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Order and Asymmetry in Jammed Systems

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ORDER AND ASYMMETRY IN JAMMED SYSTEMS

by

ZHUSONG LI

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy
The City College of the City University of New York

2015
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Supervisory Committee

THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK
Abstract

Order and asymmetry in jammed systems

by

Zhusong Li

Adviser: Mark D. Shattuck

Granular matter is composed of particles that are big enough that thermal effects may be neglected. We studied both granular flow and granular statics using numerical simulation. In granular flow, we simulated 2D granular flow in a hopper. A hopper is a container with an opening at the bottom. Simulated disks are placed in the hopper with the bottom closed and then released. We developed a new tangential force model to simulate hopper flow, that matches experiments and shows that the output flux is proportional to the bottom opening size to the $3/2$ power. We also see clogging or jamming and estimate the jamming probability. We applied our force model to a 2D rotating drum simulation and studied the statistics of avalanches. In many systems, from earthquakes to plastic deformations the avalanche size probability $F(I)$ is a power-law in avalanche size $I$. We find $F(I) \propto I^{-1.29}$ for our system. We also find that the scaled average avalanche shape is parabolic as predicted by mean-field theoretical models.

In many systems, we would like to measure the degree of crystallization. $Q_6$ is a
common order metric used to detect hexagonal symmetry, and it works very well in mono-disperse systems. However, when we consider bi-disperse and poly-disperse systems, and other non-hexagonal lattices, $Q_6$ is not as useful. We developed a new order metric, Voronoi entropy, based on Voronoi tessellation and information theory. The main idea of the Voronoi entropy is to detect and quantify unique Voronoi polyhedrons. Voronoi entropy can successfully find lattice order in bi-disperse crystal and other structures like simple cubic, body-centered-cubic, for which $Q_6$ is not sensitive.

We performed molecular dynamics (MD) simulations of binary Lennard-Jones systems to model the crystallization process during heating and cooling protocols in metallic glasses. We measured the minimum cooling rate $R^*_c$ to crystallize a liquid and the minimum heating rate $R^*_h$ to crystallize a glass formed prepared using a fast quench at rate $R_p$. We find: (1) $R^*_h > R^*_c$ in all systems. (2) The asymmetry ratio $R^*_h/R^*_c$ increases as $R^*_c$ increases. (3) The critical heating rate $R^*_h(R_p)$ has an intrinsic contribution $R^*_h(\infty)$ and protocol-dependent contribution $R^*_h - R^*_h(\infty)$ that increases with decreasing preparation cooling rates $R_p$. We show all of these findings are in agreement with classical nucleation theory.
Acknowledgements

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2.6 Avalanche magnitude versus frequency. This is done in experiment.

Comparing with simulation, a bump is found at tail and here

$$f(I) \sim I^{-1.36}.$$ In simulation, $f(I) \sim I^{-1.29}.$

2.7 Avalanche Duration versus frequency. This is done in experiment. A bump is also found at tail.

3.1 Packing fraction versus $Q_6.$ In mono-disperse system, $Q_6$ is generally increasing when packing fraction increases. This plot is a case that we prepare system very slowly, so system get crystallized and $Q_6$ arrives maximum 0.57. If we quench system fast, system will be jammed at lower fraction and $Q_6$ can’t reach 0.57, which refers to Random Close Packing.
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4.2 Shifted and normalized probability for crystallization

\( \frac{P(R_{h,c}) - P_\infty}{P_0 - P_\infty} \) versus the scaled heating or cooling rate

\[ \log_{10}(\frac{R_{h,c}}{R_{h,c}^M})^{1/\kappa_{h,c}} \]

Circles (squares) indicate data for cooling (heating) for diameter ratios \( \alpha = 1.0 \) (filled symbols) and 0.97 (open symbols). The insets show the fraction of crystal-like particles \( N_{cr}/N \) as a function of temperature \( T \) during cooling (lower left) and heating (upper right) for 12 configurations with \( \alpha = 1.0 \). The four solid, dashed, and dot-dashed curves in each inset correspond to cooling and heating trajectories with rates slower than \( R_{h,c}^* \), near \( R_{h,c}^* \), and faster than \( R_{h,c}^* \), respectively. Trajectories for which \( N_{cr}/N \) exceeds 0.5 (above the horizontal dashed line) are considered to have crystallized during the heating or cooling protocol.

4.3 Maximum value \( N_{c}^{\text{max}} \) of the number of crystal clusters \( N_c(T) \)

normalized by \( L^3/\sigma_A^3 \) (averaged over 1000 trajectories) during the cooling (squares) and heating (circles) protocols at rates \( R_c \approx 0.5R_c^* \) and \( R_h \approx 0.5R_h^* \) for LJ mixtures with diameter ratios \( \alpha = 1.0, 0.97, \) and 0.95. For all systems, the maximum number of crystal clusters is larger for the heating protocol compared to that for the cooling protocol and \( N_{c}^{\text{max}} \) decreases with increasing glass-forming ability (decreasing \( \alpha \)).
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4.5 The nucleation $I/AD_0$ (solid lines; left axis) and growth $Ua/D_0$ (dashed lines; right axis) rates as a function of temperature $T$ for increasing values of the glass-forming ability (GFA) $c = 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6,$ and $0.5$ (from top to bottom) that span the range of diameter ratios from $\alpha = 1.0$ to $0.93$. The filled circles indicate the maximum rates ($I^*$ and $U^*$) for each GFA. As the GFA increases, $I^*$ and $U^*$ decrease and the difference $T_U - T_I$ between the temperatures at which the maxima in $U(T)$ and $I(T)$ occur increases (inset).
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4.7 Asymmetry ratio $R_h^*(R_p)/R_c^*$ plotted versus the preparation cooling rate $R_p$ normalized by the critical cooling rate $R_c^*$ from MD simulations with $\alpha = 1.0$ (filled circles) and the prediction from CNT (solid line) with the same parameters used for the fit in Fig. 4.4 and the GFA parameter set to $c = 1.2$. The vertical dashed line indicates $R_p = R_c^*$. The horizontal dashed lines $R_h^*(R_p)/R_c^* = 1.18$ and 1 indicate the plateau value in the $R_p \gg R_c^*$ limit and $R_h^* = R_c^*$, respectively. The gap between the horizontal dashed and dotted lines give the magnitude of the intrinsic asymmetry ratio for this particular GFA (cf. Fig. 4.4).
**Introduction**

Granular materials are very common in daily life. Granular matter is composed of macroscopic particles, which are large enough that thermal effects on their motion are negligible. Typically, particles larger than one micron can be viewed as granular. Sand, powders, and rocks are all examples of granular materials. Often we are not interested in a single granular particle, whose motion is easily described by classical mechanics. We want to focus on systems, which are composed of many particles \( N > 10^2 \). We can still write down the equations of motion for them, but we can not solve them without a computer. We investigate both dynamics and statics. In dynamics, grains flow like a fluid. In statics or “jamming” particles form mechanically stable states that act like solids.

In chapter 1, we simulate granular flow in a hopper. A hopper is a container with an opening at the bottom for flow. In our simulations granular particles are placed in the hopper. At first, the bottom is closed, and we wait until all particles have stabilize. Then we open the bottom, and the particles begin to flow out from opening. It is similar to liquid flow with resistance. However, ordinary fluid dynamics is not sufficient to explain all the behavior seen in granular flows. One key difference between ordinary fluid flow and granular flow is jamming. In some cases, the particles clog the
opening. We compare our simulation to experiments performed by Behringer with two-dimensional disks in a hopper [1]. We developed a new force model based on the total integrated relative slip distance between particles, and the results compare well with the experiments. One key measurement in hopper flow is the discharge time. Discharge time is defined as time between the $N_{th}$ particle and the $N + K_{th}$ particle flowing out. We finished by confirming that hopper flow can be described as an approximate random process with parameters that correlated with material properties.

In chapter 2, we applied our granular model to a slowly rotating drum, and analyzed the avalanches that formed on the surface as stress built up due to the rotation. A rotating drum is a cylindrical container, which rotates on its symmetry axis with gravity perpendicular the the axis. Particles inside are slowly raised as the drum rotates and avalanche down the surface, when any part of the surface is too steep. We are interested in the statistics of the avalanches. Avalanches are common phenomena. We use an expanded meaning of avalanche as the stochastic relaxation of a system under stress build up. We are interested in the reorganization of the granular system, and we define a significant discrete reorganization as an avalanche. Dahmen et al. [48] use a simple mean-field theory to understand the correlation between avalanche size and avalanche frequency, as well as, avalanche shape. They use simplified lattice
model and found a power law distribution \( F(I) \) of avalanche sizes \( I \):

\[
F(I) \sim I^{-\alpha},
\]

(1)

where \( F \) is the frequency, \( I \) is avalanche magnitude and \( \alpha \) is the power-law exponent.

They also found that the scale invariant average shape of the avalanche energy release as a function time is parabolic. We found simulation results that are consistent with the theory of Dahmen and match experiments performed in our group by Hubard et al. [54]

In chapter 3, we are interested in how to quantitatively measure order in systems using an order metric. An order metric is defined as a quantity to describe the amount order in a system. Order often refers to a crystal lattice. We know that there are an infinite number of lattice types and detecting them using one universal method is very difficult. We focus on a system, which can form a mixture of lattices and random structures. For mono-disperse systems, the bond orientational order parameter \( Q_6 \) is used frequently. Bond orientational order metric was introduced by Steinhardt, Nelson and Ronchetti[46]. They used spherical harmonics \( Y_{lm} \) to define \( Q_l \), where \( l \) can be chosen arbitrarily. \( Q_l \) is used to detect \( l \)-fold symmetry. In a mono-disperse system, particles are packed mainly as FCC(Face centered cubic) and HCP(Hexagonal close packing). Both are 6-fold symmetric, so \( Q_6 \) works well. In chapter 4 we use \( Q_6 \) to distinguish crystal regions and disordered regions, because the crystal structure has hexagonal order. However, in bi-disperse and poly-disperse systems, where the
diameter of particles are different, particles can make other lattices, and $Q_6$ is not a good parameter to determine order in these cases. We introduce a new order metric, the Voronoi entropy, which is based on Voronoi tessellation and Shannon’s information theory[44]. Voronoi tessellation is a mathematical method to divide space into N complete disjoint parts, based on the coordination of N particles. Voronoi entropy can detect any kind of lattices. In a bi-disperse system, we found a simple cubic to BCC phase transition, for which $Q_6$ is not sensitive.

In chapter 4, we focus on simulations of the crystallization of model bulk metallic glasses (BMG) for both cooling and heating, and the asymmetry in critical cooling rate $R_c$ and critical heating rate $R_h$. Crystallization, during which a material transforms from a dense, amorphous liquid to a crystalline solid, occurs via nucleation and subsequent growth of small crystalline domains [3]. Crystallization in metals has been intensely studied over the past several decades with the goal of developing the ability to tune the micro-structure to optimize the mechanical properties of metal alloys [4, 5, 6]. However, in-situ observation of crystallization in metallic melts is limited due to the rapid crystallization kinetics of metals [7, 8, 9].

In contrast, bulk metallic glasses (BMGs), which are amorphous metal alloys, can be supercooled to temperatures below the solidus temperature $T_s$ and persist in a dense, amorphous liquid state over more than 12 orders of magnitude in time scales or viscosity [10]. Deep supercooling of BMGs provides the ability to study crystallization on time scales that are accessible to experiments [11, 12, 13, 14].
These prior experimental studies have uncovered fundamental questions concerning crystallization kinetics in BMGs. Several recent studies [38, 39, 40] focus on a microscopic description of crystallization in supercooled liquids, where a two-step mechanism for crystallization is proposed. While the existence of this process is still under debate, those studies reveal important features of crystallization and the relationship between crystallization and glass transition. Instead of studying the microscopic mechanism for crystallization, we put our emphasis upon the asymmetry of cooling and heating during crystallization. For example, when a BMG in the glass state is heated to a temperature $T_f < T_s$ in the supercooled liquid region, crystallization is much faster than crystallization that occurs when the metastable melt is cooled to the same temperature $T_f$ [15, 16]. Asymmetries in the crystallization time scales upon heating versus cooling of up to two orders of magnitude have been reported in experiments [17, 18]. The asymmetry impacts industrial applications of BMGs because rapid crystallization upon heating limits the thermoplastic forming processing time window for BMGs [19, 20, 21, 22].

Recent studies have suggested that the asymmetry in the crystallization time scales originates from the temperature dependence of the nucleation and growth rates [17], i.e. that the nucleation rate is maximal at a temperature below that at which the growth rate is maximal. According to this argument, crystallization upon heating is faster because of the growth of the nascent crystal nuclei that formed during the thermal quench to the glass. In contrast, crystallization is slower upon cooling since
crystal nuclei are not able to form at high temperatures in the melt. However, there has been no direct visualization of the crystallization process in BMGs, and it is not yet understood why the asymmetry varies from one BMG to another [23] and how sensitively the asymmetry depends on the cooling rate \( R_p \) used to prepare the glass. An improved, predictive understanding of the crystallization process in BMGs will aid the design of new BMG-forming alloys with small crystallization asymmetry ratios and large thermoplastic processing time windows. We performed MD simulation using Lennard-Jones potential [25, 26, 24]. Our system is mixture of \( N = N_A + N_B \) spheres. Simulation is done in constant volume \( V = L^3 \) with periodic boundary condition. We studied mixture with \( N_A = N_B \) and diameter ratio \( \alpha = \delta_B/\delta_A < 1 \). LJ pairwise potential is defined as:

\[
    u(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]
\]  

(2)

\( r_{ij} \) is center to center distance between particle i and j. \( \epsilon \) is parameter of system. \( \delta_{ij} = (\delta_i + \delta_j)/2 \), which is average diameter between each pair. We considered \( N = 1372 \) spheres for most cases and \( N = 4000 \) and \( 8788 \) to assess finite-size effects. We first equilibrate the system at high temperature using a Gaussian constraint thermostat. We cool the system by decreasing temperature linearly at cooling rate \( R_c \) as:

\[
    T(t) = T_i - R_c t.
\]  

(3)
When $R_c$ is below critical cooling rate $R_c^*$, the system crystallizes. When we heat a system, with a heating rate $R_h$ below critical heating rate $R_h^*$, the system crystallizes temporally. We heat system also linearly at rate $R_h$ as:

$$T(t) = R_h t.$$  \hfill (4)

Note that the critical cooling rate is consistent, but critical heating rate depends on preparing rate $R_p$. We first cool the system at rate $R_p$, then heat it using eq 4. Another interesting finding is that $R_h^*$ and $R_c^*$ are not the same and the ratio depends on $R_p$.

In chapter 5, we conclude our study, and in chapter 6 we suggest future direction.
Chapter 1

Granular flow and Jamming in hopper

1.1 Granular flow, Theory

In this chapter, we are focusing on simulating the dynamics of granular particles in two dimensional hopper. A hopper is a container with an opening at bottom as Fig 1.1. At first, the bottom is blocked while particles are added. Then the bottom is opened and the particles start to flow. We are interested in dynamical properties of the flow.

We can vary both to size of the opening \( d \) and the angle of the sloping wall \( \theta \) to change the flow rate. (See figure ??). The mass flow rate is defined as the rate that mass is flowing out per unit time \( dM/dt \), where \( M \) is the total mass. Beverloo found an empirical relation [2] correlating the velocity of flow \( v \) and the opening size \( d \) and the slope \( \theta \).

During outflow, the mass flux is \( j = \rho v \), where \( v \) is speed of the material at the funnel outlet, an \( \rho \) is the mass density. The mass flow rate is \( dM/dt = jA \), where \( A \sim DT \) is the area of the hopper opening and \( T \) is the thickness assumed small for the 2D system. We assume that material fluidized up to \( \sim D \) in the hopper. Hence using
Figure 1.1: Hopper and parameter. Disks are placed in the hopper. We have an opening at bottom with size $d$. There are two sloping walls at the bottom with angle $\theta$. At first, we close the bottom, and all disks are dropped in using our simulation. When the particles are static, we open the bottom and they start to flow. The opening size $d$ and angle $\theta$ are the critical parameters for this hopper.
energy conservation Beverloo found:

\[ v = (gD)^{1/2}. \]  \hspace{1cm} (1.1)

Then,

\[ \frac{dM}{dt} = jA = \rho vA \propto \rho vDT. \]  \hspace{1cm} (1.2)

Combining

\[ \frac{dM}{dt} = C T \rho g^{1/2}(D)^{3/2}, \]  \hspace{1cm} (1.3)

Here \( C \) is material dependent constant. Beverloo found that \( D \) needed to be replaced by the empiric expression, \( D - kd_e \), where \( d_e \) is diameter of particle, and \( k \) is a constant, which also depends on the angle of the slope. In 2D a 2D volume flow rate \( V = (1/\rho T)dM/dt \) is used to obtain:

\[ V = C g^{1/2}(D - kd_e)^{3/2}. \]  \hspace{1cm} (1.4)

First, the use of \( D - kd_e \) is because of the size of the opening must be reduced by the particle size. And we find from experiment and simulation that the angle will change the opening indirectly and \( kd_e \) depends on the angle \( \theta \). If angle is 90 degrees, the hopper is a straight channel and the whole \( D - kd_e \) can be used. But when it is not 90 degree, it causes more collisions near the opening, which will effectively reduce the opening changing the fitted value of \( k \).
One very interesting phenomena, which is different from fluid flow is jamming. In principle, given any size of opening and angle, if the particles are frictional, it is always possible to get clogged at bottom. However, the probability of getting clogged is decreasing significantly as the opening size increases. With the strong Markov process assumption, we get that probability of flow surviving $P_s(t)$:

$$P_s(t) = \exp(-t/\tau)$$  

(1.5)

This $\tau$ depends on both opening size and angle of slope. From experiment, $\tau$ is fitted as Eq 1.6:

$$\tau = A \times \exp(B \times \frac{D}{d}),$$  

(1.6)

where $A$ and $B$ are constant fitting parameters that depend on the angle and friction coefficient.

1.2 Granular flow, experiment details

We collaborate with Behringer’s group at Duke University to simulate the system in Fig 1.2, and here is brief introduction to their experiment’s result [1].

In the experiment the particles are trapped between a pair of Plexiglas plates. Two sizes of disks are placed between plates with diameters of either 0.77cm or 0.602cm, with 62% by number of the sample consisting of the smaller diameter particles. Two types are used to avoid hexagonal packing. In two-dimensional mono-disperse sys-
Figure 1.2: Experiment at Duke. 8750 bi-disperse disks are placed in the hopper. Opening size is around $4 \sim 10$ diameters with a slope between 30 to 60 degree. They measured flow rate and jamming probability times for each many conditions. Flow rate here means mass flow out from bottom per second.
tems, disks pack easily. In hexagonal lattice flow, layers slide and repacked during the process. We are more interested in random flow. With two sizes, is very difficult to get crystallization. In total, there are 8750 disks, and static friction coefficient if $0.7 \sim 0.8$. The width of the hopper is 43cm and the height above and below the opening is approximately 100cm. In their experiment, they enumerate the opening range $2.9cm \sim 7.5cm$ and three typical angle 30,45 and 60.

From the Beverloo equation, we have

$$\text{flux}^{2/3} \sim D - kd_e.$$  \hspace{1cm} (1.7)

From Fig 1.3 we see that in the experiment, $V^{2/3} \propto D - kd_e$ is well confirmed. We find that changing the angle and opening barely changed $k$, but significantly changed $C$.

The jamming probability is mainly correlated with opening size. In the experiment, we can see from 1.4 that the opening size is the exponential of the survival time. This phenomena will be discussed in next section.

### 1.3 New Force Model

We simulate hopper flow with same parameters as in the experiment. Simulations based on kinetic friction are good at simulating flow, but it can not jamming. It is straightforward that when system is jammed, there is no relative motion between disks and all kinetic friction will be zero. Without static friction it will be just like
Figure 1.3: $flux^{2/3}$ versus $D$, which compares well with Eq 1.7, $flux^{2/3} \sim D - kd_e$. In this figure, x-axis is $flux^{2/3}$ and y-axis is $D$. We can see for different angles, proportional correlation is found in experiment. Also all lines are merged at 0.95cm when flux = 0, which determines that $kd_e$ is 0.95cm.
Figure 1.4: Jamming probability versus hopper parameters. Here the jamming probability is described as the time $T$ the flow survived before jamming. In each process, the probability to not jam until time $\tau$ is measured as an exponential decay $P_{\text{survive}}(T) = \exp^{-T/\tau}$. When $\tau$ is small, system is easier to get jammed. This graph shows correlation between $\tau$ and opening size and they get exponential law.
Figure 1.5: New force model. $L_t$ is the cumulative relative tangential displacement between two particles in contact. When $L_t$ increases by a small amount $D$, the tangential force grows linearly. $D$ can be thought of as the typical size of the roughness or asperities on the surface of the particles. $D$ is on the order of $10\mu m$. When $L_t$ exceeds static region $D$, the tangential force is at the Coulomb threshold and $F_t = \mu_s N$. Then if $L_t$ increases further the force fluctuates between $N\mu_m$ and $N\mu_s$ with an average 'kinetic friction' force of $N\mu_k = N(\mu_s + \mu_m)/2$. This is done by subtracting $d = D\mu_m/\mu_s$ from $L_t$. In this region the particles are sliding and if the direction is $L_t$ is changed the force will decrease back to 0 following the static region.

Friction-less particles and it is very unlikely to jam. Also in experiment, static friction is key factor for jamming. The best way to include static friction in our simulation was a big challenge for us.

The kinetic friction force $f$ is proportional to the normal force $f = N\mu_k$. However, the static friction force can be any value in range $-N\mu_s < f_s < N\mu_s$. To overcome this difficulty we merge the two friction together to get our force model, which depends on relative motion.
We show our force model in Fig 1.5. Here we define D as the static region that is on the order of the size of the asperities on the particles, and d is fluctuating region. The horizontal axis is the accumulated relative surface motion between two particles $L_t$. If a particle moves in one direction, in region D, the friction coefficient increase linearly, and when it exceeds D, it start to oscillate between $N\mu_m$ and $N\mu_s$ with and average 'kinetic friction' force of $N\mu_k = N(\mu_s + \mu_m)/2$. This is done by subtracting $d = D\mu_m/\mu_s$ from $L_t$. In this region the particles are sliding and if the direction is $L_t$ is changed the force will decrease back to 0 following the static region. The maximum friction coefficient is $\mu_s$, the static friction coefficient. Now let us calculate the energy loss when we pull passed D 1.8:

$$W \approx \frac{\mu_s + \mu_m}{2} NL_t$$  \hspace{1cm} (1.8)

and the kinetic friction coefficient as Eq 1.9:

$$\mu_k = \frac{\mu_s + \mu_m}{2}.$$ \hspace{1cm} (1.9)

In experiments, static friction is measured by an pulling object in one direction till it moves. Kinetic friction is measured by pulling in consistent speed. In our force model, when d is small enough, it satisfies all requirement of experimental observation. In the static region and fluctuating region, the slope is same, so once we fixed D, d is also fixed. In the simulations, we select $D \sim 10^{-5}m$ which is reasonable for the
experiment. The normal force obeys Hertz law as Eq 1.10:

\[ F^n = -K\delta^{3/2} \] (1.10)

where \( K \) is a constant obtained from experiments and \( \delta \) is the overlap between two particles. The tangential force \( F^t = \mu(L_t)F^n \) with the \( \mu \) from Fig. 1.5. We simulate the dynamics from Newton’s law as Eq 1.11 and Eq 1.12:

\[
m_i \frac{d^2 \vec{r}_i}{dt^2} = \sum_{j \in \text{neighbors}} F^n_{ij} \hat{n} + F^t_{ij} \hat{s} + m_ig\hat{y} \quad (1.11)
\]

and

\[
I_i \frac{d\hat{\omega}_i}{dt} = -\frac{1}{2} \sum_{j \in \text{neighbors}} \sigma_i \hat{n} \times F^t_{ij} \hat{s}, \quad (1.12)
\]

where \( m_i \) is the mass of the \( i \)th particle, \( \vec{r}_i \) is the position of the \( i \)th particle, \( F^n_{ij} \) is the normal force on the \( i \)th particle from the \( j \)th particle, \( \hat{n} \) is the normal unit-vector pointing from particle \( j \) to particle \( i \), \( F^t_{ij} \) is the tangential force on the \( i \)th particle from the \( j \)th particle, \( \hat{s} = \hat{n} \times \hat{z} \) is the tangential unit vector and \( \hat{z} \) points out of the 2D plane of simulation, \( g \) is the gravitational constant, \( I_i \) is the moment of inertia of particle \( i \), and \( \sigma_i \) is the diameter of particle \( i \).

From Fig 1.6, we can define relative normal velocity \( V_n \) and relative tangential velocity \( V_s \) as Eq 1.13 and Eq 1.14:

\[
V_n = (\vec{v}_1 - \vec{v}_2) \cdot \hat{n} \quad (1.13)
\]
Figure 1.6: Normal and tangential velocity. \( \hat{n} \) and \( \hat{s} \) are relative normal vector and tangential vector. \( R_1, R_2 \) are radii of two grains, \( \omega_1 \) and \( \omega_2 \) are angular velocity, \( v_1 \) and \( v_2 \) are translation velocity. Relative normal and tangential velocity can be calculated by equation 1.13 and equation 1.14.
and

\[ V_s = (\vec{v}_1 - \vec{v}_2) \cdot \hat{s} + \omega_1 R_1 + \omega_2 R_2. \tag{1.14} \]

Finally we can calculate tangential displacement \( L_t \) as Eq 1.15:

\[ L_t = \int V_s dt. \tag{1.15} \]

We add damping terms to both the normal and tangential forces to eliminate non-realistic oscillation in the particle position in the elastic region of the tangential force law. \( Q_n \) is normal damping term, which is correlated by normal velocity \( V_n \) and normal displacement \( \text{delta} \). In tangential direction, we use \( Q_s \), which only related with tangential velocity \( V_s \). Our final formula are Eq 1.16 and Eq 1.17.

\[ F'_s = F_s - Q_s V_s \tag{1.16} \]

\[ F'_n = F_n - Q_n V_n \delta^{1/2} \tag{1.17} \]

We checked the kinetic energy when system jammed and it decays exponentially, as shown in Fig 1.7 and Fig 1.8. We can expand a little to explain our force model examining a model surface contacts as Fig 1.9. We can assume that on surface, there are many spikes or asperities, and friction is the effect of the interaction between asperities from the two particles as in Fig 1.9.
Figure 1.7 : Jamming. This is one configuration of jamming we get in simulation. We checked kinetic energy for the system and it decays to machine precision as 1.8, which means it is "absolute" jamming and will not break by itself.
Figure 1.8: This is kinetic energy of jamming state as Fig 1.7. We can find that kinetic energy decays exponentially. We start measuring from when the last ball drops before jamming. Here fluctuations are from energy transferring between kinetic energy and potential energy.
Figure 1.9: Surface composed of spikes or asperities. When two surfaces touch, these spikes will interacting with neighbor spikes. When the particle move relative to one another, some interactions break and also new interaction are generated. Friction is generated by these interaction. More interacting pairs give more interacting strength and higher friction between two particles. When the force is too large the Coulomb criterion is exceeded and interactions disengage in a way that dissipates energy and the particle begin to slip.
We also assumed that every pair of spikes has an effective region, and force approximately obeys hook’s law. When two spikes separates too far, this pair is not valid. Also there will be new spikes pairs generated with motion. Since surface is fairly random, number of valid spikes will fluctuate, so we will have a fluctuating friction. Kinetic friction can be regarded as average number of valid pairs and static friction is maximum valid pairs. Papanikolaou et al. [52] have introduced a new friction model based on particles with bumpy surfaces.

1.4 Flow rate simulation result

In the simulation we use the same number of disks and the same parameters as in the experiment and the results match the experiments well. We enumerate opening size between 2.7cm∼4.9cm, and angle from 30° ∼ 60°. When possible we ran simulations with 2000 disks but checked using 8750 disks for size dependence. Luckily, the 2000 disk system is big enough to approximate 8750 system for most situations. We measured flow rate and get very good fit with experiment with experiment as Fig 1.10:

In order to generate strict jamming, we choose our time step very small, which is ∼ 10^{-7}/sec. We find that for a bigger time step, the jamming probability is significantly smaller for some parameters. It can be explained by the accuracy of simulation. In practice, we close the bottom, place the disks, and wait until the kinetic energy falls below a cutoff. Then we release bottom. In the non-jamming case, we need to
Figure 1.10: Experiment and Simulation, here red is experiment result, and black is simulation result. We can see that in simulation, flux is fluctuating around experimental line, and we get a good fit.
simulate $\sim 10$ sec, but in jamming case, we need to wait until kinetic energy decays to $E_k < 10^{-10}$. In this case, we need to wait a significant longer time.

Every time step, we need to find neighbors of every disks. In the naive approach, checking every pair of disks takes $O(N^2)$, which is too slow. We use the cell-list method to break the hopper to $K \times M$ boxes, then calculate force between each pair of particles in each box, and the between neighboring boxes. In this approach, we can reduce time cost to $\sim O(N \log(N))$.

In simulation, our difficulty is the time cost for preparation and jamming. We used different energy criterion for preparation and found that the preparation does not affect the result significantly. But in the jamming case sometime the system seems jammed, but then breaks when the kinetic energy is fairly small, $E_k < 10^{-6}$. So we need to wait until kinetic energy decays to very small number, $E_k < 10^{-10}$.

Another difficulty we met in our simulation is the measurement of the jamming probability. In experiments they find that $P_{\text{jamming}} = \exp(\frac{t}{\tau})$. We can not generate sufficient data to fit the jamming probability directly due to simulation time.

In simulation, normal damping term $Q_n$ and tangential damping term $Q_s$ effect flow rate. These damping terms have a physics meaning, however it is hard to measure them and so we can only enumerate the results for different sets of $(Q_n, Q_s)$ to try to find a consistent fit to the experiment result. We have the flow-rate as a function of $(Q_n, Q_s)$ shown in Fig 1.11.

We can find a curve, on which flow rate does not change and matches the experiments.
Figure 1.11: Flow rate and a function of $Q_n$ and $Q_s$. We can see that in $Q_n, Q_s$ parameter graph, we can draw a curve on certain flux. Color refers to flux and we can enumerate all parameter set on certain line, where flux is constant.

Then in principle, we can find a particular value for $(Q_n, Q_s)$ which also can fit the jamming probability.

Granular flow in a hopper can be used to verify the properties of different materials. Each material can be described by parameter set $(\mu_k, \mu_s, Q_n, Q_s)$. Once we have these parameters, we can simulate any other physics process. Granular dynamics is an N-body problem and the theoretical approach has many difficulties. On the other hand, in the experimental approach, measuring some quantities accurately is very difficult, such as the pressure and the friction between certain disks. The advantage of simulation in granular research is that we can gather all of the micro- and macro-information of the system. Also in simulation, we can change parameter very easily,
which can be hard in experiment.

1.5 Discharge time and jamming probability

We mentioned above that the jamming probability is very difficult to get from simulation due to long simulation times. So we measured another parameter, discharge time, to try to get it indirectly. The Discharge time \( DT_m(N) \) is define as Eq 1.18:

\[
DT_m(N) = t(N + m) - t(N),
\]

where \( t(N) \) is the time when \( N^{th} \) disks drops out of the bottom. \( DT_m(N) \) is time duration between the exit of the \( N^{th} \) and \( (N + m)^{th} \) disks. Here we show distribution of \( DT_1 \) and \( DT_5 \) in Fig 1.12:

We found that the discharge time can be fitted by a gamma distribution as Eq 1.19:

\[
\Gamma(X; k, \theta) = \frac{1}{\Gamma(k)\theta^k} X^{k-1} e^{-\frac{X}{\theta}}
\]

We fit the \( k_n \) for different \( DT_n \) and we found that \( k_n \propto n \). The gamma distribution has a nice property that when \( X_i \) has a \( \Gamma(k_i, \theta) \) distribution, then we get Eq 1.20:

\[
\sum_{i=1}^{N} X_i \sim \Gamma\left(\sum_{i=1}^{N} k_i, \theta\right).
\]

So \( K_n \propto n \) means that the correlations between consecutive disks is very small,
Figure 1.12 : This graph is distribution of $DT_1$ and $DT_5$. $DT_m$ is defined as Eq 1.18, the time duration between the exit of the $N^{th}$ and $(N+m)^{th}$ disks. Discharge time is more specific measurement than flow rate, and here red line is $\Gamma$ Function fit, which is defined as Eq 1.19.
Figure 1.13: In this figure, we plot $n$ versus $k_n$. Each $k_n$ is parameter for $DT_n$ in $\Gamma$ fit in Eq 1.19. Here we can find $k_n$ is proportional to $n$ and from properties of $\Gamma$ Function in Eq 1.20, we know that it refers independence. Discharge time $DT_n$ can be regarded as sum of $n$ independent $DT_1$. 
and the flowing process can be approximately regarded as random process. From Behringer’s group, they also found that surviving probability is exponentially related to time, which also implies that hopper flow is random process.

In simulation, we tracked the discharge time, but we have not found any specific properties near jamming. Disks drop regularly and suddenly get jammed. We can rewrite surviving probability as Eq 1.21 and Eq 1.23:

\[ P_s(T) = \exp\left(-\frac{T}{\tau}\right) \]  \hspace{1cm} (1.21)

\[ P_s(N) = P_s(T_f) = \exp\left(-\frac{N}{\tau f}\right) = p'^N \]  \hspace{1cm} (1.22)

\[ p' = \exp\left(-\frac{1}{\tau f}\right); \]  \hspace{1cm} (1.23)

here \( f \) is number of disks drop per second. We derive \( p' \) that describes the survival probability for each disk. We define \( q' = 1 - p' \) as the jamming probability for each disk. Now we have a more comprehensive description for hopper flow in the view of random process. Each disk has probability \( q' \) to become jammed. If it is not trapped by jamming, then it ”chooses” a discharge time from a gamma distribution. We can benefit from this random process as follows. Jamming refers to infinite discharge time, when we face a long discharge time, if we can confirm jamming before its energy decays to \( 10^{-10} \), our simulation can be accelerated a lot. If discharge time is longer than \( T \), the probability it is not in jamming case refers to accumulated probability
that its discharge time is bigger than $T$. It can be calculated as Eq 1.24:

$$P_s(T) = p' \int_{t>T} P(t)$$  \hspace{1cm} (1.24)$$

and the probability that it jammed is $q'$. So we can calculate probability of a true jamming event as Eq 1.25:

$$P_{jamming} = \frac{q'}{q' + p' \int_{t>T} P(t)}.$$  \hspace{1cm} (1.25)$$

Since we do not know $q'$ for each system, we pick the smallest $q'$ from the experiment in our parameter region. Then we have Eq 1.26:

$$P_{jamming} > \frac{q'}{q' + \int_{t>t} P(t)}$$  \hspace{1cm} (1.26)$$

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$P_{jamming}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1×mean</td>
<td>2.13%</td>
</tr>
<tr>
<td>6.7×mean</td>
<td>50%</td>
</tr>
<tr>
<td>10×mean</td>
<td>99.29%</td>
</tr>
<tr>
<td>15×mean</td>
<td>99.9995%</td>
</tr>
</tbody>
</table>

Table 1.1: Discharge time versus jamming probability

Now we can predict jamming by discharge time as table 1.1. Now we can use this form to detect jamming much earlier than waiting for the energy to decay to $10^{-10}$. This method is not as accurate as energy criterion, but we can estimate error term too.
By using these techniques, we get some data for small-opening cases as Fig 1.15. However, another problem arises. In the whole process, we can divide them into 3 parts. At first, disks start to drop, then the flux starts to increase until a consistent flow rate. Then the disks drop at consistent flux, and we call it the consistent region. When only a few disks remain, the flux starts to fluctuate and we can not rely on them as a consistent flow. Comparing with the 8750 particle system, the 2000 particle system has a much shorter consistent region. Jamming is unlikely happens in the last part, which will cause our approximation to be inaccurate. In simulation, \( P_{jam,simulation} < P_{jam,experiment} \) as Fig 1.14.

We find that surviving probability can be fitted to exponential formula, which proves random process assumption.
Figure 1.14: Surviving probability versus time (Red line is experiment result, which refers to exponential decay. Blue line is simulation result for opening size = 2.4 cm. By comparing them, we can see that in simulation, jamming is much more difficult to generate. We have shown that flux matches well in simulation and experiment. One potential explanation of this mismatch is system size.
Figure 1.15: Jamming probability versus opening size. In experiment, jamming probability is studied using surviving probability trend as Fig 1.14. In this graph, we calculate jamming probability via whole process and since average flux is constant during flow, this jamming probability can be derived as: \( P_j = 1 - \exp \frac{N/\text{flux}}{\tau} \). We have shown in Fig 1.14 that simulation \( \tau \) is bigger than experiment \( \tau \), so the jamming probability in whole process is also smaller than experiment. We have not detected jamming when opening size > 3.5, which was detected in experiment.
Chapter 2

Avalanche in rotating drum

2.1 Background of avalanche analysis

We are interested in systems that change structure dramatically due to a small but constantly increasing force. The snow avalanche is a well known example. As snow builds up slowly the angle of the heap change and then suddenly slides down. There are many other examples in nature, like earthquakes and mudslides. We use this analogy of the avalanche to describe this type of behavior. For example, back to hopper flow, when system gets jammed, if we keep adding disks at the top, then suddenly it will collapse and start to flow again. We regard these phenomena as avalanche. One very interesting thing in avalanches is the correlation between avalanche frequency and avalanche magnitude. A research on earthquake is shown in Fig 2.1. Dahmen et al. have developed a mean field lattice model for plastic deformation under shear, in which each sites has two states, either slip or stick [49, 48]. Then they increase the stress to make avalanche. There are $N = L^d$ sites on possible and $N_{occ}$ sites are occupied, $N - N_{occ}$ sites are empty. A site $i$ slips when the stress on it exceeds $\tau_i$. And slips stops when its stress is relaxed to local arrest stress $\tau_{a,i} < \tau_{s,i}$, then it re-sticks. A slip can triggers other sites to slip and slip stops when for all
sites have stress smaller than their failing thresholds. Using mean field theory, they find a power-law correlation between avalanche magnitude and frequency. Also, they derived that for each avalanche, the average avalanche magnitude as a function of time is parabolic.

## 2.2 Rotating drum

A rotating drum is a cyclical container which can rotate. Fig 2.2 shows a 2D rotating drum. Disks are placed in the drum. Another student in our lab, Aline Hubard, has done companion experiments [54] to the simulation described in this chapter. In simulation, we use the same force model as the hopper simulation. We placed 500–2000 disks in drum. We define an avalanche using the energy. We calculate the center of mass for the disks and calculate the angle between gravity and a line connecting the center of mass to the center of the drum Fig 2.3. We call this angle $\beta$. Without an avalanche, $\beta$ grows linearly with time, and when an avalanche occurs, $\beta$
Figure 2.2: Rotating Drum in simulation. Disks are placed in the cyclical container and container is rotating under a slow speed. There is a friction force between disks and container wall, and also between contacted disks. The whole system is under the force of gravity, so we can expect that disks are rotating as a whole system for a while and it collapses. We regard such collapse as an avalanche.
Figure 2.3: $-d\beta/dt$ versus $t$. In rotation without an avalanche, $-d\beta/dt = \omega$ the rotating angular velocity. When an avalanche occurs, $-d\beta/dt$ increase above $\omega$ as the avalanche builds and then decreases back to $\omega$ as the avalanche ends. This is one avalanche configuration. We can see that $-d\beta/dt$ fluctuates during avalanche. The magnitude of avalanche is defined as equation 2.1. We subtract the rotating term $\omega$ during the calculation. We $E_t > 0$ as criterion for detecting avalanche. Any fluctuation, whose peak is smaller than zero is not considered as avalanche. We do this to reduce noise.

drops. We track $\beta$ and calculate the change of $\beta$ from on time step to the next $d\beta/dt$.

We count one avalanche as segment between two zero points. In each avalanche, we can find the, (1) duration, (2) maximum energy, (3) total energy. Total energy is calculated as Eq 2.1:

$$E_t = C \int (d\beta/dt - \omega) dt$$

(2.1)

C is scale constant. For each avalanche, we scale its maximum to 1 and also scale its duration to 1. Then we average them to get the average avalanche shape. We generated more than $10^4$ avalanches and calculated magnitude frequency and avalanche
Figure 2.4: Avalanche magnitude versus frequency. We fit the line by $f(I) \propto I^{-1.29}$. In theory, $f(I) \propto I^{-2.16}$. However, theory is based on simple lattice sites, and rotating drum is much more complicated. We get similar result in experiment.

We get a power-law with $F(I) \sim I^{-1.29}$, comparing with theory $F(I) \sim I^{-2.16}$.

For the shape average, we found that the avalanche is little asymmetric with a peak around 0.55 instead of 0.5 as Fig 2.5. Our simulation is close to the theory and confirms effectiveness of theory in this system.

### 2.3 Experiment result

Aline Hubard in our group also did a companion experiment on a rotate drum. In her experiment, two glass plates separated by about one particle diameter confine
Figure 2.5: Parabolic fit during avalanche. This is an average for $10^4$ avalanches. For each avalanche, we scaled its duration to 1 and its maximum to 1. Then we sum all up and average. We can find some spikes here. This is because for very small avalanches the duration only has few time steps. The red line is best parabolic fit for average shape. We can see that its close to symmetric parabolic mono-disperse stainless-steel spheres to a cylindrical region. We rotates the system about cylinder axis, and uses high speed video up to 1000 fps. We measure the particle positions during very slow rotation in which the flow is dominated by discrete avalanche events. We measure the avalanche size, duration and time evolution for up to $10^5$ avalanches. In experiment, avalanche magnitude satisfies power-law with \( f(I) \sim I^{-1.36} \), which is close to the simulation. We find a bump at the tail and it may be explained as a bounce of the particles after avalanche. We also find the duration frequency, which is also power-law with a bump at the longest avalanches. The Shape is also measured and close to parabolic curve.
Figure 2.6: Avalanche magnitude versus frequency. This is done in experiment. Comparing with simulation, a bump is found at tail and here $f(I) \sim I^{-1.36}$. In simulation, $f(I) \sim I^{-1.29}$.

Figure 2.7: Avalanche Duration versus frequency. This is done in experiment. A bump is also found at tail.
Chapter 3

New order metric

3.1 Order Metric

Describing soft matter systems is a big challenge. Many systems are not pure crystals or completely disordered. They can have both crystal clusters and disordered particles. For example, quantify the order of a system is very important in the glass-crystal phase transition. In systems that jam (i.e., systems that get stuck in states far from equilibrium like glasses or granular packings) order is often regarded as a parameter on par with other quantities such as pressure, temperature and packing fraction, which are not sufficient to explain some phenomena without taking order into account. Torquato introduced the concept of maximal random jamming to explain random close packing of spheres as structure[47]. In his concept, a reliable order metric is a key point and he published some papers to discuss details. We will discuss them later in the section Shortcomings of $Q_6$. An order metric can be applied globally or locally. A global order metric describes order of the whole system. A local order metric can be used to describe a single crystal cluster. In classic crystal nucleation theory, crystallization is started by local small crystal and it grows. A good local order metric is very useful in calculating nucleation rate and growth rate, which is an
3.2 $Q_6$ Family

The bond-orientation order metric $Q_6$ defined by Steinhardt, Nelson and Ronchetti [46] provides a global measure of crystallinity in a system. It is the most widely used order metric. For each sphere, a set of bonds are defined connecting its center to the centers of its nearest neighbor spheres. There are some different methods to define nearest neighbors; one of the most widely used method is based on the radial distribution function. First, we calculate radial distribution, and determine a cutoff from the first minima in curve. All neighbors closer than the cutoff are counted as nearest neighbors. We can then calculate $Q_6$ based on the spherical harmonics $Y_{lm}(\theta, \phi)$ as Eq 3.1:

$$Q_6 = \frac{4\pi}{13} \sum_{m=-6}^{6} \frac{1}{N} \sum_{i=1}^{N_b} |Y_{6m}(\theta_i, \phi_i)|^2 \right)^{1/2}$$

(3.1)

where $N_b$ is to the number of nearest neighbor bonds in the system and $\theta_i$ and $\phi_i$ are the polar and azimuthal angles of bond $i$. We only need $Y_{6m}$ to calculate $Q_6$. In the original Steinhardt, Nelson, and Ronchetti definition any spherical harmonic could be used. We choose $Q_6$, because in mono-disperse packing, FCC and HCP is the most common crystal and $Q_6$ can be maximized in hexagonal lattices.

We are also interested in local measure of orientation order. $Q_{6,local}$ is used here,
which is evaluating the bond-orientation order at each sphere individually as Eq 3.2.

\[
Q_{6,\text{local}} = \sum_{j=1}^{N} \left( \frac{4\pi}{13} \sum_{m=-6}^{6} \frac{1}{n_b} \sum_{i=1}^{n_b} |Y_{6m}(\theta_i, \phi_i)|^2 \right)^{1/2}
\]  
(3.2)

where \(n_b\) is the number of nearest neighbors of sphere \(j\).

\(W_6\) is a parameter derived from \(Q_6\) and also widely used in research. It is defined as Eq 3.3:

\[
W_l = \sum_{m_1, m_2, m_3} \left( \begin{array}{ccc}
  l & l & l \\
  m_1 & m_2 & m_3
\end{array} \right) Q_{lm_1} Q_{lm_2} Q_{lm_3}
\]  
(3.3)

It is also used to specify lattice structure as Table 3.1.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>(Q_4)</th>
<th>(Q_6)</th>
<th>(W_4)</th>
<th>(W_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>0.19094</td>
<td>0.57452</td>
<td>-0.159317</td>
<td>-0.013161</td>
</tr>
<tr>
<td>hcp</td>
<td>0.09722</td>
<td>0.48476</td>
<td>0.134097</td>
<td>-0.012442</td>
</tr>
<tr>
<td>icosahedral</td>
<td>0</td>
<td>0.66332</td>
<td>0</td>
<td>-0.169754</td>
</tr>
<tr>
<td>liquid</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1: Bond order parameters for four typical structures

The \(Q_6\) family has a different value in different lattice structures. We can find that \(Q_l\) is relatively high in lattice structures compared with liquids. In a typical monodisperse system, during crystallization, \(Q_6\) increases as temperature decreases and we can distinguish glass and crystal using \(Q_6\). \(Q_6\) during packing can be found in Fig 3.1.
Figure 3.1: Packing fraction versus $Q_6$. In mono-disperse system, $Q_6$ is generally increasing when packing fraction increases. This plot is a case that we prepare system very slowly, so system get crystallized and $Q_6$ arrives maximum 0.57. If we quench system fast, system will be jammed at lower fraction and $Q_6$ can’t reach 0.57, which refers to Random Close Packing.

3.3 Shortcomings of $Q_6$

As we showed before, $Q_6$ is very powerful in detecting hexagonal lattice structures such as FCC and HCP. And in mono-disperse particle system, hexagonal structure is the most common structure when they crystallized. However, when we face other lattices, such as cubic, the value of $Q_6$ is not that effective. From its definition, we know that $Q_l$ reaches its maximum when system is l-closest neighbor lattice. So we can use $Q_4$ for cubic and it works well. However, a new problem arise that what should we do if we don’t know the structure of a system. And in bi-disperse system and poly-disperse system, the unit cell is not unique. $Q_l$ is designed for detecting specific unique unit cells, and it can not deal with a system where there are different
kinds of unit cells. For example, when a system is mixture of hexagonal lattice and cubic lattice, neither $Q_6$ nor $Q_4$ is reasonable for calculating global order. A proper way can be using $Q_4$ in cubic area and $Q_6$ in hexagonal area and merge them in some kind of way, but it needs us to detect local structure first then pick proper order metric, which is also a problem.

Kansal, Torquato and Stillinger discussed this problem in their paper[50]. Starting with mathematical properties of an order metric, $\psi$.

(1) The order metric $\psi$ is a well-defined scalar function of the coordinates $r_1, \ldots r_N$ for any N-particle system.

(2) $\psi$ is subject to the normalization in range 0 - 1. For any two states A and B, $\psi(A) > \psi(B)$ implies that state A is more ordered than state B.

(3) $\psi$ is invariant to spatial reflections and to translation or rotation of the system as a whole.

There is are a lot of functions that possess these properties. But there are some good ones and some bad ones. Kansal, Torquato and Stillinger discussed some additional properties of good metrics.

(1) A good order metric should be sensitive to any kinds of ordering in a system and not be biased toward a specific system.

(2) A good order metric should reflect the hierarchy of ordering between prototypical systems.

(3) Order at any length scale should be detected.
(4) Both the variety of local coordination patterns and the spatial distribution of such patterns should affect the amount of order measured in a system.

Back to $Q_6$, it is not that good since it is biased to the hexagonal system, and since it is based on neighbors, it can not detect a long-range lattice. In practice, the value of $Q_6$ for a cubic lattice is smaller than hexagonal, and it’s unfair to say cubic is less ordered than hexagonal. In a bi-disperse system, when we have two kinds of particles, one is much bigger than the other, the lattice structure can be many different kinds, such as $AB_{13}$. When using $Q_6$ to calculate order metric in this system, its value is very small implying that system is very disordered even for a perfect crystal.

Another issue is the definition of nearest neighbors. In practice, we calculate radial distribution, and find first cutoff. However, this cutoff is not constant in different systems, and from the formula we know that each neighbor contributes the same portion. Adding or deleting a neighbor will change $Q_l$ significantly. We can use Voronoi tessellation to define nearest neighbors and portion; we will discuss this in the next section.

3.4 Voronoi Tessellation

In mathematics, a Voronoi diagram is a partitioning of an N-dimensional space into regions based on distance to points in a specific subset of the space. That set of points, which are called seeds, are specified beforehand, and for each seed there is a corresponding region consisting of all points closer to that seed than to any other.
Figure 3.2: This is an example for Voronoi tessellation in 2D. Each polygon refers to set of dots which is closest to seed in that polygon. The seed is the black dot in each polygon. From the definition, we know that Voronoi tessellation is unique once we get position of all these seeds.

This region is called Voronoi cell. In 2 dimension, Voronoi cell is a polygon and in 3 dimension, it is polyhedron. An example on 2D is shown in Fig 3.2.

Voronoi tessellation has very wide application in particle system analysis. We mentioned before that the definition of nearest is neighbors based on radial distribution is ambiguous. Now we can use Voronoi tessellation to fix it. First we calculate Voronoi tessellation of the system and define each particles as neighbor when they share an edge(plane in 3D) in Voronoi polygon(polyhedron in 3D). Comparing with the radial distribution definition, it is strict. We also mentioned that adding or deleting a neighbor will affect $Q_b$ a lot since all neighbors contribute same portion. Now we can
change definition of $Q_l$ as Eq 3.4:

$$Q_6 = \left( \frac{4\pi}{13} \sum_{m=-6}^{6} \left| \sum_{i=1}^{N_k} s_i Y_{6m}(\theta_i, \phi_i) \right|^2 \right)^{1/2}$$

(3.4)

Here $s_k$ is defined as area of $k_{th}$ plane of Voronoi polyhedron, which shared with $k_{th}$ neighbor. We can see that when we add a new neighbor, its shared plane is increasing continuously and $Q_6$ will also change continuously.

In a bi-disperse system, there are some different definitions of Voronoi tessellation. We can use the same definition using seed, but in some cases, the particle edges will not be in the Voronoi cell. Another definition is calculating shortest distance from surface. Then it will be sure to hold the particle. However, it is hard to calculate this tessellation in practice. We will use a third definition using tangent distance. This distance is defined as Eq 3.5.

$$d_i(x, y, z) = \sqrt{((x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2 - r_i^2)}$$

(3.5)

We can prove that in this definition, Voronoi polygon can hold sphere and it’s not curved, so we can calculate properties easily.

### 3.5 Information theory and Voronoi entropy

When we calculate Voronoi tessellation, we would like to use it to design an order metric. We know that
(1) If two particles have exact same neighbor structure, they will have exact same Voronoi polyhedron.

(2) If two particles’ neighbor structures are similar, their Voronoi polyhedrons are also similar.

(3) In mono-lattice structure, all particles have same neighbor structure, so all Voronoi polyhedron will be the same.

(4) In poly lattice structure, there will be certain number of polyhedron depends on number of different unit cell.

Voronoi polyhedron is an abstraction of neighbor structure. In a system, if its Voronoi polyhedrons are similar, we can know the system is more ordered. However, if we describe a polyhedron by its index, it has a lot parameters and we can not derive an order metric directly from them. So we abstract further and compress it to two parameters. Shape factor $\psi$ and density $\phi$. $\psi$ is defined as Eq 3.6.

$$\psi = \frac{36\pi V}{S^3} \quad (3.6)$$

here $V$ is volume of polyhedron and $S$ is surface area of polyhedron. For typical structures its value is table 3.2.

Density $\phi$ is defined as Eq 3.7.

$$\phi = \frac{V_{\text{particle}}}{V_{\text{polyhedron}}} \quad (3.7)$$
Based on this definition, we can see that both $\psi$ and $\phi$ are invariant to spatial reflections and to translation or rotation of the system as a whole. Once we calculates $\psi$ and $\phi$ for each particle, we need a method to abstract it again to a number. We find that:

(1) If two polyhedron is similar, its $\psi$ is close.

(2) $\phi$ is used to deal with loose packing. Same polyhedron with different sphere should be regarded as different.

We can calculate the distribution of $\psi$ and $\phi$ in two dimensions and get distribution as Fig 3.3 3.4 3.5. We found that for ordered systems, the distribution is concentrated and for disordered system, it's dispersed. Then we applied Shannon’s information theory to derive Voronoi entropy. In Shannon’s theory, ”information” is thought of as a set of possible messages, and the goal is to send these messages over a noisy channel, and then to have the receiver reconstruct the message with low probability of error, in spite of the channel noise. If $X$ is the set of all messages $x_1, \ldots, x_n$ that $X$ could be, and $p(x)$ is the probability of some $x \in X$, then the entropy $H$, of $X$ is

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere</td>
<td>1.0</td>
</tr>
<tr>
<td>fcc</td>
<td>0.74</td>
</tr>
<tr>
<td>hcp</td>
<td>0.74</td>
</tr>
<tr>
<td>cubic</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 3.2 : $\psi$ of typical structure
Figure 3.3: \( \psi \) and \( \phi \) distribution in liquid. Systems are prepared by growth rate 0.1 and 0.01. Here small growth rate refers to slow quenching, which can make system more crystallized. 0.1 is a big growth rate, which refers rapid quenching. 0.01 is still big. However, we can find on the plot that in 0.01, in \( \phi-\psi \) graph, the distribution is more concentrated than in 0.1, and also its entropy is smaller. We can see that system is becoming more ordered.

Figure 3.4: \( \psi \) and \( \phi \) distribution in crystal. Systems are prepared by growth rate 0.002 and 0.001. Here 0.001 is small enough to crystallize. We can see that in 0.001 and 0.002, distribution is very concentrated, which means system is crystallized.
Figure 3.5: $\psi$ distribution in liquid and crystal. Systems are prepared by growth rate 0.1, 0.005 and 0.003. Here we can find at rapid quench, $\psi$ is distributed very wide and in slow quench, $\psi$ is very concentrated.

defined as Eq 3.8.

$$H(X) = -\sum_{x \in X} p(x) \log(p(x))$$ (3.8)

Back to our system, we can use concept of Shannon entropy that if system is more ordered, we need less information to describe it. We define each state as Eq 3.9.

$$X(\psi_x, \phi_x) = \sum(\psi_x < \psi < \psi_x + d_\psi, \phi_x < \phi < \phi_x + d_\phi)$$ (3.9)

$d_\psi$ and $d_\phi$ is the scale to distinguish two polyhedron. In practice, $d_\psi \approx 10^{-2}$ and $d_{psi} \approx 10^{-2}$ is sensitive enough for detecting lattice structures.

For mono-disperse lattice, there is unique Voronoi cell, so there is only one state with probability 1. We can calculate that in Eq 3.10.

$$H(mono \text{- lattice}) = -1 \times \log(1) = 0$$ (3.10)
Figure 3.6: $AB_{13}$. All blue big particles are positioned as simple cubic structure first. 13 small yellow particles composite a FCC structured ball. And these balls are also simple cubic positioned. We can see that each blue particles has same neighbor structure, each centered yellow has same, and each boundary yellow has rotational symmetric same neighbor structure.

Note that we haven’t specified the type of lattice. Entropy becomes 0 for all kinds of lattices when they have unique unit cell. For bi-disperse system, there are more than one unit cells. For example, in $AB_{13}$, there are three kinds of Voronoi polyhedrons as Fig 3.6.

We find that there are 3 different kinds of Voronoi polyhedrons. We calculate their $\psi$ and $\phi$ as table 3.3.

<table>
<thead>
<tr>
<th>Type</th>
<th>$\psi$</th>
<th>$\phi$</th>
<th>portion</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.74</td>
<td>0.74</td>
<td>$\frac{1}{14}$</td>
</tr>
<tr>
<td>B</td>
<td>0.59</td>
<td>0.68</td>
<td>$\frac{1}{14}$</td>
</tr>
<tr>
<td>C</td>
<td>0.68</td>
<td>0.70</td>
<td>$\frac{6}{7}$</td>
</tr>
</tbody>
</table>

Table 3.3: $\psi$ of typical structure
Using definition above, we can calculate its entropy as Eq 3.11:

\[ E(X) = -\frac{1}{14}\log\left(\frac{1}{14}\right) - \frac{1}{14}\log\left(\frac{1}{14}\right) - \frac{6}{7}\log\left(\frac{6}{7}\right) = 0.221 \quad (3.11) \]

A typical liquid system has entropy around 5. So this value is significant to detect its lattice structure. And we can find that even if it is a lattice, its entropy is not 0. This is because it has 3 different types of unit cells and it is reasonable to regard it less ordered compared with a mono lattice. \( Q_6 \) for this system is 0.273. But for system below, which is totally disordered mixture of two kinds of particles has \( Q_6 = 0.305 \) as Fig 3.7. \( Q_6 \) fails here mainly because system it is a mixture of cubic and hexagonal and they affect each other. By comparison, entropy for second system is 4.3, big enough to be regarded as liquid.
3.6 Generating sphere packings

We generate packing using 500-1000 identical hard spheres. We use periodic boundary conditions to decrease size effect. We use two kinds of algorithms to generate packing. One is Lubachevsky-Stillinger hard sphere packing algorithm and MD simulation[51]. In LS algorithm, we have a single parameter $\tau$, which represents the sphere growth rate. At first, all particles have diameter 0 and it grows with each step. As the spheres grow larger, they will collide. The LS algorithm finds next nearest collision and updates the velocity and position of particles to that moment. It is an event-driven algorithm. When spheres grow larger, the collision frequency increase and a maximum packing fraction is approached. The algorithm ends when the collision frequency reaches certain amount. All the collisions are elastic collisions. When $\tau$ is small, we get ordered packings and bigger $\tau$ will make disordered packings. So we can generate a range by changing $\tau$.

In MD simulation, we use potential as Eq 3.12.

$$u(r_{ij}) = 4\epsilon[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6]$$  \hspace{1cm} (3.12)

and simulate system by time step. We varies quenching rate $R_c$ to control the order of system. At first we heat the system to liquid and decrease the temperature by certain rate. We cool the system linearly at rate $R_c$ from $T_i$ to 0 as Eq 3.13.

$$T(t) = T_i - R_c t$$  \hspace{1cm} (3.13)
We also generate bi-disperse packing and vary size ratio and portion. For certain bi-disperse lattice structures, such as $AB_{13}$, we calculate position of each particle directly and calculated its property, since it’s very hard to make such packings from simulation.

To find other phenomena, Zhang et al.[53] use patchy particles to generate FCC-BCC phase transition. In patchy particle model, each particle has some patches on its surface and the patches also have an interaction with other patches and particles.

### 3.7 Voronoi entropy in patched particles

From the definition, we know that for a pure lattice, Voronoi entropy only depends on the number and portions of unit cells. We have compared $Q_6$ and Voronoi entropy in $AB_{13}$ for example and showed $Q_6$ is effective there and but the Voronoi entropy works. We would like to find other application of Voronoi entropy and now we use the patchy particle system.

They added $z$ patches on the surface of the particles. Here is a plot for $Z=6$ in Fig 3.8. Patches are oriented towards a specific symmetry. Aligned patches experience Lennard-Jones attractive interactions. The interaction between patchy particle $i$ and $j$ includes an isotropic short-range repulsive interaction and an anisotropic attractive interaction between patches. Potential can be written as Eq 3.14.

$$u(r_{ij}, s_{i\alpha}, s_{j\beta}) = u_R(r_{ij}) + u_A(r_{ij})v((\phi_{i\alpha}, \phi_{j,\beta})$$  \hspace{1cm} (3.14)

$r_{ij}$ is the separation between particles $i$ and $j$, $u_R(r_{ij})$ is the Weeks-Chandler-Andersen
purely repulsive potential, \( u_A(r_{ij}) \) is the attractive part of the Lennard-Jones potential truncated and shifted so that it is zero at \( r_c = 2.5\sigma_{ij} \), the patch \( \sigma \) on particle \( i \) has orientation \( s_{i\alpha} = (\sigma_i/2)/\vec{c_{i\alpha}} \) with surface normal \( n_{i\alpha} \) and \( \phi_{i\alpha} \) is the angle between \( r_{ij} \) and \( s_{i\alpha} \). For the patch-patch interaction, we assume as Eq 3.15. Fig 3.9 shows potential and all parameters.

\[
v(\phi_{i\alpha}, \phi_{j\beta}) = e^{-\frac{(1-\cos\phi_{i\alpha})}{a_{i\alpha}^2}} e^{-\frac{(1-\cos\phi_{j\beta})}{a_{j\beta}^2}}
\]

which is maximized when \( \phi_{i\alpha} = \phi_{j\beta} = 0 \). We considered \( z = 3,4,6,8 \) and 12 patches on the sphere surface. This refers to trigonal, tetrahedral, simple cubic, BCC, and FCC symmetry. They changed quenching rate and investigate \( Q_6 \) and entropy for
Figure 3.9: Potential Energy in Patchy particle. The first graph shows the potential between particles and patches. The second graph shows each angles referred before. Patches add different symmetry and it helps us to generate different crystal structures other than FCC and HCP.

final state. Result can be seen in Fig 3.10 3.11.

For the $z = 6$ case, we find a trough in the diagram which $Q_6$ does not find. Careful investigation shows that at first, the system is cubic structure and at certain point it changes to BCC continuously as Fig 3.12. In the view of $Q_6$, BCC has bigger $Q_6$ than the cubic lattice, so $Q_6$ increase. But in the view of entropy, it reach a local minimum when the portion of cubic is maximum, then it increase because the two types of structures are mixed. At last it decrease again, because whole system is composed by BCC only. Voronoi entropy successfully found a lattice-to-lattice phase transition which current $Q_6$ order metric can not find. When we are given a system, we can calculate $\psi$ and $\phi$ for all particles and calculate entropy by histogram. Value of entropy shows how ordered the system is. From the distribution of $\psi$ and $\phi$ we can find what kinds of structure it has. We have calculated $\psi$ for some common lattice structures and can find structure by comparing $\psi$. However, $\psi$ is not that sensitive.
Figure 3.10: $Q_6$ in different patchy systems. Here we can see when we quench system slowly, its $Q_6$ increases. All of these are very similar to the mono disperse system. We can also see that for different patches, the trends are different.

Figure 3.11: Entropy in different patchy system. Here all of the trends are very similar as $Q_6$, except $Z=6$. We found a bump, and after careful investigation, it is mixture of simple cubic and BCC. With high quenching rate, system crystallized as simple cubic at first. When we quench it slower, it transferring to BCC and with very slow quench, system reaches BCC.
Figure 3.12: Cubic and BCC mixture. Here upper half is BCC structure and down half is simple cubic structure. System first crystallized as simple cubic and then transferring to more dense crystal BCC. In the view of entropy, such mixture increase entropy, and we successfully detect it.

enough to distinguish all kinds of different lattice structures. So a potential solution can be adding a new parameter to describe polyhedron.
Chapter 4

Asymmetric crystallization during cooling and heating in model glass-forming systems

4.1 Methods

We performed MD simulations of binary Lennard-Jones (LJ) mixtures of \( N = N_A + N_B \) spheres with mass \( m \) at constant volume \( V = L^3 \) in a cubic simulation box with side length \( L \) and periodic boundary conditions. We studied mixtures with \( N_A = N_B \) and diameter ratio \( \alpha = \sigma_B / \sigma_A < 1 \). We employed the LJ pairwise interaction potential between spheres \( i \) and \( j \):

\[
  u(r_{ij}) = 4\epsilon[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6],
\]

(4.1)

where \( r_{ij} \) is their center-to-center separation, \( \epsilon \) is the depth of the minimum in the potential energy \( u(r_{ij}) \), \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \), and \( u(r_{ij}) \) has been truncated and shifted so that the potential energy and force vanish for separations \( r_{ij} \geq 3.5\sigma_{ij} \) [29]. We varied the system volume \( V \) to fix the packing fraction \( \phi = \pi \sigma_A^3 (N_A + \alpha^3 N_B)/6V \) = 0.5236 [30] at each diameter ratio \( \alpha \). For most simulations, we considered \( N = 1372 \) spheres, but we also studied \( N = 4000 \) and 8788 to assess finite-size effects. Below, energy, length, time, and temperature scales are expressed in units of \( \epsilon, \sigma_A, \sigma_A \sqrt{m/\epsilon}, \)
and $\epsilon/k_B$, respectively, where the Boltzmann constant $k_B$ has been set to be unity.

### 4.2 Cooling and Heating Protocols

For each particle diameter ratio, which yield different glass-forming abilities, we performed MD simulations to cool metastable liquids to zero temperature and heat zero-temperature glasses into the metastable liquid regime to measure $R^*_c$ and $R^*_h$ at which the systems begin to crystallize. To measure $R^*_c$, we first equilibrate the system at high temperature $T_i = 2.0$ using a Gaussian constraint thermostat [29]. We then cool the system by decreasing the temperature linearly at rate $R_c$ from $T_i$ to $T_f = 0$:

$$T(t) = T_i - R_c t.$$  \hspace{1cm} (4.2)

To measure the critical heating rate $R^*_h(R_p)$ at finite rate $R_p$, we first prepare the systems in a glass state by cooling them from the high temperature liquid state to zero-temperature at rate $R_p > R^*_c$. To measure the intrinsic critical heating rate $R^*_h(\infty)$, we quench the systems infinitely fast to zero temperature using conjugate gradient energy minimization. For both cases, we heat the zero-temperature glasses using a linear ramp

$$T(t) = R_h t$$  \hspace{1cm} (4.3)

until $T_f = 2.0$. For both heating and cooling protocols, we carried out $N_{tot} = 1000$ independent trajectories and averaged the results.
4.3 Identification of Crystal Nuclei

To detect the onset of crystallization in our simulations [17], we differentiate ‘crystal-like’ versus ‘liquid-like’ particles based on the value of the area-weighted bond orientational order parameter for each particle [31, 32]. We define the complex-valued bond orientational order parameter for particle $i$:

$$ q_{lm}(i) = \frac{\sum_{j=1}^{N_b} A_{ij} Y_{lm}(\theta(\vec{r}_{ij}), \phi(\vec{r}_{ij}))}{\sum_{j=1}^{N_b} A_{ij}}, \quad (4.4) $$

where $Y_{lm}(\theta(\vec{r}_{ij}), \phi(\vec{r}_{ij}))$ is the spherical harmonic of degree $l$ and order $m$, $\theta(\vec{r}_{ij})$ and $\phi(\vec{r}_{ij})$ are the polar and azimuthal angles for the vector $\vec{r}_{ij}$, $j = 1, \ldots, N_b$ gives the index of the Voronoi neighbors of particle $i$, and $A_{ij}$ is the area of the face of the Voronoi polyhedron common to particles $i$ and $j$. The correlation coefficient [31] between the bond orientational order parameters $q_{lm}(i)$ and $q_{lm}(j)$, where particle $j$ is a Voronoi neighbor of $i$,

$$ S_{ij} = \frac{\sum_{m=-6}^{6} q_{6m}(i)q_{6m}^*(j)}{\left(\sum_{m=-6}^{6} |q_{6m}(i)|^2\right)^{1/2} \left(\sum_{m=-6}^{6} |q_{6m}(j)|^2\right)^{1/2}}, \quad (4.5) $$

is sensitive to face-centered-cubic (FCC) order. When $S_{ij} > 0.7$, $i$ and $j$ are considered ‘connected’. If particle $i$ has more than 10 connected Voronoi neighbors, it is defined as ‘crystal-like’. The ratio $N_{cr}/N$ gives the fraction of crystal-like particles in a given configuration. In addition, we also define a crystal cluster as the set of crystal-like particles that possess mutual Voronoi neighbors. Distinct crystal clusters that
nucleate and grow upon heating and cooling are shown in Fig. 4.1.

Not only is our detection scheme very standard compared to other studies [41, 42, 43], but also we incorporate two improvements to our scheme to address the concerns in [45] about the flaws in applying bond orientational order parameter. First, the nearest neighbors are defined by Voronoi tessellations to remove the arbitrariness associated with the cutoff distance in the standard definition. Second, in $q_{lm}$ calculations each bond between the central particle and the nearest neighbors is weighted by the area of Voronoi polyhedron facet such that $q_{lm}$ is a continuous function of particle coordinates.
Figure 4.2: Shifted and normalized probability for crystallization \( \frac{P(R_{h,c}) - P_{h,c}^\infty}{P_{h,c}^0 - P_{h,c}^\infty} \) versus the scaled heating or cooling rate \( \log_{10}(R_{h,c}/R_{h,c}^M)^{1/\kappa_{h,c}} \). Circles (squares) indicate data for cooling (heating) for diameter ratios \( \alpha = 1.0 \) (filled symbols) and 0.97 (open symbols). The insets show the fraction of crystal-like particles \( N_{cr}/N \) as a function of temperature \( T \) during cooling (lower left) and heating (upper right) for 12 configurations with \( \alpha = 1.0 \). The four solid, dashed, and dot-dashed curves in each inset correspond to cooling and heating trajectories with rates slower than \( R_{h,c}^* \), near \( R_{h,c}^* \), and faster than \( R_{h,c}^* \), respectively. Trajectories for which \( N_{cr}/N \) exceeds 0.5 (above the horizontal dashed line) are considered to have crystallized during the heating or cooling protocol.
4.4 Probability for Crystallization

For each diameter ratio and rate, we measure the probability for crystallization

\[ P(R_{h,c}) = \frac{N_X}{N_{\text{tot}}} \],

where \( N_X \) is the number of trajectories that crystallized with \( N_{cr}/N > 0.5 \) during the heating or cooling protocol and \( N_{\text{tot}} \) is the total number of trajectories (cf. insets to Fig. 4.2). We find that the data for \( P(R_{h,c}) \) collapses onto a sigmoidal scaling function as shown in Fig. 4.2:

\[
\frac{(P(R_{h,c}) - P^\infty_{h,c})}{P^0_{h,c} - P^\infty_{h,c}} = \frac{1}{2} \left[ 1 - \tanh \left( \log_{10} \left( \frac{R_{h,c}}{R^M_{h,c}} \right)^{1/\kappa_{h,c}} \right) \right], \quad (4.6)
\]

where \( P^\infty_{h,c} \) is the probability for crystallization in the limit of infinitely fast rates \( R_{h,c} \to \infty \), \( P^0_{h,c} \) is the probability for crystallization in the \( R_{h,c} \to 0 \) limit, \( R^M_{h,c} \) is the rate at which \( P(R_{h,c}) = (P^0_{h,c} + P^\infty_{h,c})/2 \), and \( \kappa_{h,c} \) is the stretching factor. We find that \( \kappa_c \approx 0.25 \) and \( \kappa_h \approx 0.2 \) for \( \alpha = 1.0 \), and these factors increase by only a few percent over the range in \( \alpha \) that we consider. We define the critical heating and cooling rates \( R^*_h \) and \( R^*_c \) by the rates at which \( P(R_{h,c}) = 0.5 \), *i.e.*

\[
R^*_h = R^M_{h,c} 10^{\kappa_{h,c} \tanh^{-1} \left[ \frac{P^0_{h,c} + P^\infty_{h,c}}{P^0_{h,c} - P^\infty_{h,c}} \right]}, \quad (4.7)
\]

As shown in the insets to Fig. 4.2, for \( R_{h,c} \ll R^*_h \) most of the configurations crystallize during heating or cooling. In contrast, for \( R_{h,c} \gg R^*_h \), none of the configurations crystallize.
Figure 4.3: Maximum value $N_c^{\text{max}}$ of the number of crystal clusters $N_c(T)$ normalized by $L^3/\sigma_A^3$ (averaged over 1000 trajectories) during the cooling (squares) and heating (circles) protocols at rates $R_c \approx 0.5R^*_c$ and $R_h \approx 0.5R^*_h$ for LJ mixtures with diameter ratios $\alpha = 1.0, 0.97, \text{and } 0.95$. For all systems, the maximum number of crystal clusters is larger for the heating protocol compared to that for the cooling protocol and $N_c^{\text{max}}$ decreases with increasing glass-forming ability (decreasing $\alpha$).

4.5 Results

An advantage of MD simulations is that they can provide atomic-level structural details of the crystallization dynamics that are often difficult to obtain in experiments. In Fig. 4.1, we visualize the nucleation and growth of clusters of crystal-like particles during the heating and cooling simulations. In both cases, the number of clusters reaches a maximum near $T \approx 0.5$. In Fig. 4.3, we show the maximum number of clusters $N_c^{\text{max}}$ (normalized by $L^3/\sigma_A^3$) that form during the heating and cooling protocols. We find that more crystal clusters form during the heating protocol compared to the cooling protocol for all particle diameter ratios studied, which is supported
by the measured time-temperature-transformation (TTT) diagram. In addition, we will show below that the asymmetry ratio $R_h^*/R_c^* > 1$, and that the ratio grows with increasing GFA (increasing diameter ratio) and decreasing $R_p$. We find that CNT can qualitatively describe the dependence of the asymmetry ratio on the GFA, as measured by the critical cooling rate $R_c^*$, for both our MD simulations and recent experiments on BMGs, as well as on the preparation cooling rate $R_p$ for the MD simulations.

4.6 Intrinsic Asymmetry Ratio

The critical heating and cooling rates can be obtained by fitting the probability for crystallization $P(R_{h,c})$ as a function of $R_h$ or $R_c$ to the sigmoidal form in Eq. 4.6. We first investigate the minimum value for the asymmetry ratio $R_h^*(\infty)/R_c^*$, which is obtained by taking the $R_p \to \infty$ limit. (The asymmetry ratio $R_h^*(R_p)/R_c^*$ for finite preparation rates $R_p$ will be considered in Sec. 4.7.) In Fig. 4.4, we plot $R_h^*(\infty)/R_c^*$ versus $R_c^*$ (for diameter ratios $\alpha = 1.0, 0.97, 0.96, 0.95, \text{ and } 0.93$). We find that $R_h^*(\infty) > R_c^*$ for all systems studied, which is consistent with classical nucleation theory (CNT). As shown in Fig. 4.1, more crystal nuclei form during the heating protocol than during the cooling protocol. In addition, CNT predicts that the growth rates for crystal nuclei are larger during heating compared to cooling. In Sec. 4.6.1, we will show that both factors contribute to an increased probability for crystallization during heating.
Figure 4.4: Intrinsic asymmetry ratio $R^*_h(\infty)/R^*_c$ versus the critical cooling rate $R^*_c$ (for diameter ratios $\alpha = 1.0, 0.97, 0.96, 0.95,$ and $0.93$) normalized by $R_0 = 1K/s$ on a logarithmic scale. The inset shows the intrinsic asymmetry ratio versus $\log_{10} R^*_c/R_0$ on an expanded scale. The filled circles indicate data from the MD simulations and filled squares indicate data from experiments on Zr- and Au-based BMGs [17, 18]. The prediction (Eq. 4.12) from classical nucleation theory (solid line) with $A' = (8\pi AD_0^4)/3a^3 = 0.5$ (in units of $\varepsilon^2/(m^2\sigma_4^4)$), $\Sigma = 0.26,$ and $Q_{eff} = 2.6$ interpolates between the MD simulation data at high $R^*_c$ and experimental data from BMGs at low $R^*_c$.

In Fig. 4.4, we also show that the asymmetry ratio $R^*_h(\infty)/R^*_c$ increases as the critical cooling rate $R^*_c$ decreases, or equivalently as the glass-forming ability increases. In the MD simulations, we were able to show a correlation between the asymmetry ratio and the critical cooling rate over roughly an order of magnitude in $R^*_c$. In Sec. 4.6.1, we introduce a model that describes qualitatively this dependence of the asymmetry ratio on $R^*_c$. 

\[
\log_{10}(R^*_h(\infty)/R^*_c) \approx \frac{8\pi AD_0^4}{3a^3} \left(\frac{R^*_c}{R_0}\right) - \frac{2}{3} \left(\frac{R^*_c}{R_0}\right)^2
\]
4.6.1 Classical Nucleation Theory Prediction for the Asymmetry Ratio

In classical nucleation theory (CNT), the formation of crystals is a nucleation/growth process: fluctuations in the size of crystal nuclei that allow them to reach the critical radius \( r^* \), and then growth of post-critical nuclei with \( r > r^* \). To form a critical nucleus, the system must overcome a nucleation free energy barrier:

\[
\Delta G^* = \frac{16\pi}{3} \frac{\Sigma^3}{\Delta G^2},
\]

(4.8)

where \( \Delta G \) is the bulk Gibbs free energy difference per volume (in units of \( \epsilon/\sigma^3 \)) and \( \Sigma \) is the surface tension between the solid and liquid phases (in units of \( \epsilon/\sigma^2 \)).

We assume that \( \Delta G = c(T_m - T) \) [36], where \( T_m \) is melting temperature, \( T_m - T \) is the degree of under-cooling, and \( c \sim L_v/T_m \) is a dimensionless parameter that characterizes the thermodynamic drive to crystallize and will be used to tune the GFA of the system (where \( L_v \) is the latent heat of fusion). Within CNT, the rate of formation of critical nuclei (nucleation rate) is given by:

\[
I = AD_0 \exp\left(-\frac{Q_{\text{eff}}}{T}\right) \exp\left(-\frac{\Delta G^*}{T}\right),
\]

(4.9)

where \( A \) is an \( O(1) \) constant with units \( \sigma^5 \), \( D_0 \) is the atomic diffusivity with units \( \sigma_A^2 \sqrt{\epsilon/m} \), and \( Q_{\text{eff}} \) is an effective activation energy for the diffusivity (with units of \( \epsilon \)). After the nucleation free energy barrier \( \Delta G^* \) has been overcome and crystal nuclei
reach $r \geq r^*$, the growth rate of crystal nuclei is given by

$$U = \frac{D_0}{a} \exp \left( - \frac{Q_{\text{eff}}}{T} \right) \left[ 1 - \exp \left( - \frac{\Delta GV}{T} \right) \right],$$  

(4.10)

where $a$ the characteristic inter-atomic spacing.

In Fig. 4.5, we plot the nucleation $I/AD_0$ and growth rates $Ua/D_0$ with $Q_{\text{eff}} = 2.6$ and $T_m \approx 1.40$ from MD simulations of binary LJ systems [34], $\Sigma = 0.26$, which is typical for BMGs [17], while varying the GFA parameter from $c = 1.2$ to 0.5 (corresponding to diameter ratios from $\alpha = 1.0$ to 0.93.) Both $I(T)$ and $U(T)$ are
peaked with maxima $I^*$ and $U^*$ at temperatures $T_I$ and $T_U$. In Fig. 4.5, we show that as the GFA increases, $I^*$ and $U^*$, as well as $T_I$ and $T_U$ decrease. However, $T_I$ decreases faster than $T_U$, so that the separation between the peaks, $T_U - T_I$, increases with GFA.

To determine the critical heating and cooling rates, $R^*_h$ and $R^*_c$, we must calculate the fraction of the samples $N_X$ that crystallize and the probability for crystallizing $P(R_{h,c}) = N_X/N_{tot}$, where $N_{tot}$ is the total number of samples, upon heating and cooling. Within classical nucleation theory, the probability to crystallize upon cooling from $T_i$ to $T_f$ is given by [35]:

$$P(R_c) = \frac{4\pi}{3R_c^4} \int_{T_i}^{T_f} I(T') \left[ \int_{T'}^{T_f} U(T'')dT'' \right]^3 dT'. \quad (4.11)$$

We assume that $T_i$ is above the liquidus temperature $T_l$, and $T_f$ is below the glass transition temperature $T_g$, where the time required to form crystal nuclei diverges. We can rearrange Eq. 4.11 to solve for the critical cooling rate at which $P(R_c^*) = 0.5$:

$$\left( R_c^* \right)^4 = \frac{8\pi}{3} \int_{T_i}^{T_f} I(T') \left[ \int_{T'}^{T_f} U(T'')dT'' \right]^3 dT'$$

$$= A' \int_{T_i}^{T_f} dT' \exp \left( -\frac{Q_{eff}}{T'} \right) \exp \left( -\frac{\Delta G^*}{T'} \right)$$

$$\left[ \int_{T'}^{T_f} \exp \left( -\frac{Q_{eff}}{T''} \right) \left[ 1 - \exp \left( -\frac{\Delta GV}{T''} \right) \right]dT'' \right]^3,$$  

(4.12)

where $A' = (8\pi AD_0^4)/(3a^3)$ and we assumed that $A$, $D_0$, and $a$ are independent of temperature. A similar expression for the intrinsic critical heating rate $R^*_h(\infty)$ can
be obtained by reversing the bounds of integration in Eq. 4.12.

In Fig. 4.4, we plot the intrinsic asymmetry ratio $R_h^*(\infty)/R_c^*$ predicted from Eq. 4.12 versus the critical cooling rate $R_c^*$ after choosing the best value $A' = 0.5$ that interpolates between the MD simulation data at high $R_c^*$ and experimental data from BMGs at low $R_c^*$. We find that CNT qualitatively captures the increase in the asymmetry ratio with increasing GFA over a wide range of critical cooling rates from $1K/s$ (experiments on BMGs) to $10^{12}K/s$ (MD simulations of binary LJ systems). A comparison of Figs. 4.4 and 4.5 reveals that the increase in the intrinsic asymmetry ratio is caused by the separation of the peaks in the growth and nucleation rates $U(T)$ and $I(T)$ that occurs as the GFA increases. Thus, we predict an enhanced value for $T_U - T_I$ in experiments on BMGs since the critical cooling rate in experiments is orders of magnitude smaller than in the MD simulations.

The fact that $R_h^*(\infty) > R_c^*$ is also reflected in the asymmetry of the “nose” of the time-temperature-transformation (TTT) diagram. In Fig 4.6, we show the probability $P$ that the system has crystallized at a given temperature $T$ after a waiting time $t$ for monodisperse LJ systems. We find that $T_{\text{min}} \sim 0.5-0.6$ is the temperature at which the waiting time for crystallization is minimized and that the time to crystallize is in general longer for $T < T_{\text{min}}$ compared to $T > T_{\text{min}}$. Because crystallization on average occurs at a higher temperature during heating and a lower temperature during cooling, the asymmetry in the TTT diagram indicates that slower rates are required to crystallize during cooling than during heating, i.e. $R_c^* < R_h^*$. 
Figure 4.6: The time-temperature-transformation (TTT) diagram during cooling is visualized by plotting the probability to crystallize $P$ (increasing from light to dark) from 96 samples as a function of temperature $T$ and waiting time $t$ for LJ systems with diameter ratio $\alpha = 1.0$. A sample is considered crystalline if the number of crystal-like particles satisfies $N_{cr}/N > 0.5$. The initial states are dense liquids equilibrated at $T = 2.0$. Each initial state is cooled (at rate $R_c \gg R^*_c$) to temperature $T < T_i$, where $T_i \approx 1.4$ is the liquidus temperature, and then run at fixed $T$ for a time $t$.

4.7 Asymmetry Ratio for Finite $R_p$

In Sec. 4.6.1, we assumed that the initial samples (i.e. the zero-temperature glasses) for the heating protocol were prepared in the $R_p \to \infty$ limit and, thus were purely amorphous. How does the asymmetry ratio $R^*_h(R_p)/R^*_c$ depend on $R_p$ when the preparation cooling rate $R_p$ is finite and partial crystalline order can occur in the samples? In this section, we show results for the asymmetry ratio $R^*_h(R_p)/R^*_c$ for monodisperse systems using a protocol where the samples are quenched from equilibrated liquid states to zero temperature at a finite rate $R_p$ and then heated to temperature $T_f$ at
rate $R_h$. (See Sec. 4.2.) Note that when $R_p/R_c^* \approx 1$, some of the samples crystallize during the cooling preparation, yet these samples are still included in the calculation of the probability $P(R_h^*(R_p))$ to crystallize. In Fig. 4.7, we show the results for the asymmetry ratio $R_h^*(R_p)/R_c^*$ from MD simulations. We find that $R_h^*(R_p)/R_c^*$ grows rapidly as $R_p$ approaches $R_c^*$ from above and reaches a plateau value of $\sim 1.2$ in the limit $R_p/R_c^* \gg 1$.

The critical heating rate $R_h^*(R_p)$ at finite $R_p$ can also be calculated from CNT using an expression similar to Eq. 4.12 with an additional term that accounts for cooling the equilibrated liquid samples to zero temperature at a finite rate. In Fig. 4.7, we show that the asymmetry ratio $R_h^*(R_p)/R_c^*$ predicted using CNT agrees qualitatively with that from the MD simulations. The number of crystal nuclei that form during the quench increases with decreasing $R_p$, which causes $R_h^*(R_p)/R_c^*$ to diverge as $R_p \to R_c^*$. The predicted intrinsic contribution to the asymmetry ratio for $R_p \sim R_c^*$ is small, and $R_h^*(R_p)/R_c^*$ is dominated by the preparation protocol. In contrast, the asymmetry ratio $R_h^*(R_p)/R_c^* \approx 1.2$ is dominated by the intrinsic contribution in the $R_p \gg R_c^*$ limit. As shown in Fig. 4.4, the size of the intrinsic contribution to the asymmetry ratio can be tuned by varying the GFA, which controls the separation between the peaks in the nucleation $I(T)$ and growth $U(T)$ rates.
Figure 4.7: Asymmetry ratio $R_h^*(R_p)/R_c^*$ plotted versus the preparation cooling rate $R_p$ normalized by the critical cooling rate $R_c^*$ from MD simulations with $\alpha = 1.0$ (filled circles) and the prediction from CNT (solid line) with the same parameters used for the fit in Fig. 4.4 and the GFA parameter set to $c = 1.2$. The vertical dashed line indicates $R_p = R_c^*$. The horizontal dashed lines $R_h^*(R_p)/R_c^* = 1.18$ and $1$ indicate the plateau value in the $R_p \gg R_c^*$ limit and $R_h^* = R_c^*$, respectively. The gap between the horizontal dashed and dotted lines give the magnitude of the intrinsic asymmetry ratio for this particular GFA (cf. Fig. 4.4).
Chapter 5

Conclusions

We did mainly simulation research on granular system, both in dynamics and jamming.

In chapter 1, we invented new force model, and perform simulation with new force model to make hopper flow. We get correlation between opening size and flux as:

$$V = Cg^{1/2}(D - kd_e)$$  \hspace{1cm} (5.1)

Same correlation was found in both experiment and simulation. Our new force model also made system jammed, which formal method didn’t. We used discharge time to derive jamming probability, and strongly supported random process assumption on hopper flow.

In chapter 2, we used same force model on particles in rotation drum. We collected avalanche data and found power law correlation between avalanche frequency and avalanche magnitude. Analysis on avalanche shape is done and get parabolic curve. Same results are found on both theory and experiment.

In chapter 4, We performed MD simulations of binary Lennard-Jones systems to model the crystallization process during heating and cooling protocols in metallic
glasses. We focused on measurements of the ratio of the critical heating $R_h^*$ and cooling $R_c^*$ rates, below which crystallization occurs during the heating and cooling trajectories. We find: 1) $R_h^* > R_c^*$ for all systems studied, 2) the asymmetry ratio $R_h^*/R_c^*$ grows with increasing glass-forming ability (GFA), and 3) the critical heating rate $R_h^*(R_p)$ has an intrinsic contribution $R_h^*(\infty)$ and protocol-dependent contribution $R_h^*(R_p) - R_h^*(\infty)$ that increases with decreasing cooling rates $R_p$ used to prepare the initial samples at zero temperature. We show that these results are consistent with the prediction from classical nucleation theory that the maximal growth rate occurs at a higher temperature than the maximal nucleation rate and that the separation between the peaks in nucleation $I(T)$ and growth $U(T)$ rates increases with the GFA. Predictions from CNT are able to qualitatively capture the dependence of the asymmetry ratio on the GFA as measured through $R_c^*$ for both our MD simulations and recent experiments on BMGs as well as on $R_p$ for the MD simulations. Thus, our simulations have addressed how the thermal processing history affects crystallization, which strongly influences the thermoplastic form-ability of metallic glasses.

In chapter 3, we invented new order metric Voronoi entropy based on Voronoi tesselation and information theory. Voronoi entropy is totally different from traditional order metric which is highly based on certain symmetry. We successfully distinguish lattice from liquid in bi-disperse system, which $Q_6$ can’t and we found simple cubic-BCC phase transition in patched particle system, which $Q_6$ still can’t find. We can easily prove that Voronoi entropy can detect any lattice structure. However, we faced
some difficulties in accuracy. Possible solution will be discussed in next section.
Chapter 6

Future Directions

6.1 Application of force model

We can apply new force model on jamming research. In current jamming research, we mainly use Lubachevsky-Stillinger hard sphere model, Lennard-Jones potential, and conjugate gradient(CG) method. It can be used directly on friction correlation on jamming. We have showed that new force model can make jamming and can reduce energy to zero. Packing fraction and packing properties in friction particles are interesting research area and comparing with CG, new force model is much faster, and more reasonable to set and change friction coefficient.

6.2 Better Voronoi Entropy

We have mentioned that Voronoi Entropy is good in theory, but not that good in practice. One problem is shape factor $\psi$ is not very discriminate. Since we are mainly focusing jammed system, Voronoi polyhedron are mostly similar. And many polyhedrons have same $\psi$, which means they are indistinguishable in $\psi$. These problem arise, mainly because we over-compressed information of polyhedron. One possible solution is adding more information to specify polyhedrons.
Another approach is calculating pair correlation. We can compare every pair of polyhedrons. We can define similarity of Polyhedron A and B as:

\[ f(A, B) = \frac{V(a, b')}{V(a)} \]  

(6.1)

first, we scale A’s and B’s volume to 1, which is refers to a and b. Then we find a combination of rotation and translation for b, that make overlap of a and b maximum. The more a and b similar, the bigger f is. Once we calculate f for all pairs, we can do lattice particle detection, which we did in asymmetry research. Similarity bigger than certain number is defined as strong connection. If a particle i has more than certain neighbors with strong connection, we select it as lattice particle. Comparing with \( Q_6 \) it is more sensitive for all lattice, mainly because it didn’t compress information.

We can also use Voronoi entropy in quasi-crystal. We can find that in quasi-crystal, there are only limited types of Voronoi polygon(polyhedron). So we can predict that it’s entropy will be similar with multi-unit cell system.
Bibliography
Bibliography


