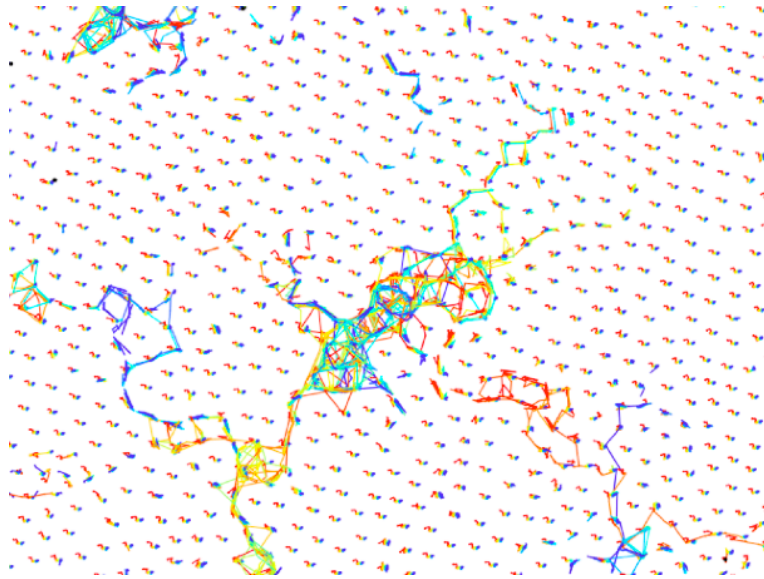


Fig. 3.10 Microscopic movement causing data distortion

3.3.4 Collective movement reduction algorithm

The algorithm reduces the collective movement of the particles. The first version of the algorithm was based on the assumption that the whole system is stationary and would not have collective mass flow. However, after few trials, the first version of the algorithm failed because of the open system and the fact that some particle moved a long distance after a long time. Therefore, the second version of this algorithm, it chooses the least mobile particles, say 10% ranked lowest on the displacement rank which are the ones that only vibrates around its stable position, and subtract the averaging movements of those 10% particles. The resulting trajectory in Fig. 3.11 clearly states the validity of this algorithm since it successfully subtracted all the movement of the microscope.

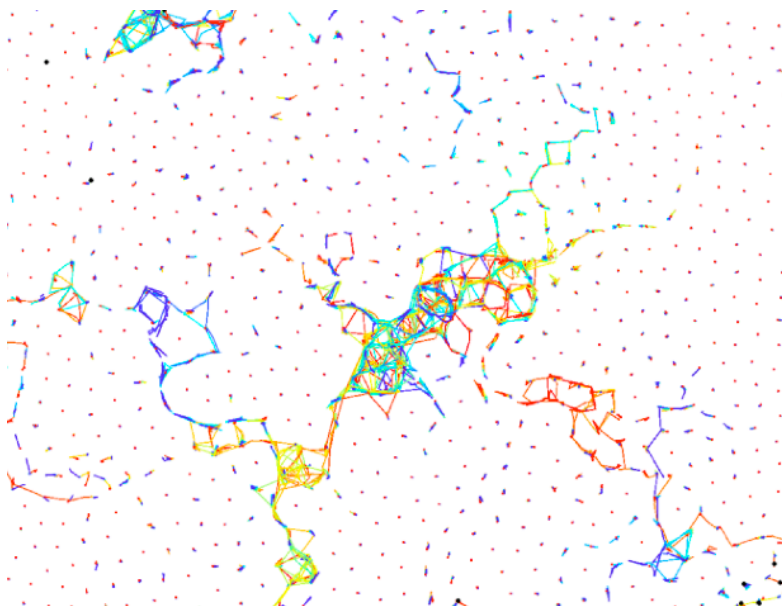


Fig. 3.11 Particle trajectory after the subtraction



Chapter 4 Hopping Events in Glass Dynamic

4.1 Hopping and creeping

From the Previous trajectories, quick observation can be made that the mobile particles are having long-range motion and the immobile ones are just vibrating around its original position. Then we can consider separating this kind of motion with the vibrational motion since these are the ones that can really contribute to the system dynamic. Here we consider a sequence of n time steps t_k , where $k = 1, 2, 3 \dots n$, for analyzing motions of particles. A particle i displacement $\Delta \vec{r}_{ik} = \vec{r}_i(t_{k+1}) - \vec{r}_i(t_k)$ can be subdivided into the hopping and creeping parts (see Fig. 1a-1b). If $t_{k+1} - t_k \geq \delta t$, where δt is the average hopping time of the particles in the binary system, the string-like motion can be captured with an appropriate coarsening time Δt_c

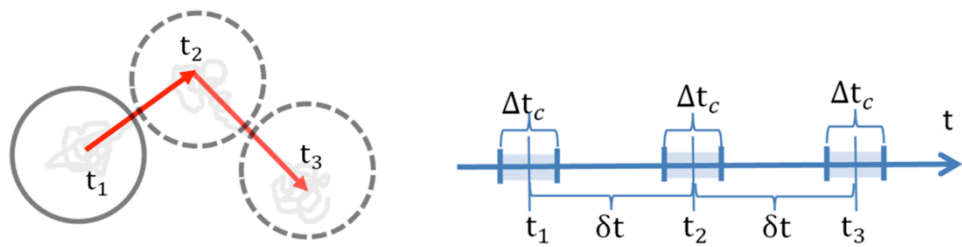
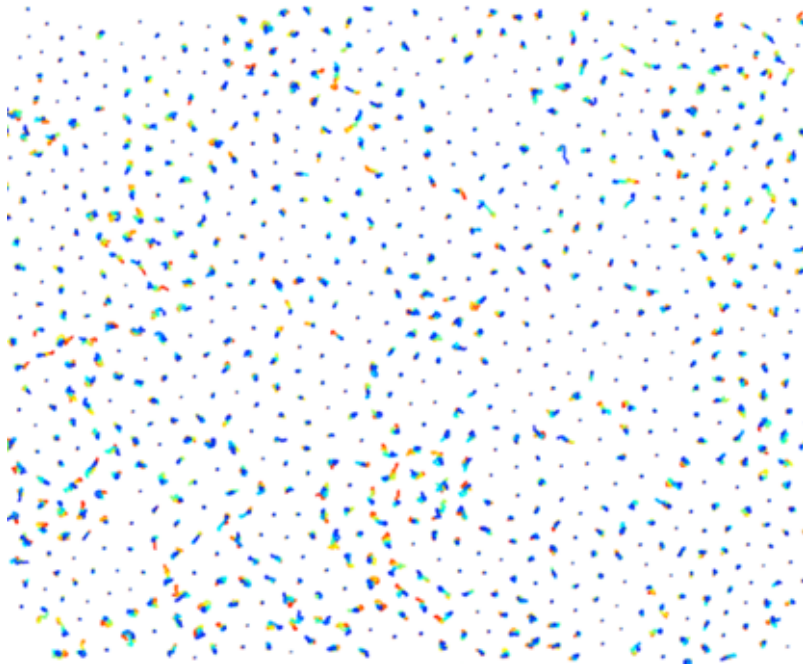


Fig. 4.1: a) particle motion (grey line) with hopping event (red line); d) time sequence, hopping and coarsening times for analyzing particles trajectories;

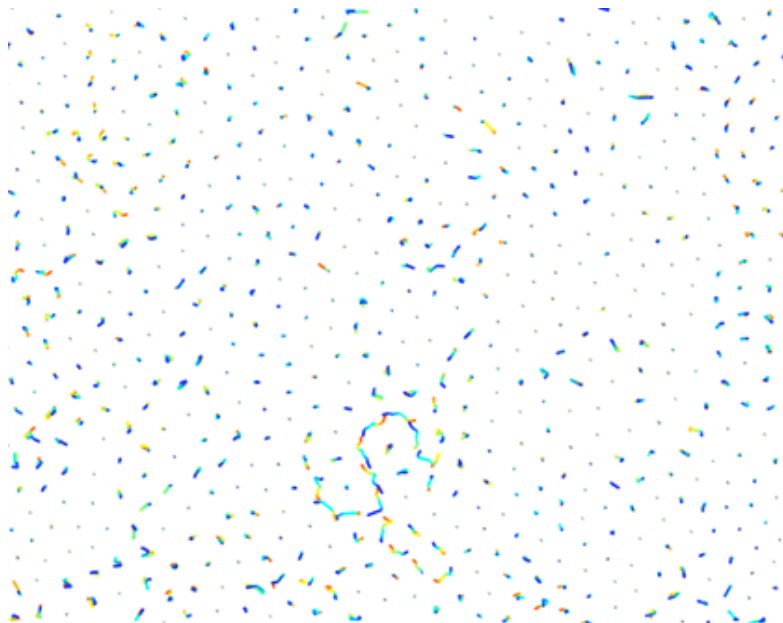
The visualization of the particle trajectories using different time length and



coarsening time is displayed in Fig 4.2 where clear and straightforward intuition given. With larger and larger observation time, the motion of the particles changed from mainly random vibration around its stable position to hopping to the next stable state and finally they exhibit long-range string-like motion that contribute to the dynamics of the system,



(a)



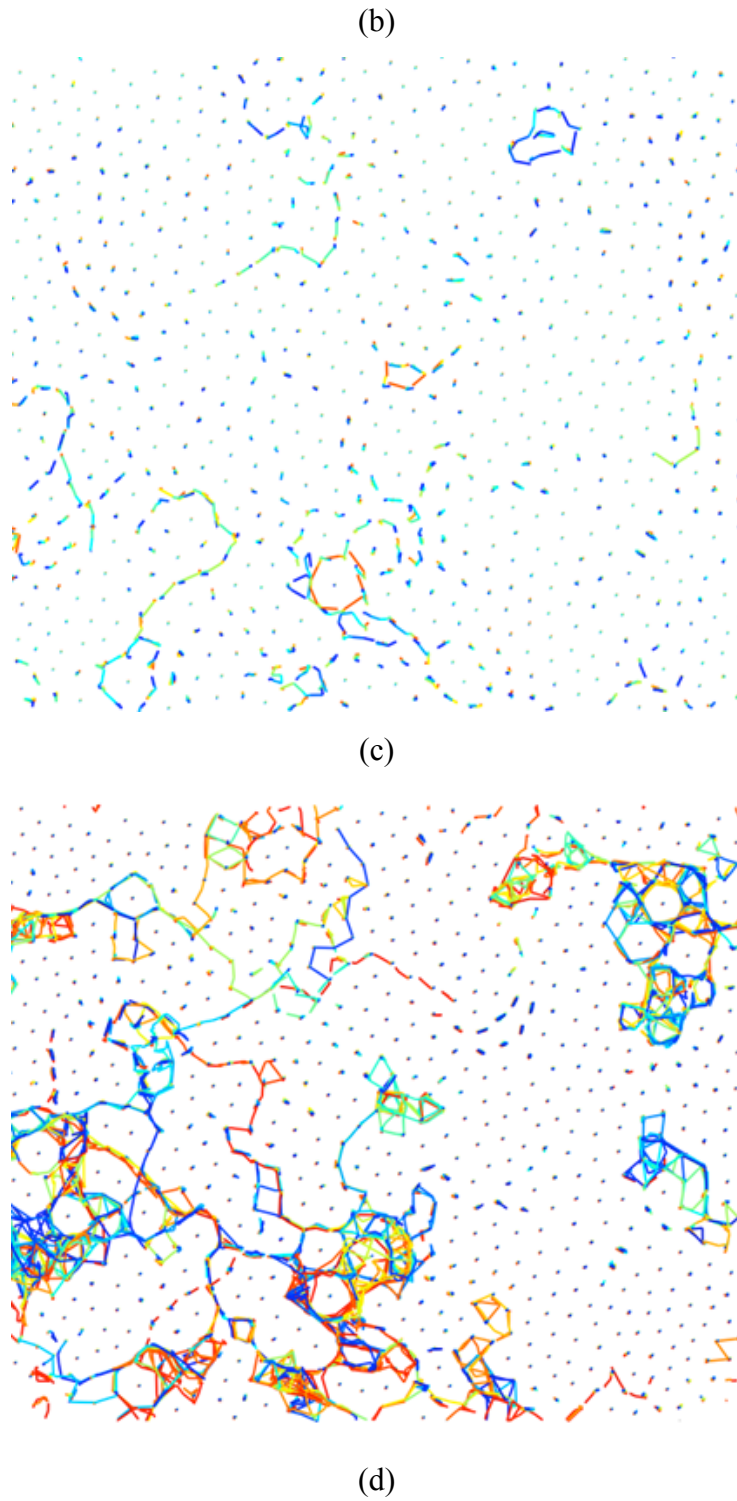


Fig 4.2 particle trajectory for various time lengths with increasing coarsening time

a) $\Delta t_c = 7.5$ s, $n_{seg} = 80$, $T = 600$ s; b) $\Delta t_c = 120$ s, $n_{seg} = 10$, $T = 1200$ s; c) $T = 6000$ s, $\Delta t_c = 600$ s, $n_{seg} = 10$; d) $T = 600000$ s, $n_{seg} = 80$; Note that $n_{seg} = T/\Delta t_c$.



Fig. 4.2 a) - 4.2 d) are the coarse-grained particle trajectories of the centers of about 800 closely packed spherical particles for various durations T and Δt_c from a colloidal experiment ($\rho = 0.75$). Each trajectory consists of a number of segments n_{seg} joining time-averaged particle positions colored according to time with red (blue) being the earliest (latest). Fig. 4.2 a) shows the trajectory plot with short duration and coarsening time ($T = 600$ s and $\Delta t_c = 7.5$ s), where all particles were oscillating around their metastable sites. However, when T and Δt_c are long enough ($T = 1200$ s and $\Delta t_c = 120$ s (see Fig. 4.2b)), the first string-like motion can be observed. If T and Δt_c are further increased, more string-like motions occurred at a different time can be captured by the coarse-grained trajectory and all oscillating motions can be averaged out in the trajectory plot (see Fig 4.2 c-4.2d).

4.2 Mean Square Displacement (MSD) for hopping and creeping

To determine the roles of hopping and creeping motions in the mean squared displacement (MSD), we defined the hopping and creeping displacements of a particle as the followings:

$$\Delta \vec{r}_{ik}^H = \Delta \vec{r}_{ik} \theta(|\Delta \vec{r}_{ik}| \geq r_d) \text{ and } \Delta \vec{r}_{ik}^N = \Delta \vec{r}_{ik} \theta(|\Delta \vec{r}_{ik}| < r_d), \quad (4.2.1)$$

where the hopping distance r_d is defined by the dip of the histogram (see Fig. 4.3).

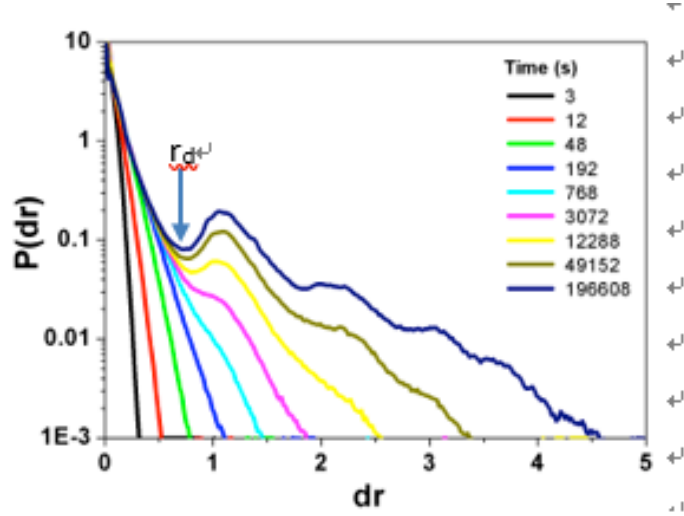


Fig. 4.3 Histogram of displacement using semi-log scale with different time separations

From the histogram, one can clearly see the difference between common vibrational movement and the rare hopping events that only become obvious in a longer time separation. The peak around 1.3 sigma in the dr signifies that typical hopping distance and the dip around 0.9 sigma gives us a good criteria to separate hopping or vibration. This histogram is very typical in experiment where all the experimental data with longer time exhibit same trend where clear dip and peak position can be located around 1 sigma, which can also prove existence of the hopping motion in colloidal glass system.

We count $\Delta \vec{r}_{ik}^H$ and $\Delta \vec{r}_{ik}^N$ from initial frame to final frame with a fixed time interval $\Delta t = t_{k+1} - t_k$. However, if $\Delta t = t_{k+1} - t_k < \delta t$, most of the hopping events cannot be captured. Therefore, we need to select Δt in which all of the first hopping events in the particles can be taken into hopping distance before the occurrence of the second hopping events.



The total displacement of a particle caused by the hopping and creeping motions up to the time of t_n can thus be determined by:

$$\vec{l}_i^H(t_n) = \sum_k \Delta \vec{r}_{ik}^H \text{ and } \vec{l}_i^N(t_n) = \sum_k \Delta \vec{r}_{ik}^N. \quad (4.2.2)$$

Therefore, the total displacement of the particle $\vec{l}_i(t_n)$ is:

$$\vec{l}_i(t_n) = \vec{l}_i^H(t_n) + \vec{l}_i^N(t_n), \quad (4.2.3)$$

By using eq (2), we can determine the contribution of hopping and creeping events on MSD. The interrelationship between the total MSD $g(t)$, $g^H(t)$ and $g^N(t)$ is:

$$g(t) = g^H(t) + g^N(t) + g^{corr}(t), \quad (4.2.4)$$

where the $g^{corr}(t)$ is the correlation function of hopping and creeping MSD, $g^H(t)$ and $g^N(t)$.

4.3 Ratio of MSD-hop and MSD-creep

We also compare the significance of hopping and creeping motions in a long time MSD by:

$$R^H(t) \equiv \frac{g^H(t)}{g^H(t) + g^N(t)}. \quad (4.3.1)$$

To further improve the accuracy of Δr_{ik}^H , the hopping displacement $\Delta \langle \vec{r}_{ik} \rangle_{\Delta t_c}$ is determined by the following way:



$$\Delta \langle \vec{r}_{ik}^H \rangle_{\Delta t_c} = \Delta \langle \vec{r}_{ik} \rangle_{\Delta t_c} \theta(|\Delta \langle \vec{r}_{ik} \rangle_{\Delta t_c}| \geq r_d), \quad (4.3.2)$$

where Δt_c is the coarsening time for removing the oscillating motion part in the hopping displacement, and the net displacement that is not part of the hopping motion will be substituted into the creeping term:

$$\Delta \vec{r}_{ik}^N = \Delta \vec{r}_{ik} - \Delta \langle \vec{r}_{ik}^H \rangle_{\Delta t_c}. \quad (4.3.3)$$

Therefore, the error in Δr_{ik}^H induced by the oscillation can be averaged out by Δt_c .

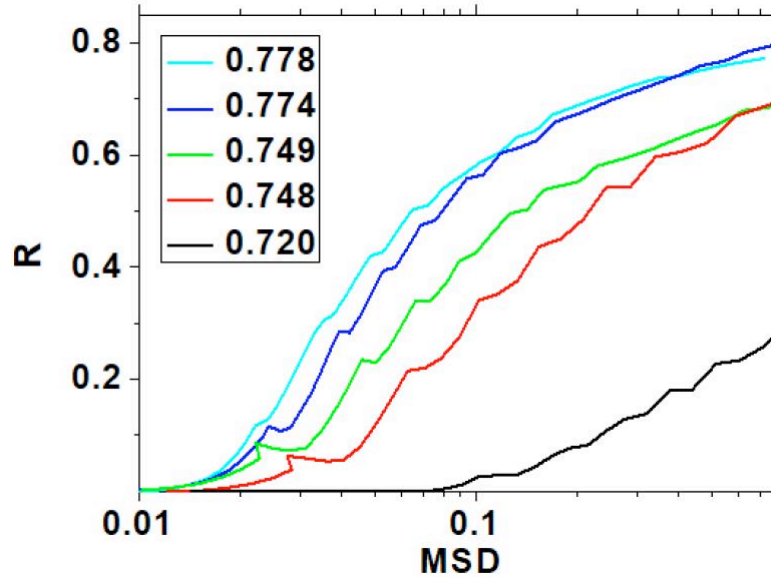


Fig4.4 R-value versus MSD with various density data

From the Fig 4.4, one can clearly see that the dominance of the hopping motion in the dynamics of the system. For high density case, at long time scale with $\text{MSD} \approx 1$, the R value can be larger than 85%. For medium density case (0.74), the R value can go to nearly 70%, which still shows the dominance of the hopping events in the dynamics of the glassy system.



From lower density (0.720) to increasingly higher density (0.778) cases, the R value increase substantially. Not only did the density-dependence of the R-value can be clearly observed, the relationship between the R value with increasing MSD is also interesting. At lower MSD, the vibration contributes to majority of the motion. As time goes by, more and more hopping events occurs and the R-value would rise. From the trend of the R-curve, the R-value would be likely to stabilize and approach to certain value which is close to 1. The underlying implication is direct that the glassy system dynamic is dominated by hopping motion in long-time, or to be more specific, high-MSD scale.



Chapter 5 Return and Escape Events

5.1 Return and dynamic slow down of the glass system

The dynamic of the glass is strongly dominated by the hopping events. However, this does not illustrate the whole picture of the glass dynamic problem since it is not giving enough information for explaining the dynamic slow down of the system. Therefore, the next step of the research is to develop a quantitative understanding of what factor really induced the dynamic slow down of the glass system.

According to DPLM theory, the dynamic slow down of the glass system is largely due to the returning events after the particle hopping events. As the hopping motion contributes to the total MSD, that is to say, the hopping motion induces the dynamic property of the system, the majority of the hopping events are followed by returning events in system close to the dynamic slow down (For colloid, it is having a higher density and for polymer glass it is having a lower temperature that is closer to T_g).

5.2 Definition of Hop, Return and Escape Events

Though the hopping events are strictly defined in the previous chapter with Equation 4.2.1. Graphic representation is used for better illustration of the event and helps to gain much more intuition for understanding returning and escaping events. Fig

5.1 defines the hopping events as having a displacement larger than the hopping threshold, which was also defined in the previous chapter, in a given time limit.

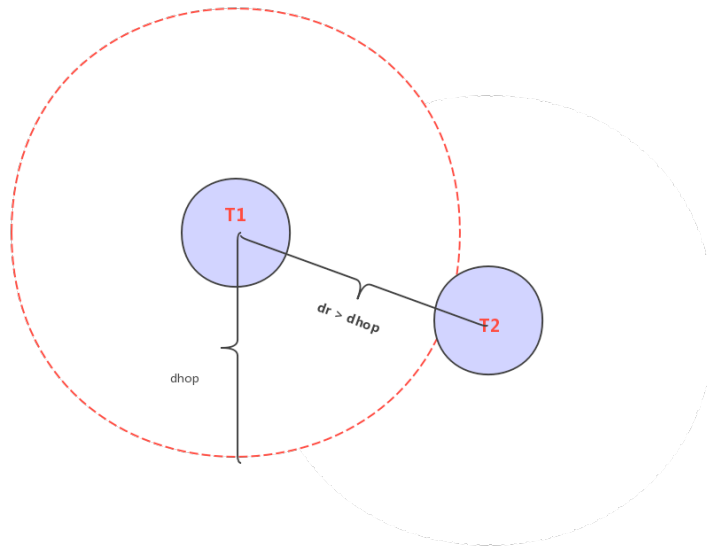


Fig. 5.1 Hopping Event definition

After we define the hopping motion, the other two special events can be defined by dividing the subsequent motion after this particle hop into 2 categories. The first one is the returning event. Simple as its name suggests, it is the event that the particle ‘returns’ back to its position after hopping motion. A simple illustration can be found in the Fig. 5.2. The T3 is long respect to the T1 and T2 since one particle can wait till a long time vibrating around its new meta-stable position before it returns to the previous meta-stable position. The returning position would be valid if the particle returns to the half of the hopping threshold within the previous position of the particle before hopping. As long as the particle is found within that range, it counts as a returning event.

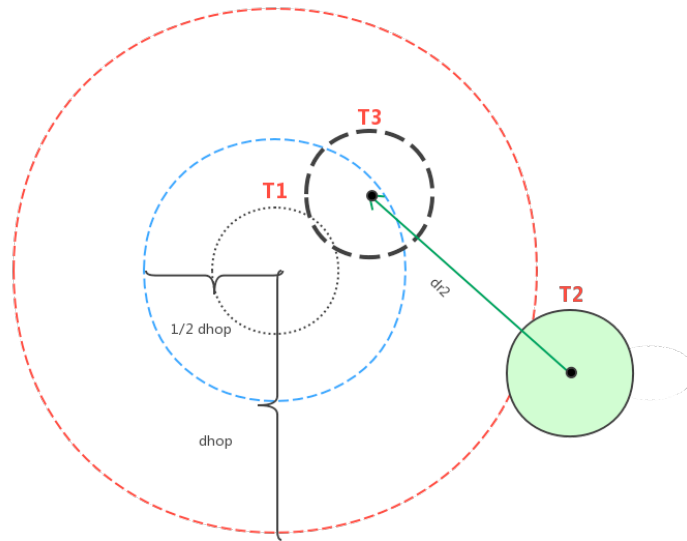


Fig. 5.2 Returning event definition

Apart from the returning, a particle can also hop to other positions which are not in the vicinity of the original position. This process can also take a long time compared with T1 and T2 separation. The Fig. 5.3. gives a clear description of the situation when a particle escapes from its original position as well as hopping position. Though for the sake of saving space, the plot drawn showed opposite escaping direction from the hopping direction. However, the escaping direction is not known to have any preferred direction since the string-like motion can be in all random other places except returning.

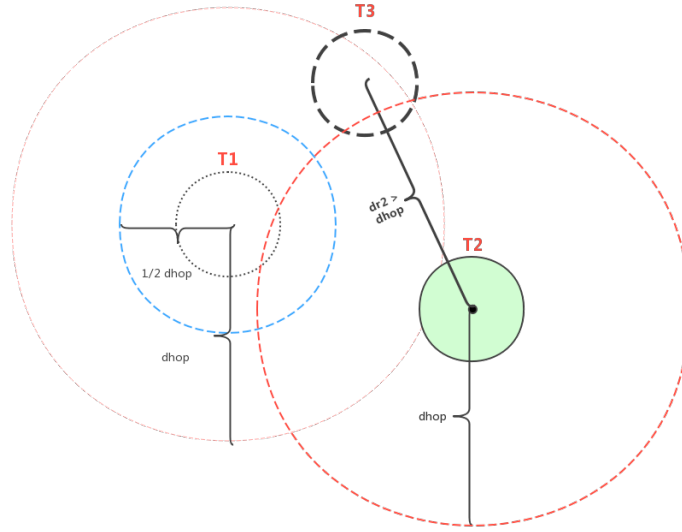


Fig. 5.3. Escaping Event definition

The returning combination of the two subsequent motions largely affects the dynamic of the system. In ideal cases, all the particles would exhibit one of the above-mentioned subsequent moves after a hopping incident. However, due to realistic limitations like finite observation time as well as the impurity of the data (Some of the particles remains at the position last seen due to fill-in process), the returning and escaping event can only reach 90% of the hopping events. Though there are few particles remaining in the same position after hopping, the 90% found is already sufficient to illustrate how the dynamic property being affected by this phenomenon.

5.3 Return and Escape Probability

The influence of the returning and escaping events are measured by their probability of happening. By comparing the returning and escaping probability for all range of density of the experimental data, the results are plotted in the Fig. 5.4

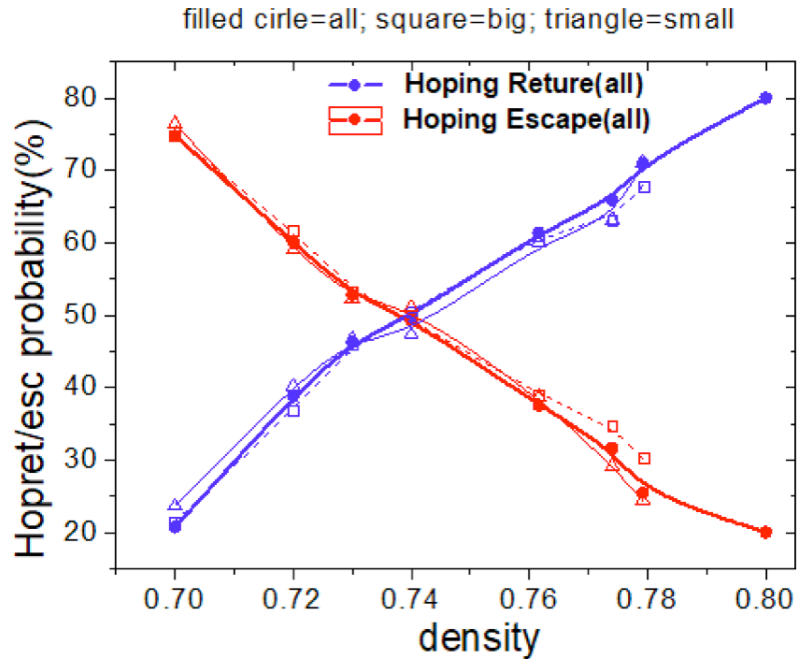


Fig. 5.4 X-curve of return and escape probability

This figure is one of the most important results in this whole project. With a clear trend of rising return probability and dropping escape probability. The upper limit of our experimental data was around 0.8 and higher density is hardly achievable to gain a reasonable MSD. The dynamic would be too slow and the time it takes to get sufficient data for densities above 0.8 would be more than 3 months, which is not a worth-paying price. The lower bond of the experiment density lies around 0.7 where the escaping probability is approaching 80%. The crossing point is around 0.74 where the hopping and return probability is equal indicating half of the particle hop eventually goes back to the original position. With the clear upward trend of return probability, extrapolation can be drawn that with even higher density (Approaching T_g in glassy system), the return probability can approach 100%, that is almost all the particle hops returned finally, causing the dynamic slow down.



Chapter 6 Conclusions and Future Recommendation

6.1 Conclusions

6.1.1 Dominance of Hopping motion in the glass dynamic in colloidal systems

Through the in-depth analysis of the R-value (Ratio of MSD-hop and MSD-hop+creep) as well as the X-curve showing the hopping return probability, convincing conclusion can be drawn that the DPLM model is well supported by the experimental data. From the R-value curve we can see that the glass dynamic is well dominated by the hopping motion instead of the creeping motion as at even low density, the R-value can go over 50% and at high density region the R-value raise to over 80%. The implication is clear that there is a positive correlation between the system density of the colloidal glass and the dominance of the Hopping motion in the total dynamic of the system. This may well imply that in other glass systems, it is also true that when temperature approaches T_g , the contribution from the hopping motion would far exceed the contribution of the creeping motion, which controls and plays an important role in the dynamic slow-down phenomenon.

6.1.2 Dominance of Returning Events after hopping motion

Though clear trend has shown that the glass dynamic is dominated by the hopping motion instead of creeping motion, it is not sufficient to cause the kinetic arrest of the glass system. However, combined with the dominance of the returning events when approaching T_g , the picture became much clearer.



As the Chapter 5 result shown, after a particle hops, there is a high chance that it is going to return back to its original position in later time, especially in higher density cases. This is like solid that single voids would vibrate around its energy trough. As in the low density cases, they have a higher probability to escape away. It is like liquid where particles escape too fast that they are indistinguishable.

The dominance of returning probability in high density gives strong implication of how glassy states' dynamic lie between liquid and solid. Combined with the dominance of the hopping motion, it became strong evidence explaining the dynamic slow-down of 14 orders of magnitude.

If we extrapolate even higher density cases, that is analogous to pushing the temperature towards the kinetic arrest limit T_g , the Hopping motion would be strictly dominate and eventually all the dynamic property would be contributed by the hopping motions. Meantime, the returning probability would also approach to 1, which is saying that except for few extremely scarce case, the particle hopped would return back to its original position before the hopping motion. **Combining these two pieces of information together, a dynamic arrest can be predicted and substantiated.**

6.2 Future recommendations

6.2.1 Exponential waiting time of subsequent event after hopping

Though the results are sufficient to support the DPLM theory in return probability and hopping motion dominance in glassy system, further work can be done to further justify the validity and accuracy of the theory. One thing particular from the simulation results from DPLM model is the exponential



waiting time of the returning and escaping events. Further investigations and analysis can be done to verify this particular trend.

6.2.2 String pattern recognition—Closed Loop and Open String

Also, from the experimental trajectories plots, observations can be made that the string-like motion can be further categorized into two bins. One is the regular string which ‘head’ and ‘tail’ of the string can be easily located. The other part of the trajectory pattern is the ‘loop’ where the hopping motion forms a closed-loop structure and repeat itself. It is worth studying the underlying reason for why these two particular structure of string exist and how does it contribute to the kinetic arrest problem.

6.2.3 Quasi-void Identification and quantitative measurement

Moreover, one concept has been vague and non-quantified since the beginning of this project. It is the quasi-void that is causing the particles to hop in high density, which is the co-effect of several neighbouring particles. It has be postulated that at every string-like motion, there is a quasi-void propagating through the string and leading to this hopping and returning events. However, we did not defined it quantitatively so that one can count the number of quasi-void affecting the behavior of the glassy system. Further investigation can be done on the existing data to measure the qausi-void with a more strict and quantifiable manner.





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