Structural Characteristics and Applications of Hard-particle Packings

via Event-driven Molecular Dynamics Simulations

by

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ABSTRACT

In this dissertation, several computational results of jammed packings of hard particles are presented, including the investigation of disordered hard-non-sphere in 2 dimensions and hard-ellipsoid packings in 3-dimensions. In the first part, an introduction of the dissertation will be provided. In the introduction, a briefly review is for the researches and results associated with hard particle packings over last 10 years. In the second part of this dissertation, the detailed discussion of the mathematical algorithms will be presented to model hard-particle systems, and in particular, an algorithm event – driven (collision-driven) molecular dynamics (EDMD) is deep studied. This algorithm is always employed to generate disordered jammed packings of hard spheres, ellipsoid, superdisks and superballs and all of the packings in our paper. In the third part, to generating maximally random jammed (MRJ) packings of binary superdisks in two-dimensions is achieved by EDMD algorithm and the fundamental characteristics of the packing structure has been analyzed. In these MRJ packings, other parameters of packing system are considered for the effect of structure characteristics (i.e., size ration, number ratio etc.). Then, through analysis of the local packing structure, a relative accurate local theoretical prediction method is proposed and the verification is provided subsequently. In the fourth part of this dissertation, the several different binary ellipsoids MRJ packing in 3-dimensions are produced as extension. By using these packing structures, it is able to be systematically discussed the characteristics of the binary ellipsoids and the structures will be applied in the subsequent sintering simulation as initial configurations. In the

conclusion part, a concluding is remarked and several future directions of the research of packing are provided.

ACKNOWLEDGEMENTS

I am indebted to a number of people who have made my stay at Arizona State University both productive and enjoyable. I thank my family and friends for their support and love, without which I could not have finished this dissertation.

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CHAPTER 1 INTRODUCTION

Granular materials, defined as large conglomerations of discrete macroscopic particles, are widely distributed in our nature, such as nuts, rock, coal, sandy soil, rice and gravel. They are one of the indispensable elements for our environment and linked with our daily lives. Also, granular materials are very commercially important in applications as diverse as soil in agriculture, concrete in the civil engineering, the medicinal powder in the pharmaceutical industry and the composite cathode material powder in solid oxide fuel cell of energy production. As material scientist Patrick Richard said, "Granular materials are ubiquitous in nature and are the second-most manipulated material in industry (the first one is water)"[3].

Packing issues, such as how densely given particles can fill in the space, have been perennial studied as an entry point for understanding the characteristics of the granular material. In addition, packing problems are very useful in the analysis of heterogeneous materials, colloids and granular media[2]. They even appear in numerous biological contexts, spanning a wide spectrum of length scales as well, which includes macromolecules crowded condition within living cells, the packing of cells to form tissue and the protein structure[2]. Thus, research into packing is directly applicable and even can be dated back to several centuries ago. In 1611, Kepler proposed a question: what is the densest way to stack equal-sized balls? His conjecture was the face-center cubic (fcc) arrangement[2]. Then in 1831, Gauss first verified the fcc packing is the densest Bravais lattice packing[4]. Although the packing problems are easy to be proposed, they are very difficult to be solved rigorously. It was not until 2005 that Hales proved the general

Kepler's conjecture that there isn't any other arrangement of spheres in three-dimensional Euclidean space whose coverage area can exceed that of the fcc packing[5]. Even the two-dimensional simpler analog of Kepler's problem, the densest packing of identical circles in a plane, proved only 70 years ago[6][7]. Hence, packing problems arouse more and more interest and has been a source of fascination in materials science, physics and other areas.

Investigation of the characteristics of dense particle packing, as a way of packing analysis, can not only help us understand the symmetry, structure and macroscopic physical properties of condensed-matter phases, liquids, glasses and crystals, but also bring us a good and basic insight into the structure properties of granular materials and other like-particle systems[2]. For the packing problems, most studies of the densest packings in two dimensions and three dimensions focused on circular or spherical shapes. It was Torquato who first well defined the random close packing (RCP) and introduced a new concept of maximally random jammed (MRJ) state, which is more precise and break the impasse that the original picture of RCP cannot be made mathematically precise with the support of conclusion via a molecular dynamics study of hard spheres[8]. Donev et.al then discussed the densest packing fraction of several different basic packings, such as hard circular particles, hard sphere monodisperse and binary-disperse system[9]. Later, the packing faction and other characteristics of order and disordered ellipse and ellipsoids packing in mono and binary system had been studied by Donev[10][11][12]. However, it is only more recently that non-circular and non-spherical shapes (e.g., superdisks) have been investigated in different Euclidean space R^d by introduced deformation parameter.

Yang et.al investigated many essential characteristics of optimal and maximally random jammed packing of superballs and superdisks[1][13][14].

In Refs. [1][14], they showed the dense and maximally dense packing of superballs, which is a family of nonspherical particles with versatile shapes. Specially, a d-dimensional superball is a centrally symmetric body in R^d occupying the region

$$|x_1|^{2p} + |x_2|^{2p} + \cdots + |x_d|^{2p} \leq 1,$$

Where x_i ($i = 1,\ldots,d$) are Cartesian coordinates and $p \geq 0$ is the deformation parameter, which indicates to what extent the particle shape has deformed from that of d-dimensional sphere (p=1). Thus, the superdisk and superball are the cases for two-dimensional (d=2) and three dimensional (d=3). The geometric shapes are shown in Figure 1 and Figure 2 [13]. They shows convex particles ($p \geq 0.5$) with both cubic-like and octahedral-like shapes as well as concave particles ($0 \leq p \leq 0.5$) with octahedral-like shapes.

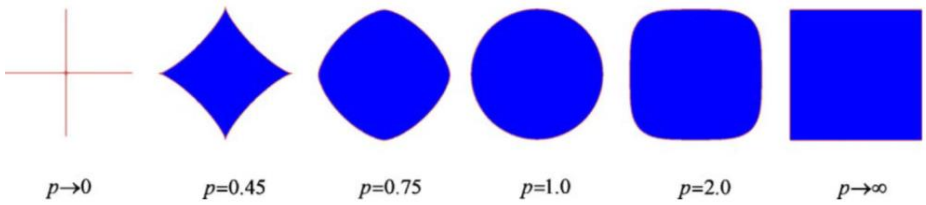


Figure 1: Superdisks with Different Values of Deformation Parameter p[15]

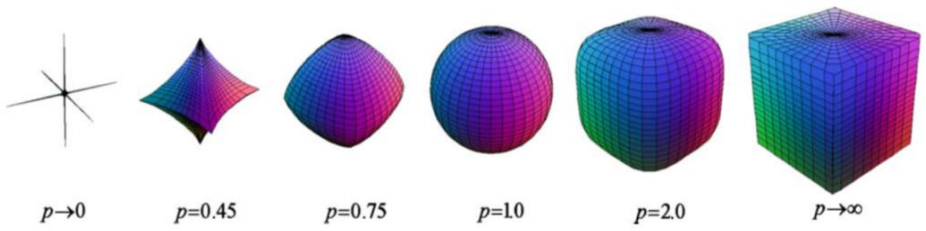


Figure 2: Superballs with Different Values of Deformation Parameter p[15]

It is necessary to mention several definitions in packing studies. Packing is defined as a large conglomeration of non-overlapping (i.e., hard) particles in either a finite-sized container or in d-dimensional Euclidean space R^d. Packing fraction ϕ, one of important parameters used for characterizing the packing structure, is the fraction of space covered by the hard particles. "Jammed" packings are defined as those particle configurations in which each particle is in contact with its nearest neighbors in a such way that possess mechanical stability[2]. In general, for a given particle shape, the associated packings have a diversity of densities and degrees of order. The maximally jammed packing of equal-size particles, usually achieved by ordered arrangements depending on the particle symmetry, are the thermodynamic stable phases of the associated shapes in the infinite-pressure limit and also determine the high-density equilibrium phase behavior of such hard-particle systems. On the other hand, the maximally random jammed (MRJ) packings can be viewed as prototypical glasses in that they are maximally disordered while simultaneously being mechanically rigid. Roughly speaking, MRJ packings can be obtained by compressing liquid configurations at the largest possible rate to a strictly jammed (i.e., mechanically stable) configuration.

A number of schemes can be used to simulate the densest packing of hard particles. Based on the molecular dynamics simulation in which the motions and the interactions of each particle have been simulated as a function of time, there are two main approaches – time-driven and event-driven molecular dynamics. Time-driven molecular dynamics (TDMD) is more suitable for soft particles and more efficient in the dense system. In this approach, time changes in small steps and the equations of motion are integrated[15]. However, an alternative rigorous algorithm is event-driven molecular dynamics (EDMD), based on a rather general discrete model. In EDMD, the advancing time in TDMD is replaced by the binary collision event and it has higher efficiency in dilute system because the simulation is advanced to the time of the collision event with the smallest scheduled time (the impending event) and gets rid of the useless steps without any collision. Thus, in the densest packing research, the EDMD has been efficiently implemented to simulate the evolution of system from dilute to jammed.

In this paper, we generate both packings of binary superdisks in two-dimensions and bi-disperse ellipsoids in three-dimensions that represent the MRJ state of these particles by using the aforementioned approach EDMD and investigate their characteristics. Since one cannot enumerate all possible packing even for a small number of particles, it is desirable to devise a small set of parameters that can characterize packings well. For example, size ratio is one of the common parameter in binary system and deformation parameter p is always used for investigation of non-sphere particle system. Thus, we picked up several common and important parameters, such as size ratio, number ratio, aspect ratio and deformation parameter, for the investigation in the packing

system. According to several related research and papers, for superdisks, the relation between deformation parameter *p* and packing fraction had been intensively studied despite the simplicity the exhibit rich packing characteristics. However, the effect of size ratio, number ratio and packing faction hadn't been systematically investigated in binary superdisk system. Furthermore, we proposed a local organization principle for the prediction of the global packing fraction in a system[16]. We find that the distribution of local contact angle possesses assumes a universal Gaussian form associated with the minimal curvature of the particle surface. This principle allows us to devise formulas that provide accurate estimates of the MRJ packing fraction, which is subsequently verified by simulation results.

For research of the superdisks in R^2, it really helps that people understand the features and characteristics of this type of particles packing and it is easier to conclude under the simple dimension condition. In three-dimension, the effect of characteristics as size ratio, number ration and aspect ratio in binary hard ellpsoids packings is still a very interesting area. On the other hand, ellipsoids packing is more practical in the application of industry and engineering. For example, in this paper, the three- dimensional packing structures are models of granular materials and powder compact for sintering.

CHAPTER 2 EVENT-DRIVE MOLECULAR DYNAMICS (EDMD) ALGORITHM

2.1 MD Introduction

Original molecular dynamics (MD) approach are very popular in numerical simulation and have been implemented to study the characteristics and properties of particle packings and granular materials for many years. However, it is not very often to be discussed in detail for non-spherical particle packings (i.e., superballs). In this section, the details of this method are provided.

MD method was used to study the basic multiple hard sphere particle system as the beginning, which is rich in behavior. Then the approaches were developed and were implemented in a soft sphere particles system. In the soft spherical particles system, the interactions among particles are other spherically symmetric particles and the continuous potential energy between them. For these two different types of system, hard particles and soft particles, the algorithms are very different as well and it is necessary to work on both sides separately for a given particle system. For example, Newton's law of motion has been used and integration of its ordinary differential equations is needed for the soft particles. However, for hard particles, the interaction potential is singular and one only needs to find out the binary collision-events between a pair of particles or between a particle and hard wall of container instead of integration of ordinary differential equations[15]. In other words, we don't have to take the information of every small time step but each discrete collision events which is also a process impetus for hard particle.

For hard particles system, although there are two popular approaches for simulation, the algorithm that we call “event-driven” molecular dynamics (EDMD), advanced by collision event, is preferred because of the distinctive characteristics of this system and it is opposed to the time-driven method as we mentioned in which tiny time steps is “driving force” and the equations of motion are integrated whenever the time changes in the soft particle system. For event-driven algorithms, we are faced with the task of scheduling a series of events that are predicted to happen in the future and arranging them as a selection of the impending time from small to large order in the event list. Subsequently, the simulation moves forward to the time of the impending event with the shortest time interval and that event is processed. Then the future event list is updated and the identical process is repeated.

In the MD simulation, event-driven molecular dynamics (EDMD) method was first used for the very basic hard circular particles system, and then has been developed and improved in different ways, in particular, to increase the efficiency of the approach, such as delayed particle updates, the cell method, etc.. However, before the broadly applying event-driven simulation approach, most of the non-spherical particles have used the time-driven method, which is much easier to apply than the event-driven but inferior in both accuracy and efficiency, especially at higher densities. The reason event-driven approach had not yet been broadly applied for non-spherical particles is that it is very demanding for running a higher accurate EDMD algorithm for diverse particle shapes and large enough system[15]. Today, the running requirements of computers have already been satisfied, such as faster speeds and suitable implementation involves a

significant level of code complexity. Thus, in the following parts, we discuss in detail about an advanced event-driven molecular dynamics algorithm (EDMD) for a hard non-spherical particle system.

2.2 The Improved EDMD for Non-spherical Particles System

Several improvements of current EDMD approach have been made by Donev, Toqurato and Stillinger[15]. The algorithm is based on classical event-driven method that we mentioned above for a spherical particles system. Based on the classical one, we introduced several innovations and strengths of the current EDMD related to our simulation and results in this paper. The improved EDMD specifically allows different symmetric particles by using quaternions to present all of different orientations, unlike original hard-particle algorithms which have been restricted to the simple dimension or direction. Thus, in three-dimensional space, it is possible to make changes to different particle shapes and orientations which are very helpful for the study of different types of packing structure. The components about the shape of the particle are separated from the original concepts, so that it is convenient to adapt the algorithm to different geometric shapes. In contrast, classical EDMD was used for simple sphere packing system and there is no need to consider the effect of each particle shape in system. However, it is more complicated for the application of EDMD in a non-spherical system. One of the big adjustments is searching method.

2.2.1 Searching Method

In our research, we didn't concern the deformation of the boundary and the boundary condition is the very simple one, periodic boundary condition. Thus, we don't present how to handling the boundary problem in current EDMD. However, the searching method is the strength of this EDMD which provide a very higher efficiency for searching neighbors of the particle of interest.

2.2.1.1 Cell Method

Cell method is a traditional method for neighbor search in particle systems. It partition the whole simulation domain into N disjoint cells and each cell has a list of all the particles whose centroid are within it. Then, for a given particle *i*, its neighbors are supposed to be in the same cell as *i* or the neighbor cells. For example, if all the cells that we defined are square, each cell has night neighbor cells including itself (under periodic boundary condition). For the same reason, the cube cell has 27 neighbor cells including itself in three dimensional space. Thus, only those particles belonging to the neighboring cells or the central cell are considered as the neighbors of the particle of interest. For the shape of the cells, it can be chosen arbitrarily if the following principle can be satisfied: the cells can cover the whole simulation domain and it is easily to identify the neighbor cells for any given cell. A very important point in the cell method is that the partitioned cells in the simulation domain are independent of the motion of the particles so that the fixed cells can be relied on to identify the neighbors rigorously even the particles are in motion.

In EDMD, the event could be the collision event which is between the particle and the hard wall of container, or a binary collision. The event could also be a particle leaving the original cell. For the binary collision, each particle predicts the collision only with the particles in the (first) neighbor cells of its current cell. It is clear that the collision event cannot happen with a particle not in the neighbor cell until the particle of interest leaves the original cell. If so, there has a transfer for a particle from old cell to the new cell.

2.2.1.2 The Near-neighbor List Method

The cell method is very efficient for the equal size spherical particles, particularly at moderate densities. However, it becomes inefficient for the non-spherical particles, whose aspect ratio is far from 1. The reason is that one cannot choose the proper cells which is sufficient small to ensure the average that one particle per cell but relative large cells which contain many particles because of the large diameter of the particle. Thus, so little computational effort is saved by implementing the cell method. For the same reason, it is true even for spheres when large poly-dispersity is present since the cells need to be at least sufficient large to enclose sphere in the system, and therefore many small spheres will be inside one cell.

As we mentioned before, the main limitation of the cell method is not flexible enough and the shape of the cell cannot be adjusted to the diverse shapes of the particles. The main strength is that the partitioning into cells is static and the independent of the motion of the particles so that we can save time for update the cell following the motion

of particles. However, we have to sacrifice our advantage to correct the drawback for more general application. The preliminary idea is that each particle is inside a bounding neighborhood, namely, the bounding neighborhood completely surrounds the particle and the shape of the neighborhood is in some sense sensitive to the position and the shape of the particle of our interest. Then, any two particles with overlapping bounding neighborhoods are considered to be neighbors and the collision time or other interaction only calculated between such pairs. Thus, each particle should have a list to store the neighbors, so that one can easily find the potential interaction between its neighbors. Since the constructing and maintaining of such systems are very expensive in computation, sometimes we just choose the same bounding neighborhood shape as the original particle but elongate the axis, namely, a large size. Also the near-neighbor lists method in event-driven molecular dynamics (EDMD) has the similarity with the cell method in some degree. In other words, we just change the neighbor cells to the list of bounding neighborhood (see the details in Ref.[15]). Thus, in this paper, we focus on the non-spherical particle packings and the NNLs method is what we actually used in the simulation.

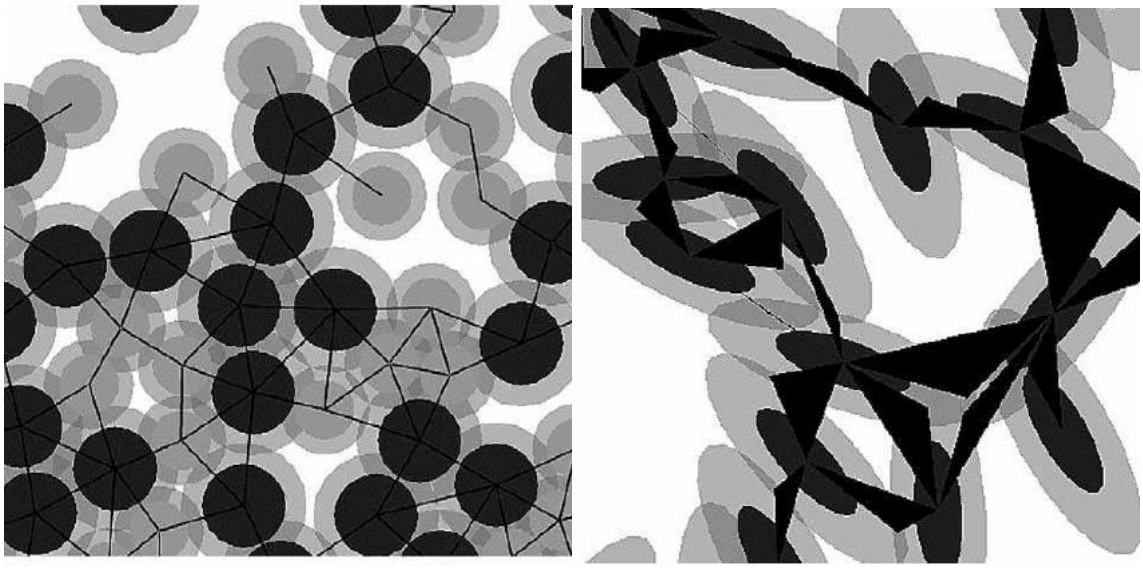


Figure 3：Visualized NNLs method for disks and ellipses. The real particles are darker and the bounding neighbors are lighter. For the upper panel binary disks, their neighbors are connected by the lines. For the lower panel binary ellipses, their neighbors are connected by the dark triangle, whose vertices are the centroids of the two ellipses and the contact point of this pair. (Reference A. Donev, S. Torquato. F. H. Stillinger, Neighbor list collision-driven molecular dynamics simulation for nonspherical hard particles, I. Algorithmic details, Journal of Computational Physics 202 (2005) 737-764)[15]

2.2.2 Overlap Potential

The verification of the nonoverlap conditions for particles is an essential part in any algorithm which aims at generating the hard particle system. For spheres particles motion in EDMD, it is very simple for predicting the time of collision by finding the first positive root of a quadratic equation. But it is more complicated for non-spherical particles. Essentially, one can find the predicted collision time between two neighbors p1(t) and p2(t) if they can find the first non-zero root of the overlap potential ζ (t) = ζ [p1(t), p2(t)] (see the details in Ref.[17]).

The overlap potential ζ (p1,p2) is a function associated with information of the positions, orientations and shapes of the particles and the value of the function indicate

whether the two particles overlap or not. Also, the inequality containing the particle information is based on *shape function* ζ

$$\zeta(r) = [u(r)]^2 - 1 \leq 0 ,$$

where is strictly convex. For this overlap potential, we have a criterion to determine the situation of pair of particles,

$$\begin{cases} \zeta[\, p1(t), p2(t)\,] > 0 \text{ if particle one p1 and particle two p2 are disjoint} \\ \zeta[\, p1(t), p2(t)\,] = 0 \text{ if particle one p1 and particle two p2 are externally tangent} \\ \zeta[\, p1(t), p2(t)\,] < 0 \text{ if particle one p1 are overlapping} \end{cases}$$

In our simulation, the collision is defined as the pair of particles is contact and we could easier find out the time of impending event (i.e., the collision) by solving the overlap potential equation $\zeta(t)$. More details of EDMD algorithm and overlap potential in our simulation are provided in Ref. [15][17][18][19]. Interested readers are strongly encouraged to read these original papers to learn more about the algorithm.

CHAPTER 3 LOCAL PRINCIPLES FOR 2D MAXIMALLY RANDOM JAMMED SUPERDISKS PACKING

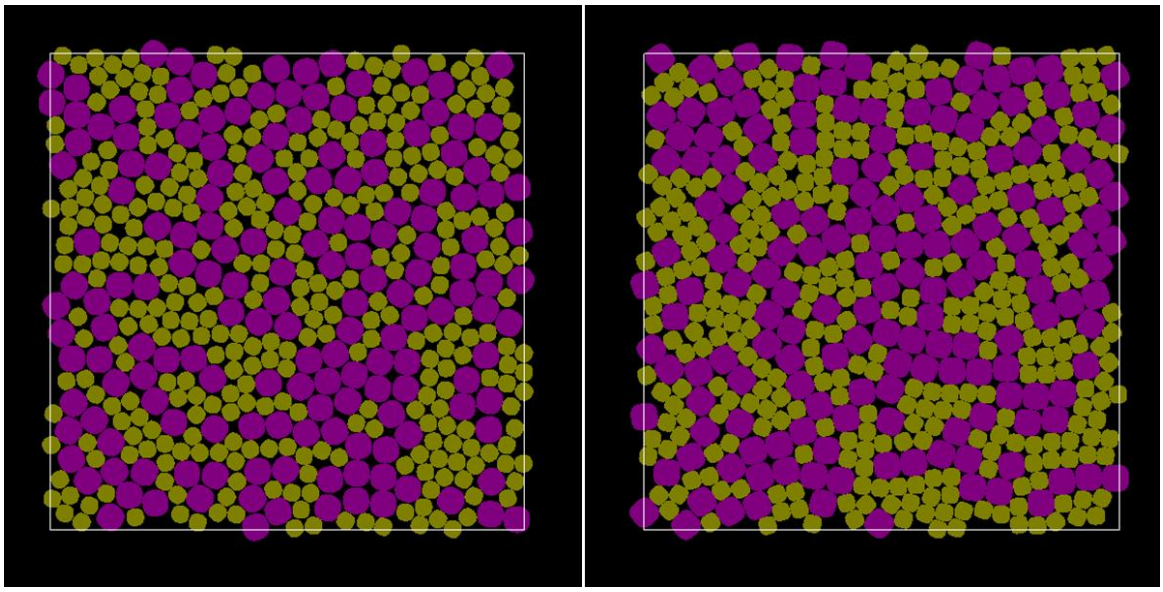
Maximally random jammed (MRJ) packings can be viewed as prototypical glasses in that they are maximally disordered while simultaneously being mechanically rigid. The prediction of the MRJ packing fraction ϕ, among other packing properties, for given particle characteristics such as shape and size distribution still poses many theoretical challenges.

In general, for a given particle shape, the associated packings can possess a diversity of densities and the degrees of order. The maximally dense packing of congruent particles, usually achieved by ordered arrangements depending on the particle symmetry, is the thermodynamic stable phases of the associated shapes in the infinite-pressure limit and also determines the high-density equilibrium phase behavior of such hard-particle systems.

3.1 MRJ Binary Superdisk Packing Generating and Analysis

Recently, the non-spherical particle system has been intensively studied for understanding the structure and properties of several novel particle shapes (i.e., superdisks). One of the common characteristic parameter for packing study is the packing fraction ϕ, which is the fraction of space covered by the hard particles. For superdisks, the relation between deformation parameter p and packing fraction aroused interest from dozens of researchers. Also, the effect of size ratio, number ratio and packing fraction are worthy to be systematically investigated in binary superdisk system as well. Thus, in this

paper, we generated several different binary mixtures superdisk system in two dimensions and did not use monodispersed superdisk systems here because they are easily crystallized into ordered packings. Here, size ratio and number ratio are the variables because we already have abundant data sets for deformation parameter p in other papers. For the superdisk, convex ($p>0.5$) and concave ($p<0.5$) represents the versatile family of square symmetry but only convex is considered since it is more general than the others.



(a) (b)

Figure 4: Typical configurations of MRJ packings of binary superdisks for two different values of the deformation parameter p. Figure (a) shows p = 0.85 at the number ratio NR=0.5 and size ratio SR=1.5 case, figure (b) shows p = 1.5 at the number ratio NR=0.5 and size ratio SR=1.5 case (where number ratio is the ratio of number of red (large size) to the number of yellow particles (small size), the size ratio is the ratio of the length of semi-major axis of red particle to the yellow particle).

3.1.1 The Effect of Size Ratio on the Characteristic of the Structure

The packings generated by event driven molecular dynamics algorithm as shown in Figure 4.

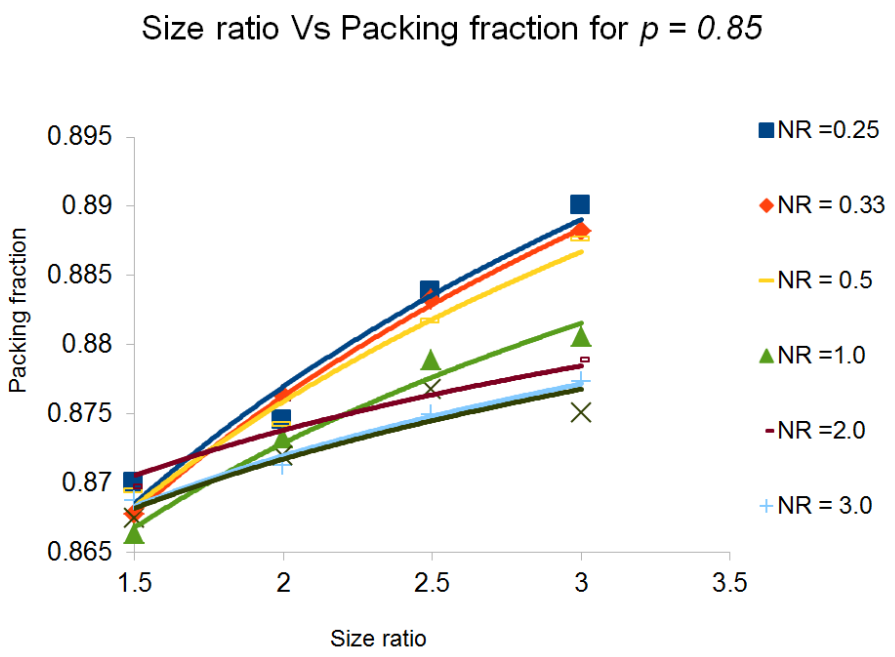


Figure 5: Size Ratio Versus Packing Fraction for p=0.85

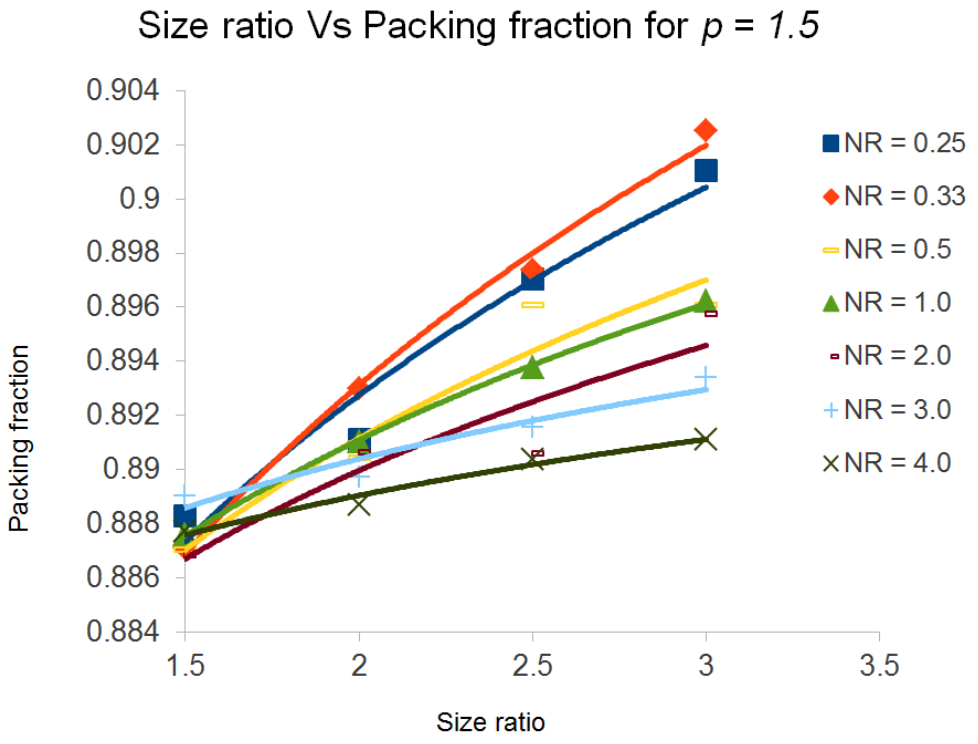


Figure 6: Size Ratio Versus Packing Fraction for p=1.5

The size ratio SR of the two superdisk species is defined as the ratio of the diameter of large superdisk over that of a small superdisk. As the Figure 5 and Figure 6 shown above, we choose several different size ratio, 1.5, 2.0, 2.5, 3.0, as our horizontal scale. Although we find that statistical fluctuation associated with the packing characteristics (i.e., packing fraction) exist because of the 500 particle numbers in the small system, the trend of the figures is obvious. In both figures with p = 0.85 and p = 1.5, they all reveal that the packing fraction increases monotonically as size ratio moves away from the ratio1.5. It is worthy of mentioning that, the increased packing fraction is highly dependent on the number ratio. This is discussed after the analysis of the effect of number ratio.

3.1.2 The Effect of Number Ratio for Characteristic of the Structure

Number ratio, which is defined as the ratio of the quantity of the large superdisks over that of the small superdisks, is another important variable in superdisk binary packing. Because of the same reason mentioned above, the statistical stability is the limitation in such small system. However, the effect of the size ratio to the packing fraction is still clear and can be analyzed. In this part, the number ratios are 0.25, 0.33, 0.5, 1.0, 2.0, 3.0, 4.0. These figures reveal that the packing fraction with a fixed size ratio decreases monotonically with the increase of number ratio. In other word, the packing fraction will get smaller if the number of large size particle increases. It also comforts to our guess: a large number ratio of larger size particles will lead to not enough number of smaller particle to fill in the spare space.

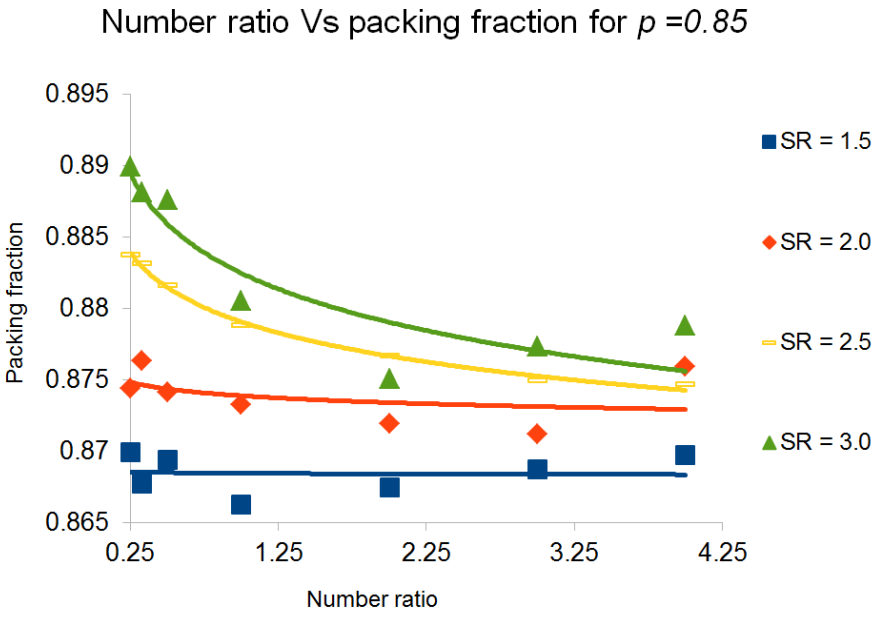


Figure 7: Number Ratio Versus Packing Fraction for p=0.85

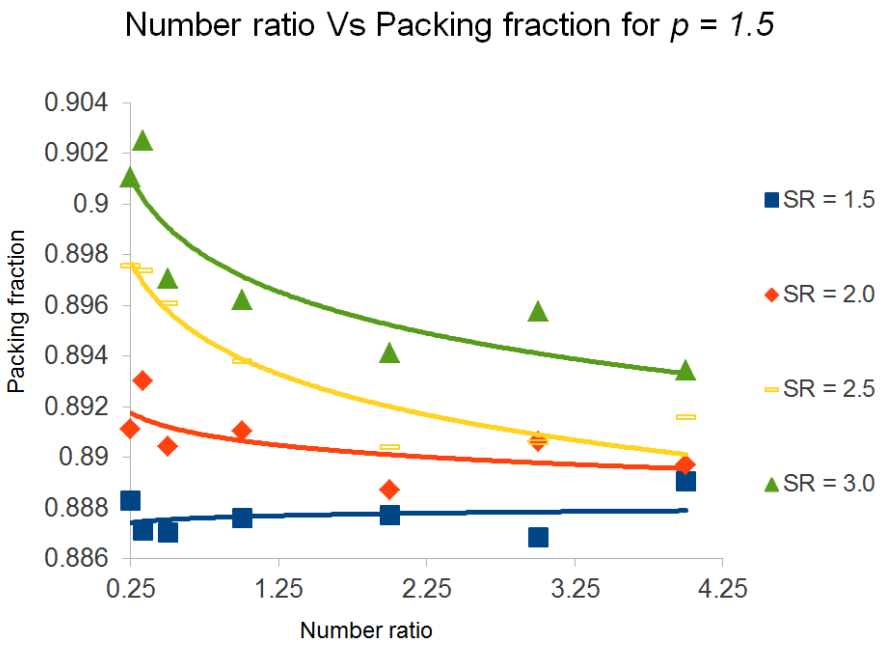


Figure 8: Number Ratio versus Packing Fraction for p=1.5

In general, these two factors, number ratio and size ratio, function together in the effect of the packing fraction. As the Figure 7 and Figure 8 shown above, the packing fraction doesn't have much fluctuation with the change of number ratio if the size ratio is around 1, since the number ratio is not that important for densities if the size of binary particles is almost the same. However, if at the proper large size ratio,

Different number of each species particle will give us totally different packing fraction. As the similar steps of analysis, the packing fraction can be affected intensively by the number ratio if the size ratio is higher enough. On the other hand, a relative high size ratio and low number ratio can provide us a pretty high packing fraction for the binary non-spherical particle packing.

3.2 Theoretical Prediction

Prediction of the packing properties for characteristics of given particle or system, such as shape and size distributions, is a long-standing and notoriously difficult problem. The determination of the maximal packing fraction ϕ_{max} for non-space-filling particles has been a source of fascination for centuries. Recently, general organizing principles and conjectures have been proposed that enable one to predict dense packing arrangements and thus, lower bounds on ϕ_{max} based on the characteristics of the particle shapes. The estimation of the MRJ density ϕ_{MRJ} is even more challenging. This can be seen from the fact that the prediction of ϕ_{max} only requires the consideration of relatively simple ordered arrangements of a small number of particles in a fundamental cell; while for ϕ_{MRJ}, it is necessary to take into account complex disordered configurations with a large number of particles with strong positional and orientational correlations.

A number of schemes to predict the density of disordered particle packings representative of the MRJ state have been developed. However, one of the defining characteristics, i.e., the packing are strictly jammed, were not explicitly incorporated. In this paper, we employ a "geometric-structure" approach [16]to devise a local organizing principle for MRJ packings of non-spherical particles. Through comprehensive computational and analytical studies of the MRJ packings of the family of superdisks with a rich spectrum of shapes extrapolating circles to squares in two-dimensions (as shown in Figure 9), we find that the distribution of local contact angles (i.e., one made by a principal axes of the particle and a line connecting its center to a contact point on the

particle surface), after proper re-scaling, possesses a universal Gaussian form for all particle shapes. Specifically, the mean value of the distribution corresponds to the contact angles associated with the minimal surface curvatures for different particle shapes. We show that such a distribution results from the two competing characteristics of the packings, i.e., maximal disorder and jamming, and thus, is an intrinsic property of MRJ state and applicable to other particle shapes in higher dimensions. This local organizing principle allows us to devise a formulism that provides accurate estimates of the MRJ packing fraction for a wide range of nonspherical shapes, which are verified by simulation results.

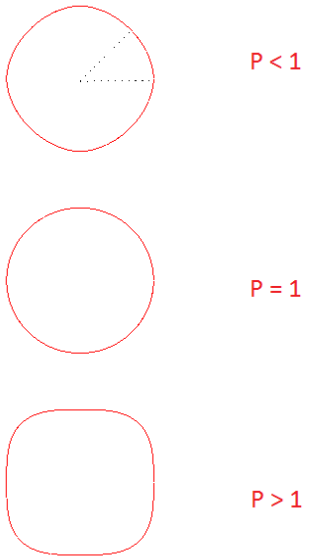


Figure 9: The Different Geometric Shape for Different Value of Deformation Parameter *p*

3.2.1 Universal Distribution of Contact

In the binary non-spherical particle system, the size ratio and number ratio are very important variables for the final packing fraction. However, we can find out even these two factors are the same in our binary superdisk system, the packing fraction still

can change with different shape (i.e., deformation parameter p). Actually, deformation parameter had been studied a lot for the packing fraction and other properties of a given structure[13]. For these kinds of packing, it is supposed to have a principle to predict the packing fraction which is worthy to do in industry or engineering.

We first have the high-quality strictly jammed packing configurations of the families of binary superdisks with number ratio $\alpha = n_L / n_S \in [4.0,0.5]$ (where n_L and n_S are respectively the number of large and small particles) and dispersity $\beta = R_L/R_S \in [4.0,0.5]$ (where R_L and R_S are the corresponding semi-axis of large and small particles, respectively) that we generated in 2.1 section by using the EDMD method. A superdisk is a region defined via the following equation:

$$|\frac{x}{a}|^{2p} + |\frac{y}{b}|^{2p} \leq 1 ,$$

where p is the deformation parameter. As p increases or decreases from unity to infinity, a superdisk continuously changes its shape from a circle to a square.

Then, for the local analysis, we pick up two contact particle from our binary systems, as shown in the Figure 10 and Figure 11 for p=0.85 and p=1.5, respectively.

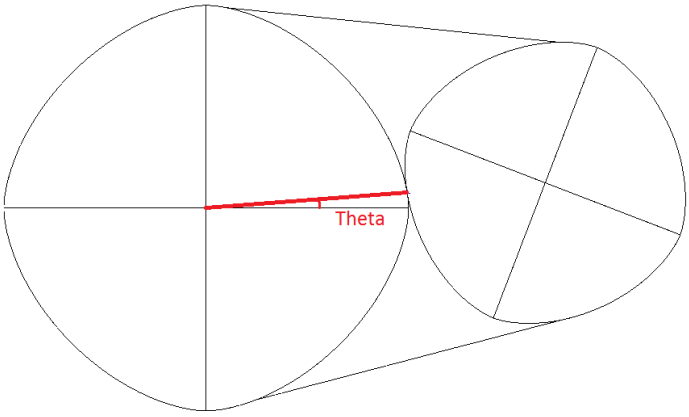


Figure 10: The Contact Angle for Binary Superdisk When p=0.85

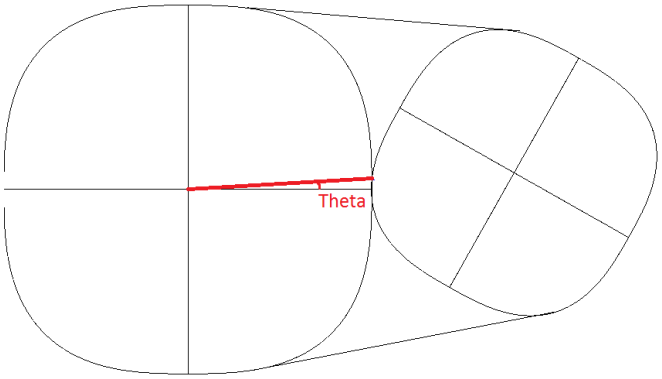


Figure 11: The Contact Angle for Binary Superdisk When p=1.5

When p=1, the equation plots as a circle (a=b) or an ellipse ($a \neq b$). In our work, p changes from 0.85 to 3. For superdisk, because it is four fold symmetric, the curvature K of point on superdisk edge serves as a period function of the corresponding angle θ of the point. The period is $T = \pi/4$. Figure 12 shows the correlation with $a = b = 1$ and

p=0.9, 1, 1.6. For all p values, the curvature K at each point is equal to the curvature of the corresponding symmetry point in the first quadrant, for which its curvature is given by

$$K(\theta) = \frac{ab(2p-1)(\cos\theta\sin\theta)^{(2p+1)/p}}{(a^2(\cos\theta)^{\frac{2}{p}}\sin^4\theta + b^2(\sin\theta)^{\frac{2}{p}}\cos^4\theta)^{\frac{3}{2}}}$$

Assume a=b=R, so the reduced curvature can be expressed as

$$K^* = K(\theta)\cdot R = \frac{(2p-1)(\cos\theta\sin\theta)^{(2p+1)/p}}{((\cos\theta)^{\frac{2}{p}}\sin^4\theta + (\sin\theta)^{\frac{2}{p}}\cos^4\theta)^{\frac{3}{2}}}$$

For p<1, the minimal curvature increases with deformation parameter p. For p>1, the minimal curvature is zero. When p approaches to 1, K tends to 1/R, the reciprocal of the radius of the perfect disk. For p<1, there is no definition of the curvature at $\theta = n\pi/2$, $n = 0, \pm1, \pm2,$ ... etc.

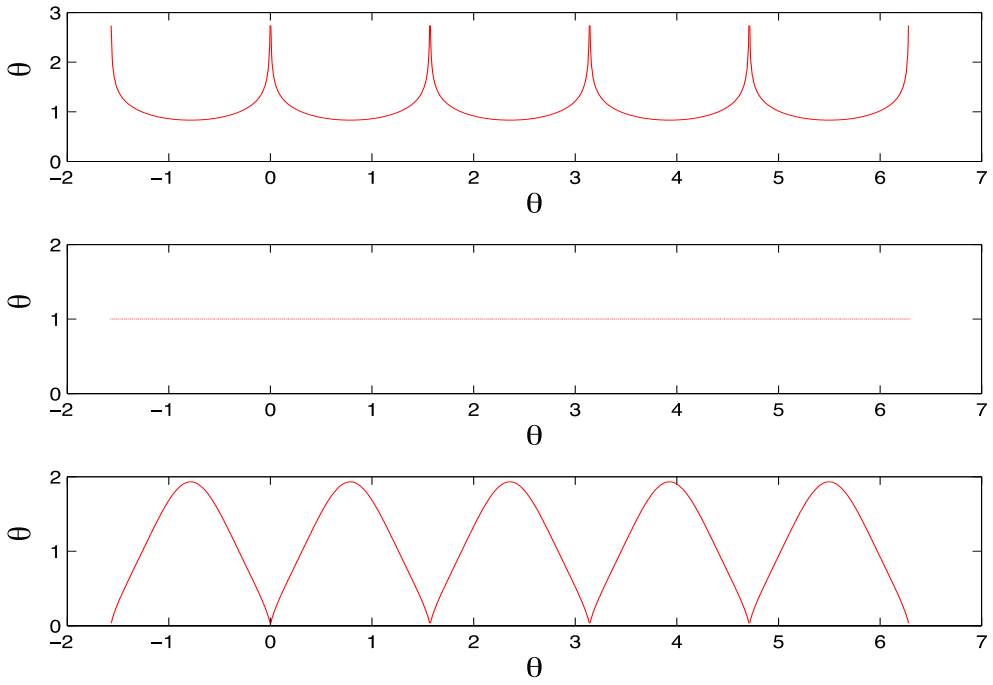


Figure 12: Angle Dependent Curvature of Points on Superdisks with a=b=1.

When the superdisks packing is well jammed, two contacted superdisks locate at two fixed centroid positions and have two rotational angles. Throughout of the analysis, $\theta_m$and $\theta_n$are the two angles of the contacted point when the contacted superdisks m and n are translated to the origin and rotated back, respectively.

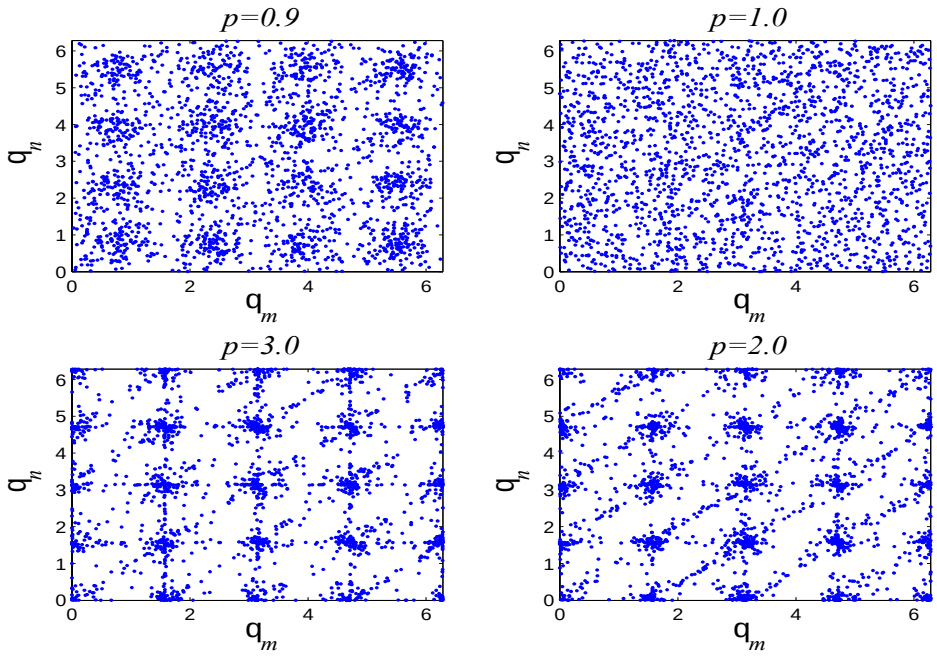


Figure 13: Contacted Points Expressed by Contacted Angles in Different p Values

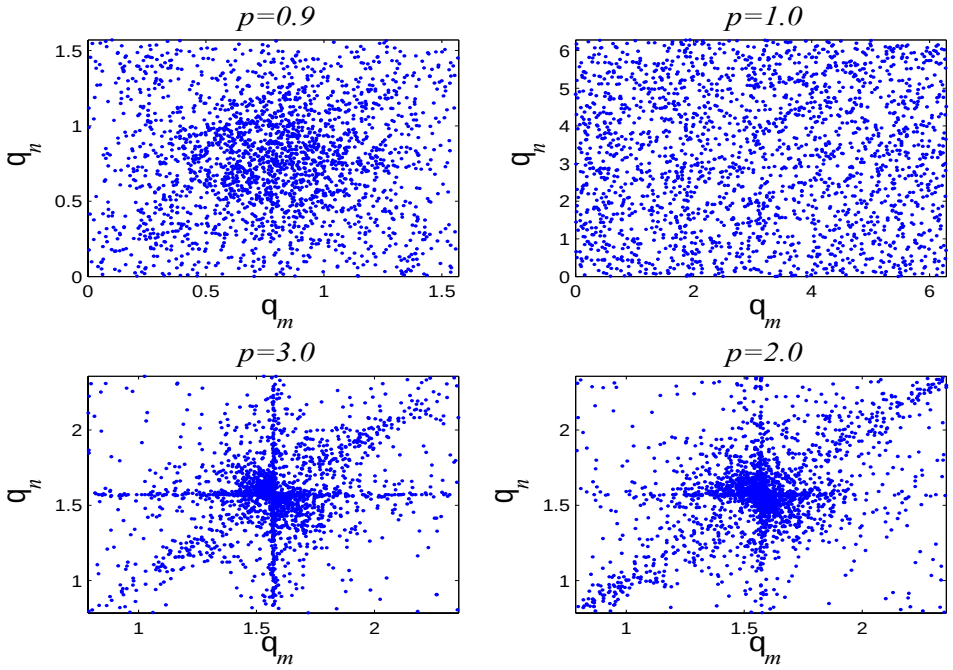


Figure 14: Contact Points Expressed by Angles after Angle Transfer

For p=1, the distribution is naturally even due to the higher symmetry of circles than superdisks. For other cases, the most probability distribution locates at the points with the angle of the combinations of the minimal values of curvatures. For p<1, high points density appears at $(\frac{n\pi}{4}, \frac{m\pi}{4})$ with $m, n = 1, 3, 5, \text{etc}$. For p>1, high points density is at $(\frac{n\pi}{4}, \frac{m\pi}{4})$ with $m, n = 2, 4, 6, \text{etc}$. Figure 13 shows the basic results. Visually, the points density at these points increases with p when p>1, and decrease with p when 0.5<p<1. We will terrify it in the following section. Due to that the curvature is a periodic function of the angles, it is convenient for us to transfer all the angles to a complete period. We have many choices and select $[0, \frac{\pi}{2}]$ for p<1 and $[\frac{\pi}{4}, \frac{3\pi}{4}]$ for p>1. Figure 14 is the picture after transformation. Clearly, the distributions of contacted points are regular. By using One-Sample Kolmogorov-Smirnov Test method, we find the distribution of angle for each p obeys qui-normal distribution (shown by the online red real lines in Figure 15).

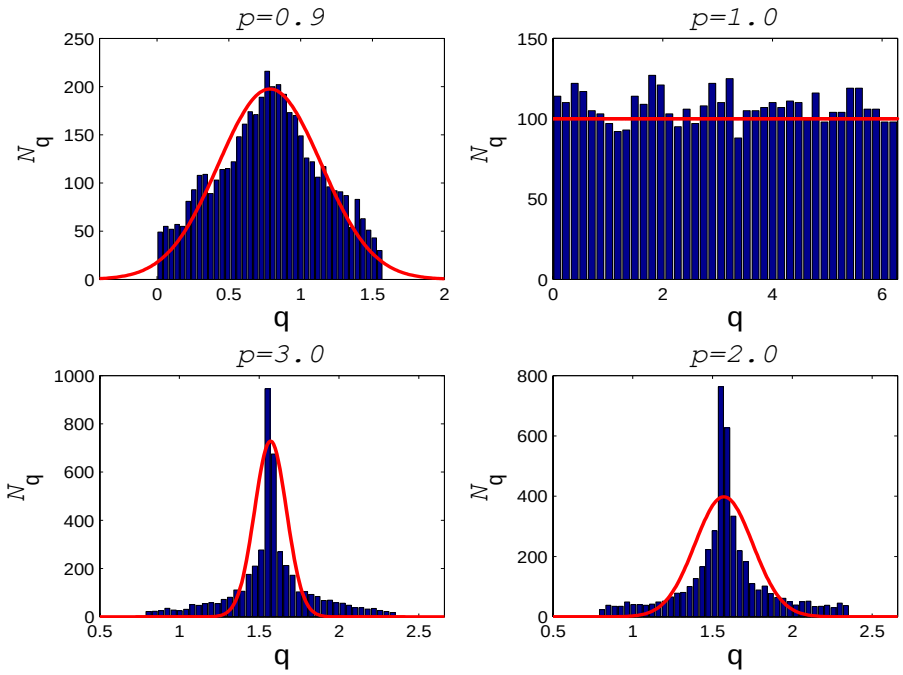


Figure 15: Statistical Distributions of Contacted Points: Contacted Angle Statistics

The normal distribution function reads

$$f_\theta = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(\theta-\mu)^2}{2\sigma^2}}$$

For p<1, we have $\mu = \frac{\pi}{4}$. For p<1, we have $\mu = \frac{\pi}{2}$. We evenly divide the range of $[0, \pi/2]$ into 40 sections and statistic the contact numbers in each section. The result is shown in Figures. N_θ is the number of contacted points in each section.

3.2.2 Predictive Formula for Packing Fraction

We sign the local packing fraction as

$$\phi_{local\_BB} = \phi_{local\_BB}(\theta) = \phi_{local\_BB}(K^*)$$

$$\phi_{local\_BS} = \phi_{local\_BS}(\theta) = \phi_{local\_BS}(K^*)$$

Here, the ϕ_{local_BB} is the local packing fraction when the two contacted particles are all large size in the binary system and it is equal to the ϕ_{local_SS}, which is the local packing fraction for two small size contacted particles. The ϕ_{local_BS} is the second condition which is the local packing fraction for two different size contacted particles.

So,

$$\phi_{local} = \frac{N_S}{N} \cdot \phi_{local_{BS}}(\theta) + \frac{N_B}{N} \cdot \phi_{local_{BB}}(\theta)$$

Or

$$\phi_{local} = \frac{N_S}{N} \cdot \phi_{local_{BS}}(K^*) + \frac{N_B}{N} \cdot \phi_{local_{BB}}(K^*)$$

N_B is the number of relative big superdisks in the configuration and N_S is the number of relative small superdisks in the configuration. Then the packing fraction of a maximal jammed superdisk configuration is obtained by

$$\phi = < \phi_{local} > = \int_{\theta_1+}^{\theta_2-} \phi_{local}(\theta) f_\theta d\theta$$

or

$$\phi = < \phi_{local} > = \int_{K_1^*}^{K_2^*} \phi_{local}(K^*) f_{K^*} dK^*$$

During the calculation, we choose $\theta_1 = 0$ and $\theta_2 = \pi/2$. Of course, an alternative choice is $\theta_1 = 0$ and $\theta_2 = \pi/4$.

Then the packing fraction of a maximal jammed superdisk configuration is obtained by

$$\phi = < \phi_{local} > = \int_{\theta_1}^{\theta_2} [\frac{\alpha}{\alpha+1} \phi_{local1}(\theta) + \frac{1}{\alpha+1} \phi_{local2}(\theta)] f_\theta d\theta \ ,$$

Where α is number ratio, $\phi_{local1}(\theta)$ and $\phi_{local2}(\theta)$ are the local volume fraction for big and big particle, big and small particle, respectively. For p<1, θ_1= 0 and θ_2 = π/2; for p>1, θ_1= π/4 and θ_2 = 3π/4.

3.3 Simulation Verification

This organizing principle is a global packing fraction theoretical prediction method for the maximally random jammed packings. To verify the method by using computational simulation, a rigorous algorithm, which has a high efficiency and accuracy, is necessary. In general, there are two basic approaches in molecular dynamics. One is time-driven molecular dynamics (TDMD), which is inspired by MD simulation of soft particle system. An alternative rigorous approach, event-driven molecular dynamics (EDMD), is advanced by collision event instead of time step.

The improved EDMD, which is mentioned at the beginning of this paper, is used to guide us to generate the analytical construction of MRJ packing configuration of superdisks. The small non-overlapping particles are initially placed in the periodic simulation box with random

positions and orientations. Then the particles are given random translational and rotational velocities and their motion follow as they collide elastically and also expand uniformly with an expansion rate, which is larger at moderate densities and smaller at the higher densities. After the assigned steps, a jammed state with a diverging collision rate is reached and the density reaches a locally maximum value. Thus, the simulation algorithm can generate a same rigorous MRJ state packing as the system used in the prediction method.

3.3.1 Generate of Packing Data Sets

In order to verifying the prediction in a more general way, several sets of data are obtained from simulation by choosing representative parameters. The number of particles, N, in the system is a very important parameter in MRJ system. Jiao et.al (2010) studied several different particle number, N = 250, 500, 625 and 2500, and found that the statistical fluctuations associated with the packing characteristics are sufficiently diminished when N > 500. Here, N=500 is chosen so that we can obtain a relative stable data and save the cost of time as well. Deformation parameter is also considered as two different cases. Superdisk has convex shape ($p>0.5$) and concave shape ($p<0.5$) but it's not continuous only at p = 1, which is a circular disk. Thus, we chose two smaller than 1 (i.e., p = 0.85 and p=0.95) and two larger than 1 (i.e., p = 1.5 and p=2.0) [16] so that we can analyze all the conditions on the continuous segment. In addition, besides these two common parameters, there are two ratios in two dimensions packing system. Size ratio β of the two superdisk species is defined as the ratio of the diameter of large superdisk over that of a small superdisk and we choose β = 1.2 and 1.8.. Let α denote the number ratio,

which is defined as the number of large superdiks over the number of small one and we choose $\alpha = 0.5$ and 2.0.

3.3.2 Comparison of Prediction and Simulation

The predicted equation provide us the estimated MRJ packing fraction for a variety of binary superdisk packings. To verify its accuracy, we obtain the ϕMRJ data sets from the packing structure that we generate in 2.3.1 part. The Table 1 shows us the data of theoretical local prediction, the simulation, the error between them and the standard deviation. The estimates agree with simulation results extremely well, with most of the deviations within 1.5%. Also, we make four figures of the packing fraction verses deformation parameter in different number ratio and size ratio by using the data sets. Figure 16 shows us the results of our prediction comforts to the data from the computer simulation as well.

Table 1 Comparison of MRJ Packing Fractions

	Predicted data	**Simulation(average of 10 sets of Data)**	**Error**	**Standard Deviation**
P=0.85;SR=1.2;NR=1.2;	0.860859	**0.86751**	**0.77%**	**0.00079**
P=0.85;SR=1.2;NR=2:1;	0.860298	**0.86765**	**0.85%**	**0.00047**
P=0.85;SR=1.8;NR=1.2;	0.872244	**0.87308**	**0.10%**	**0.00074**
P=0.85;SR=1.8;NR=2:1;	0.865991	**0.87093**	**0.57%**	**0.00054**

P=0.90;SR=1.2;NR=1:2	0.854446	**0.86027**	**0.68%**	**0.00038**
P=0.90;SR=1.2;NR=2:1	0.854112	**0.86085**	**0.79%**	**0.0009**
P=0.90;SR=1.8;NR=1:2	0.86563	**0.86676**	**0.13%**	**0.00063**
P=0.90;SR=1.8;NR=2:1	0.859704	**0.86463**	**0.57%**	**0.00077**
P=1.5;SR=1.2;NR=1:2	0.88312	**0.88748**	**0.49%**	**0.00055**
P=1.5;SR=1.2;NR=2:1	0.886116	**0.88683**	**0.08%**	**0.00076**
P=1.5;SR=1.8;NR=1:2	0.895067	**0.88929**	**0.65%**	**0.0006**
P=1.5;SR=1.8;NR=2:1	0.892089	**0.88802**	**0.46%**	**0.00075**
P=2.0;SR=1.2;NR=1:2	0.910302	**0.91037**	**0.0075%**	**0.00131**
P=2.0;SR=1.2;NR=2:1	0.9125	**0.91064**	**0.20%**	**0.00134**
P=2.0;SR=1.8;NR=1:2	0.909766	**0.90473**	**0.55%**	**0.00075**
P=2.0;SR=1.8;NR=2:1	0.912231	**0.9034**	**0.97%**	**0.00116**

SR: size ratio; NR: number ratio Big/small. $\phi_{predicted}$: Packing-fraction derived from our ND formula.

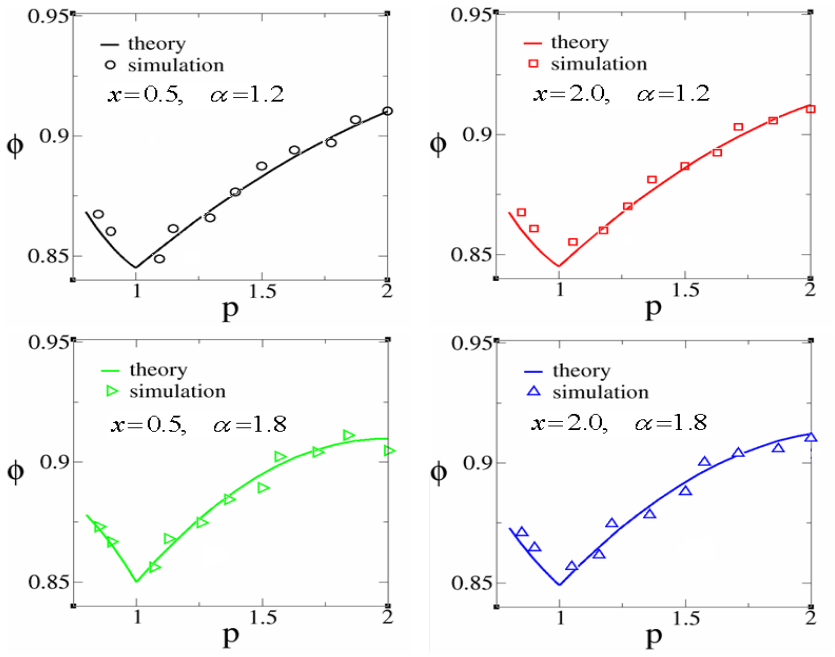


Figure 16: Comparison of the MRJ Packing Fraction Estimated Using the Prediction Equation and Obtained from Simulations for Various Binary Superdisk Packings.

Furthermore, we predict global packing fraction in different size ratio and number ratio and analyze the influence of these factors to the packing fraction as shown in Figure 17 and Figure 18. Through comparison of these results to the simulation results (Figure 6 and Figure 8), we found the trend are extremely similar and the data error between the predicted and the simulated is within 3% even for such small and relative large statistically fluctuation system.

In summary, we have devised a quantitative local organizing principle for MRJ packings of superdisks in two dimensions, which include a rich family of shapes. Specifically, the distribution of the contact angles defined for a single particle for all different shapes, when properly re-scaled, possesses a universal Gaussian form, who mean value is associated with the minimal surface curvatures. This local organizing

principle allows us to devise a formulism to accurately estimate the MRJ packing fraction for a wide range of nonspherical shapes.

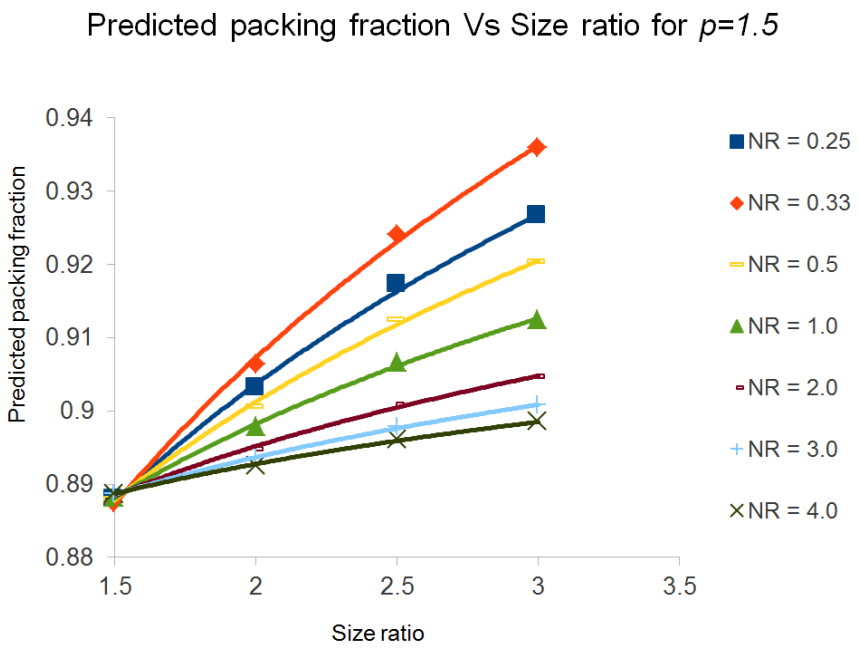


Figure 17: Predicted Packing Fraction versus Size Ratio for p=1.5

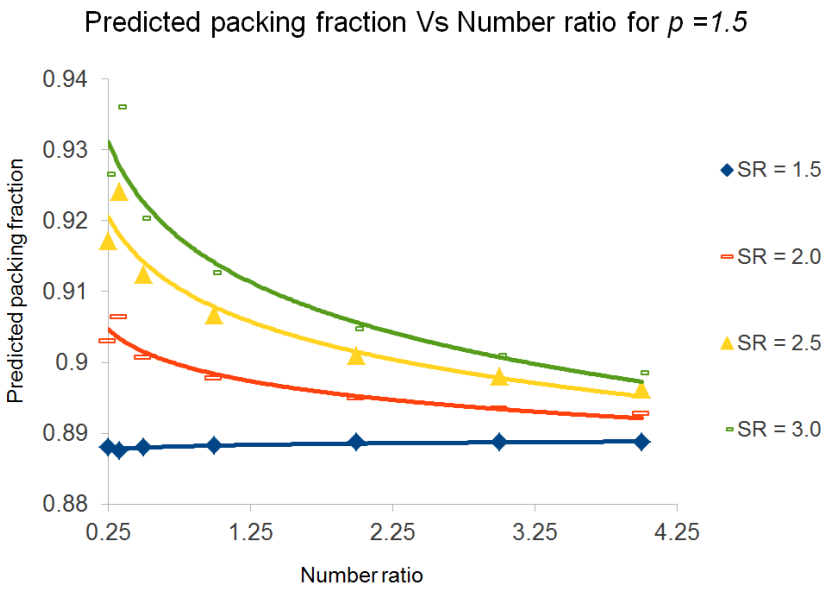


Figure 18: Predicted Packing Fraction versus Number Ratio for p=1.5

CHAPTER 4 3D MRJ FOR BINARY ELLIPSOIDS

In three dimensions, the packing system is more practical because the R^3 packing structure not only can be used as a structure of a specific granular material, but also can be an initial configuration for further research. Thus, non-spherical jammed packing characteristics in higher dimensions become a new focus and considerably more complex than in two dimensions. Non-spherical particles introduce rotational degrees of freedom not present in the simple sphere packings and can dramatically change the jamming characteristics from those of sphere packings. As the relative simple non-spherical particle, ellipsoids are very popular for preliminary research of the structure characteristics. A three-dimensional ellipsoid is a centrally symmetric body occupying the region

$$(\frac{x}{a})^2 + (\frac{y}{b})^2 + (\frac{z}{c})^2 \leq 1 ,$$

Where a, b and c are the semiaxes of the ellipsoid. Thus, we can see three different types ellipsoids, oblate, prolate, or scalene, by just changing the semiaxes and we could have many variable when we study the ellipsoids. It is noteworthy that MRJ-like packings of nearly spherical ellipsoid can be obtained with $\phi \approx 0.74$, which has only recently been proved that the densest packing fraction (face-centered cubic lattice). That indicates that there exist ordered ellipsoid packings with appreciably higher densities. It is true that the densest known ellipsoid packings were discovered by Donev(2004). Although the effect between packing fraction and aspect ratio of some ordered ellipsoids

packings or densest optimal packing had been studied [14], the binary ellipsoid are barely systematical discussed. In this paper, we generate different

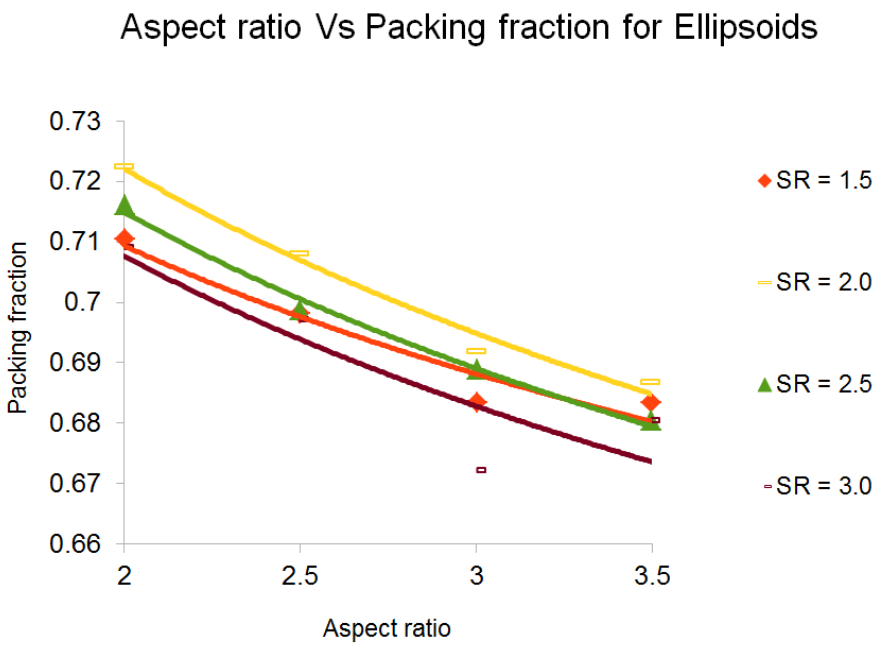


Figure 19: Aspect Ration versus Packing Fraction for Ellipsoids

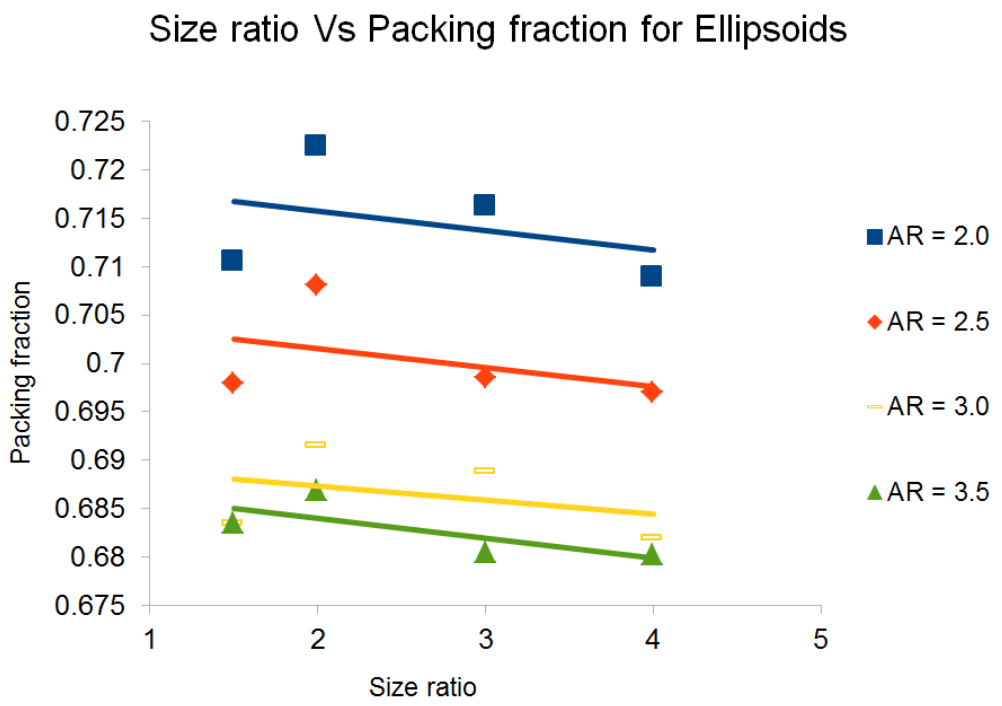


Figure 20: Size Ratio versus Packing Fraction for Ellipsoids

ellipsoid packings by change the aspect ratio and size ratio when number ratio and shape factor are equal to 1. The semiaxes here are 1, α^{β} and α, where α is aspect ratio and β is shape factor.

From the Figure 19, we find that the packing fraction decreases following the increasing aspect ratio. Note that the binary ellipsoids data in this figure tend to show a very similar behavior for mono-prolate spheroids in Ref. [12]. And Figure 20 shows at unit number ratio and shape factor case, the size ratio has little influence on the packing fraction no matter what the aspect ratio is.

CHAPTER 5 CONCLUSION AND FUTURE WORK

In this dissertation, we have reviewed two different molecular dynamics methods, in particular, the improved event-driven molecular dynamics algorithm (EDMD). EDMD is a particle system simulation method driven by the event instead of the time advancing in time-driven MD. In this method, numbers of particles are given with random positions, translational, rotational velocities and orientations and uniformly expand at a fixed expansion rate after certain relaxation cycles. Since for compression in reality, such as a pile of sands, we only can get a densest packing by relaxing the packing after every compressed operation, which conforms to the physical principle. Hence, in the relaxation process, the collision event is the "driven force" and the simulation advance through following the schedule of the impending event. In this algorithm, the impending event is updated by finding the first non-zero root of calculation of the overlap potential, which is a very efficient way. However, the time cost of the update nearest impending event in computation is very expensive. Thus, the near-neighbor lists (NNLs) searching method is applied in current EDMD. This searching method first adapts to non-spherical particle system and it successfully built a neighborhoods list so that one can update the impending event only among its neighbors. This current EDMD has highly decreased the cost of time and possess higher efficiency and accuracy for non-spherical particle packing simulation. Thus it is adjustable for different shape of the particle, which cannot be implemented by other algorithms.

By using this algorithm, we have generated MRJ binary superdisks in two dimensions and binary ellipsoids in three dimensions. For MRJ binary superdisks, the

effect of size ratio and the number ratio to the packing structure are considered. We found that at a fixed number ratio, the packing fraction increases with the increasing of the size ratio. Then at a fixed size ratio, where size ratio > 1, the packing fraction trend to decrease with the number ratio get larger. They are reasonable because at the same number ratio, the large size ratio, the more small size particle can fill in the spare volume among the large particles and at the same size ratio, the larger number ratio, the fewer small size particle fill in the volume.

Even more exciting is that we have devised a quantitative local organizing principle for MRJ packings of superdisks in two dimensions, which include a rich family of particle geometric shapes. Furthermore, the distribution of the contact angles defined for a single particle for all different shapes, when properly re-scaled, possesses a universal Gaussian form. The mean contact angle corresponding to the minimal surface curve and the distribution becomes narrower as the particle shape deviates more from that of a sphere. We provide arguments that such a distribution arises from the two competing requirements defining the MRJ state, i.e., maximal disorder and jamming. This organizing principle is then employed to provide accurate estimates of the MRJ packing fraction ϕ_{MRJ} for a variety of binary superdisk systems, with different particle shape, size and number ratios.

For 3-dimensions binary elliposids, we only consider a very simple case in which the shape factor and the number ratio are all units and the trend on the figures are very similar to the mono-system. In addition, we found that the size ratio is not very important

for packing fraction if the number ratio and shape factor are 1. Besides, these packing systems that we generated by event driven molecular dynamics not only can be the structures of granular materials but also can be the initial configurations in sintering which is a very hot area of research.

In the future, we would like to further explore the characteristics of poly-disperse MRJ non-spherical particle system in two dimensional space, which hasn't been studied yet. For three dimensions, not only poly-disperse systems are interesting, but also the superellipsoids or the poly-disperse superellipsoids system, especially the "disperse" follows the normal distribution or even distribution, etc. In addition, the extrapolated prediction from two dimensions and mechanical analysis for these new structures is very practical as well.

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