Determining random packing density and equivalent packing size of superballs via binary mixtures with spheres

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Abstract

We propose a new approach to determining the random packing densities of superballs via binary mixtures with spheres. The main idea of the approach is to suppress order formations in non-spherical particle packings via the polydispersity of particle shapes, which avoids using order metrics. The packing density of superballs in a mixture can be segregated using a linear fitting method with the concept of equivalent packing size (or size ratio with unit spheres) which represents the effective size (or volume) of a non-spherical particle in a binary mixture with spheres. We systemically study the packing properties of binary mixtures consisting of spheres and superballs and obtain the equivalent packing sizes of superballs. Our results show that the equivalent packing size ratio always corresponds to the minimal packing density or specific volume (reciprocal of packing densities) variation, and is independent of the solid volume fraction. The specific volumes of mixtures with the equivalent packing size ratio are always the upper bound for all the solid volume fractions. The linear relationship between the specific volume and solid volume fraction is only observed in the mixtures with superballs of small surface shape parameters (shapes close to a sphere), which results from the highly disordered nature in the mixtures. Moreover, the ideal random packing densities of mono-sized superballs obtained via the linear fitting method are surprisingly close to those of the MDRPs (maximally dense random packings), further verifying that the MDRPs of non-spherical particles correspond to the ideal random packings whose degrees of order are at the same level with that of the random close packing of spheres. Our work leads to a better understanding towards the random and binary packings and sheds new light on the essence of the MDRP. Our work also guides the optimal particle size distributions of powders in chemical engineering process.

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1. Introduction

Random packings (or highly disordered packings) are conventional in nature and industry, and are served as useful models in liquids, glasses, metalloids and granular materials (Torquato and Stillinger, 2010; Liu and Nagel, 2010; Parisi and Zamponi, 2010; Damasceno et al., 2012; Zhong et al., 2016; Baule et al., 2018; Torquato, 2018). Packing density (or packing fraction), which is defined as the ratio of the volume of all particles to that of the container, is a direct and essential parameter in describing random packing systems. The random packing density of mono-sized spheres is about 0.64, which is a stable value obtained under various packing protocols and definitions, such as the random close packing (RCP) (Burryman, 1983), the maximally random jammed (MRJ) packing (Torquato et al., 2000), and the jamming point (O’Hern et al., 2002). However, the random packing densities of some non-spherical particles which are easy to crystallize are not so robust, because the packings of these particles generated via different methods are on various degrees of order to maintain the mechanical stability or jamming. For example, many face-to-face joints are observed in the close packing of tetrahedra (Li et al., 2013), and small ordered clusters are abundant in the jammed packing of cubes (Smith et al., 2014; Liu et al., 2017). In other words, the packings of these particles generated via different methods are not on the same degree of randomness and are not all highly disordered packings.

Recently, we proposed the concept of the maximally dense random packing (MDRP) (Meng et al., 2016; Liu et al., 2016), which provides a platform to compare the random packing densities of differently shaped particles on the same random state. The MDRP is defined as the densest packing in the random state in which the particle positions and orientations are randomly distributed. The packing density of the MDRP corresponds to a sharp transition in the order map, which characterizes the onset of nontrivial spatial correlations among the particles (Meng et al., 2016; Liu et al., 2016). The MDRP is also regarded as a glass state of hard particle systems with an artificial constraint and is always random (Liu et al., 2017). Compared to the other packing states, the MDRP is a simpler and geometrically based one, providing a better platform which shows uniform particle shape effects on the random packing densities. Uniform and decoupled effects of surface shape and aspect ratio on the random packing densities of superellipsoids which are elongated or compressed superballs were observed on the MDRP state (Liu et al., 2018a). Meanwhile, uniform shape elongation effects on the random packing densities of rod-like particles including cylinders were also observed on the MDRP state (Liu et al., 2018b). However, on the other packing states, the shape effects are not so uniform, as discussed in Liu et al., 2017; Liu et al., 2018a; Liu et al., 2018b. As a newly proposed concept in the random state, further evidence is needed to confirm the physical meanings of the MDRP state.

Generally, two approaches are applied to obtain the packing density of the MDRP. One is the enumeration method (Meng et al., 2016; Liu et al., 2016). A large number of packings are generated by common packing algorithms, then the random packings are selected via specific order parameters, and the MDRP is chosen as the maximally dense one among all the random packings. The other is the inverse Monte Carlo (IMC) method (Liu et al., 2017), in which the MDRP is directly generated via slowly compressing a dilute packing and an artificial order constraint is applied to suppress the formation of ordered structures. Nevertheless, choosing or constructing appropriate order parameters which effectively identify the main order forms in packings of various shapes could be difficult, and a universal order metric for particle packing is still absent so far (Torquato, 2018). In this work, we propose a new method to obtain the random packing densities of non-spherical particles via the binary mixtures with spheres. Importantly, this method does not need any order parameters and the order structures are suppressed by shape dispersity. In previous packing researches, the size dispersity has been often used to suppress order formations in the mono-shaped particle packings in two dimension, such as the binary packings of disks (Xu et al., 2005, Donev et al., 2007), superdisks (Jiao et al., 2010), ellipse (Schreck et al., 2010), and circulo-particles (VanderWerf et al., 2018). However, the random packing densities of their mono-sized packings are still debatable and cannot be obtained from the mixtures with size dispersity. In this work, we use the shape dispersity to suppress the order structures and estimate the random packing densities of mono-sized particles. The influence of particle size is eliminated via the concept of equivalent packing diameter (EPD) proposed by Yu and his colleagues (Yu and Standish, 1993a; Zou and Yu, 1996).

The EPD of a non-spherical particle is a crucial character of non-spherical particles in binary and polydisperse mixtures. The EPD is the diameter of the sphere which gives the minimum packing density when mixed with the non-spherical particle at any given solid volume fraction (Yu and Standish, 1993a). We note that the “solid volume fraction” here is the volume of non-spherical particles divided by the total volume of all particles (including the non-spherical particles and spherical particles) in the binary mixtures. It is not the volume fraction of all solid particles which has been used interchangeably with "packing fraction" or "packing density" in literature. The EPD of a non-spherical particle should be independent of the packing method and solid volume fraction of a component (Yu and Standish, 1993a; Zou and Yu, 1996). If a particular particle, whose shape is not much different from a sphere, is mixed by spheres with the EPD, a linear relationship between the global specific volume (reciprocal of packing densities) and the solid volume fraction of one component can be observed, i.e., the linear packing model (Yu and Standish, 1993a). However, this model may fail for non-spherical shapes which are much far away from spheres, as discussed in Yu and Standish, 1993b. The concept of EPD makes it possible to relate the shape polydisperse mixtures of non-spherical particles to size polydisperse mixtures of spheres. Some empirical models were successfully developed via the EPD concept to predict the packing densities of the mixtures consisting of non-spherical coarse (Yu et al., 1993; Yu et al., 1996) and fine (Yu et al., 1997; Zou et al., 2011) particles.

We focus on the random packing densities of superballs in this work. The superballs are powerful geometrical models to study the shape effects on particulate systems. The surface function of a superball in the local Cartesian coordinates is defined as

\[ (|x|^p)^2 + (|y|^p)^2 + (|z|^p)^2 = R^{2p} \]  \hspace{1cm} (1)

where \( p \) is the surface shape parameter and \( R \) controls the particle size. The superballs degenerate to a sphere with the radius to be \( R \) when \( p = 1.0 \). Moreover, the superballs degenerate to ideal octahedra and cubes when \( p \) equals to 0.5 and infinity, respectively. Fig. 1

![Fig. 1. Some typical superballs with different surface shape parameter p. The size parameter R for all the superballs is R = 1.0. The heights along the x, y and z directions are all 2R = 2.0. The superballs degenerate to a sphere with the radius to be R = 1.0 when p = 1.0.](image)
shows some typical superballs with different surface shape parameter $p$. The size $R$ for all the superballs in Fig. 1 are $R = 1.0$. The heights along the $x$, $y$, and $z$ directions are all $2R = 2.0$ and the volume of each superball is $V_p = \frac{2R^2\Gamma(1/2p)^2}{(3p^2\Gamma(3/2p))}$, where $\Gamma(x)$ is the Euler gamma function. The superball systems have been recently well studied in terms of phase behavior (Batten et al., 2010; Ni et al., 2012), percolation behavior (Lin and Chen, 2018), tortuosity and thermal conductivity (Xu et al., 2018), electrical (Audus et al., 2015), rheological and diffusive (Royer et al., 2015) properties. Meanwhile, the densest known superball packings are the Bravais lattices with different lattice vectors (Jiao et al., 2009).

As for the disordered packing of superballs, the packing density always increases as the particle shapes shift from spheres (Jiao et al., 2010; Delaney and Cleary, 2010; Zhao et al., 2017; Liu et al., 2018a). However, the packing properties of superball systems generated via different packing methods differ when the surface shape parameter $p$ is large. Jiao et al. (2010) generated the MRJ packings of superballs via the DTS algorithm (Donev et al., 2005), which is an event-driven molecular dynamics packing algorithm generalizing the Lubachevsky-Stillinger (LS) sphere packing algorithm (Lubachevsky and Stillinger, 1990). They found that the local geometry of the MRJ packings was necessarily nontrivially correlated. The increase in the orientational order associated with the increasing $p$ values. Via a Discrete Element Method (DEM), Delaney and Cleary (2010) generated the disordered jammed packings of superballs when $p$ is small ($p = 1.0, 1.5$). However, they observed that the jammed packings with larger values of $p$ ($p = 2.0, 2.5$) exhibited clear signs of ordering. The surface shape parameter $p$ also made the distributions of particle orientations more square-like with the increase of $p$ in the disordered packings generated via another DEM method under gravity (Zhao et al., 2017). In order to investigate the shape effects on the same random states for superballs, Liu et al. (Liu et al., 2018a) generated the maximally dense random packings (MDRPs) of superballs with lower packing densities and no obvious ordered structures via the IMC method (Liu et al., 2017). They found that the maximal random packing density was obtained at $p \approx 0.7, 2.0$. They also concluded that there was a competition between the randomness and jamming or mechanical stability (Liu et al., 2017; Liu et al., 2018a; Liu et al., 2018b) in the packings. However, the fundamental relationship between the disordered jammed packings and MDRPs of superballs is still not clear.

In this work, we propose a new approach to determining the random packing densities of superballs via binary mixtures with spheres. The main idea of the approach is to suppress order formations in non-spherical particle packings via the polydispersity of particle shapes, which avoids using order metrics. The packing density of superballs in a mixture can be segregated using a linear fitting method with the concept of EPD. Here we use the adaptive shrinking cell (ASC) algorithm (Torquato and Jiao, 2009a; Torquato and Jiao, 2009b) to generate the jammed mixtures of spheres and superballs with different superball-to-sphere size ratios and solid volume fractions. Firstly, we analyze the packing properties of mixtures with different size ratios. We verify the properties of the EPD and compute the specific volume variations and order parameters to explain the different packing properties for different surface shape parameters. Then we estimate the EPDs of superballs with various surface shape parameter $p$ and study the linear properties of specific volumes. The Voronoi analysis is also carried out to analyze the local packing properties of binary mixtures. Finally, the linear fitting method is used to estimate the ideal random packing density of mono-sized superballs and the results are compared with literature results. The rest of the paper is organized as follows: in Section 2, we introduce the ASC algorithm used to generate packings and the parameters applied to describe the mixtures. The simulation results are discussed in Section 3, and concluding remarks are provided in Section 4.

2. Methodology

We use the adaptive shrinking cell (ASC) algorithm (Torquato and Jiao, 2009a; Torquato and Jiao, 2009b) to generate the jammed mixtures of spheres and superballs with different size ratios and solid volume fractions. The ASC algorithm was devised to generate the densest packings (Torquato and Jiao, 2009a; Torquato and Jiao, 2009b) and the MRJ packings (Jiao and Torquato, 2011; Chen et al., 2014; Liu et al., 2018b) of hard particles. It is a Monte Carlo (MC) compression process with random particle movements and allows the simultaneous change of different lattice vectors of the simulation box at the same time. In this work, the compression rate $\Gamma$ is set to be 1.0, which results in a fast compression to maintain the maximal degree of randomness. We note that the final packings are approximations to the MRJ states, while the specific compression rate for the MRJ state of different shaped particles may varies and the final packings may not be strictly jammed. However, the packing densities of the approximations, which are the main concerns in this work, are close to those of the MRJ packings. More details about the ASC algorithm we use can be found in Liu et al., 2018b. For effective and economic computation, the total amount of particles in all the systems we generated is $N_{MDR} = 420$, which is verified to be large enough for systems with periodical boundary conditions in three directions. All the data shown below are averaged over five times and the error bars in the figures below represent the standard deviations.

Generally, in a binary mixture of $N_{sb}$ superballs and $N_s$ spheres, the solid volume fraction of superballs $X_{sb}$ can be calculated as

$$X_{sb} = \frac{V^s}{V^s + V^b} = \frac{N_{sb}V^s_{sb}}{N_{sb}V^s_{sb} + N_s V^s}$$  \hspace{1cm} (2)$$

where $V^s_{sb}$ and $V^s$ are the total volumes of superballs and spheres, $V^s_{sb}$ and $V^s$ are the volume of a superball and a sphere, respectively. The superball-to-sphere size ratio $\alpha$ is defined as

$$\alpha = \frac{d^s_{sb}}{d^s}$$  \hspace{1cm} (3)$$

where the $d^s_{sb}$ and $d^s$ are the equivalent volume diameter (EVD) of the superball and sphere, respectively. The EVD of a particle is the diameter of a sphere whose volume is the same as that of the particle, i.e.,

$$d^s_{sb} = \sqrt[3]{\frac{6V_{sb}}{\pi}}, \hspace{0.5cm} d^s = \sqrt[3]{\frac{6V^s}{\pi}} = 2R_s$$  \hspace{1cm} (4)$$

In all the mixtures we studied, the EVD of spheres are a constant value with $d^s = 2R_s = 2.0$, i.e., unit spheres. The EVD of a particle usually differs from the EVD. A large size ratio $\alpha$ means that the superballs in the mixtures are much bigger than the spheres. Finally, the global packing density $\varphi$ and specific volume $V$ of the binary mixture are calculated as

$$V = \frac{1}{\varphi} = \frac{V^s}{V^s_{sb} + V^s}$$  \hspace{1cm} (5)$$

where the $V^s$ is the volume of the container which is a cubic box with periodical boundary conditions in three directions in this work.
3. Results and discussion

In this section, we first investigate the packing properties of the mixtures consisting of spheres and superballs with different size ratios for the surface shape parameter $p = 1.0, 1.5, 5.0$. Then we obtain the equivalent packing size ratio for all the superball shapes we study and investigate the packing properties of mixtures with the equivalent packing size ratio. Finally, the linear fitting method in binary mixtures is used to estimate the ideal random packing densities of mono-sized superballs.

3.1. Mixtures with different size ratios

3.1.1. The packing density and specific volume

As mentioned above, the EPD of a non-spherical particle is the diameter of the sphere which gives the minimal packing density when mixed with the non-spherical particle at a given solid volume fraction (Yu and Standish, 1993a). Fig. 2 shows the global packing densities of binary mixtures versus the size ratio $\alpha$ for different solid volume fraction of superballs $X_{sb}$. The surface shape parameters $p$ we studied here are $p = 1.0, 1.5, 5.0$, representing the sphere, the superball which is close to a sphere, and the superball which is much different from a sphere and close to a cube, respectively. As can be seen in Fig. 2, the minimal packing density is always obtained at $\alpha_c = 1.0, 1.5, 5.0$ for $p = 1.0, 1.5, 5.0$, respectively. Here the $\alpha_c$ is noted as the equivalent packing size ratio (EPSR) and the EPD of a superball $d_{p_{sb}}$ can be represented as

$$d_{p_{sb}} = \frac{d_{v_{sb}}}{\alpha_c}$$  \hspace{1cm} (6)

where $d_{v_{sb}}$ is the EVD of a superball defined in Eq. (4). Moreover, we further verify the conclusion that the EPD of a non-spherical particle is independent of the solid volume fraction of a component (Yu and Standish, 1993a; Zou and Yu, 1996), regardless of whether the non-spherical particle is close to the sphere or not.

The specific volumes $V$ of binary mixtures of spheres and superballs versus the solid volume fraction of superballs $X_{sb}$ for different size ratio $\alpha$ are shown in Fig. 3 for $p = 1.0, 1.5, 5.0$, respectively. In all the three figures, the specific volumes of the mixtures with the EPSR $\alpha_c$ are always the upper bounds at any given solid volume fraction. Both enlarging and shrinking the superballs from the EPSR without changing the solid volume fraction of superballs in the mixture will decrease the specific volume of the mixture, i.e., the mixtures will be packed more densely. However, the surface shape influences the linear properties of the specific volume curves for $\alpha = \alpha_c$. The specific volume curves for $\alpha = \alpha_c$ with $p = 1.0, 1.5$ are almost linear, but the specific volume curve for $\alpha = \alpha_c$ with $p = 5.0$ is apparently nonlinear and concave upward. Therefore, a question is raised: How does the surface shape influence the packing properties of binary mixtures consisting of spheres and superballs? The question will be answered in terms of the specific volume variation and the order parameters, which will be demonstrated below.

3.1.2. The specific volume variation

We calculate the so-called specific volume variation $\Delta V$, which is used to represent the change in space occupied when the particles are unmixed and mixed (Li et al., 2018). The $\Delta V$ connects the unmixed superball and sphere packings with their mixtures. In this work,

![Fig. 2. The global packing density $\varphi$ of binary mixtures consisting of spheres and superballs versus the size ratio $\alpha$ for different solid volume fraction $X_{sb}$. The surface shape parameters $p$ are (a) 1.0, (b) 1.5, and (c) 5.0, respectively.](image-url)
\[ \Delta V = \frac{V_{sb}^b + V_{s}^b - V_{sb}^p - V_{s}^p}{V_{sb}^p + V_{s}^p} \]  

(7)

where \( V_{sb}^b \) is the volume of a cubic container filled with \( N_{sb} \) superballs. The packing density and specific volume of mono-sized superball packings are

\[ V_{sb} = \frac{1}{\rho_{sb}} = \frac{V_{sb}^b}{V_{sb}^p} \]  

(8)

Similarly, the packing density and specific volume of sphere packings are

\[ V_{s} = \frac{1}{\rho_{s}} = \frac{V_{s}^b}{V_{s}^p} \]  

(9)

Therefore, the \( \Delta V \) can also be represented as

\[ \Delta V = \frac{V_{sb}^b V_{sb}^p + V_{s}^b V_{s}^p - V (V_{sb}^p + V_{s}^p)}{V_{sb}^p + V_{s}^p} \]  

(10)

Substituting Eq. (2) into Eq. (10), we get

\[ \Delta V = V_{sb} X_{sb} + V_{s} (1.0 - X_{sb}) - V \]  

(11)

Fig. 4 shows the specific volume variation \( \Delta V \) versus the size ratio \( \alpha \) for different solid volume fraction \( X_{sb} \). All the minimal specific volume variations are obtained at \( \alpha = \alpha_c \approx 1.0, 1.2, 1.5 \) for \( p = 1.0, 1.5, 5.0 \), respectively. As shown in Fig. 4(a) and (b), the minimal values of \( \Delta V \) are almost equal to zero for different solid volume fraction \( X_{sb} \) when \( p = 1.0 \) and \( 1.5 \), meaning that there is no volume variation between the unmixing and mixing packings and the particles in the mixtures will not produce any interaction (Li et al., 2018). According to Eq. (11) with \( \Delta V = 0.0 \), we get

\[ V = V_{sb} X_{sb} + V_{s} (1.0 - X_{sb}) \]  

(12)

which is a linear relationship between the global specific volume \( V \) and the solid volume fraction of superballs \( X_{sb} \), as also observed in Fig. 3(a) and (b). Moreover, all the values of \( \Delta V \) for different size ratio \( \alpha = \alpha_c \) and different solid volume fraction \( X_{sb} \) are larger than zero, meaning that the superballs (\( p = 1.0, 1.5 \)) and spheres interact with each other. The volume of the container filled with binary mixtures \( V^b \) is smaller than the sum volume of the containers filled superballs (\( p = 1.0, 1.5 \)) and spheres separately, i.e., mixing helps to saving space for packing particles, which is in accordance with our common sense.

However, as shown in Fig. 4(c), the minimal value of \( \Delta V \) varies and are always negative when the \( X_{sb} \) changes from 0.0 to 1.0 for \( p = 5.0 \). In other words, the volume variation between the unmixing and mixing states arises, and the superballs (\( p = 5.0 \)) and spheres interact with each other even for the EPSR \( \alpha_c \). The linear relationship between the global specific volume \( V \) and the solid volume fraction of superballs \( X_{sb} \) will not be observed, as also observed in Fig. 3(c). Moreover, \( \Delta V < 0.0 \) means that the volume of the container filled with binary mixtures \( V^b \) is larger than the sum volume of the containers filled with superballs (\( p = 5.0 \)) and spheres separately, i.e., binary mixtures are packed looser than unmixed particles and we need a larger container to pack the mixed particles. Mixing leads to more space for packing particles, which is against our common sense. This phenomenon is caused

![Fig. 3. The specific volume \( V \) of binary mixtures consisting of spheres and superballs versus the solid volume fraction of superballs \( X_{sb} \) for different size ratio \( \alpha \). The surface shape parameters \( p \) are (a) 1.0, (b) 1.5, and (c) 5.0, respectively.](image-url)
by the distinctive degrees of order among the binary mixtures with different solid volume fractions, which is discussed below.

3.1.3. The order parameter

Considering that the packings of mono-sized superballs are not always highly disordered and the degrees of order increase when the superball is much closer to an ideal cube (Smith et al., 2014; Liu et al., 2017; Liu et al., 2018a; Jiao et al., 2010), we also evaluate the order degrees of superballs in the binary mixtures we studied. Here we use the normalized cubatic order parameter $b_4^S$, which evaluates the degrees of cubatic orientational order. More details about the $b_4^S$ are described in Appendix A. Fig. 5(a) and (b) show the normalized cubatic order parameter $b_4^S$ of binary mixtures of superballs ($p = 1.5$; 0) and spheres versus the solid volume fraction $X_{sb}$ for different size ratio $a$. The $b_4^S$ increases with the increase of $X_{sb}$ in both figures, i.e., the degree of order increases when more superballs are added to the mixtures. All the values of $b_4^S$ for $p = 1.5$ are smaller than 9.0, which is a small value indicating that all the mixtures with $p = 1.5$ are highly disordered. However, some of the values of $b_4^S$ for $p = 5.0$. $X_{sb} \geq 0.8$ are larger than 20.0, meaning that these mixtures are much ordered than the mixtures with $p = 1.5$. Therefore, the distinctive packing properties of the binary mixtures with various surface shape parameters results from that the mixtures are not on the same level of randomness. The mixtures with large surface shape parameter are apparently not random packings when the solid volume fraction of superballs is large, but the mixtures with small surface shape parameters are all highly disordered.

3.2. Mixtures under the equivalent packing size ratio

3.2.1. The equivalent packing size ratio

In this section, we obtain the EPSR $a_c$ for more superballs. Considering that the EPSR $a_c$ corresponds to the minimal packing density obtained and is independent of the solid volume fraction, we generate the mixtures with various size ratio $a$ for different surface shape parameter $p$. The solid volume fraction of superballs $X_{sb}$ is always 0.5. As shown in Fig. 6(a), the $\phi - \alpha$ points are fitted by cubic polynomial functions and the EPSR $a_c$ is then obtained at the minimal point of the fitted cubic polynomial functions (Yuan et al., 2018). Fig. 6(b) shows the EPSR $a_c$ as a function of the surface shape parameter $p$. The $a_c$ for spheres ($p = 1.0$) is 1.0 and rises with the increase of $p$. The maximum of $a_c$ is obtained at about $p = 4.0$ with $a_c \approx 1.51$. The values of $a_c$ for all the superballs are larger than 1.0, meaning that the superballs are larger than spheres in the mixtures with the minimal packing density at any given solid volume fraction.

3.2.2. The packing density and order parameter

We generate the binary mixtures with different solid volume fraction $X_{sb}$ at $a = a_c$ for each superball shape we study. Some typical packing configurations are demonstrated in Fig. 7. The mixtures with large solid volume fractions ($X_{sb} = 0.9; 1.0$) and large surface shape parameters ($p = 2.5; 5.0$) are not random enough with local or global ordered structures, while the other mixtures are highly disordered. We also plot the diagrams of $\phi - X_{sb}$, $\tilde{S}_4 - X_{sb}$, $\phi - p$, and $\tilde{S}_4 - p$ in Fig. 8. As can be seen in Fig. 8(a), the packing density $\phi$ rises with the increase of $X_{sb}$ for all the sur-
When the \( X_{\text{sb}} \) increases from zero to unity, the normalized cubatic order parameter \( \tilde{S}_4 \) changes little if \( p \) is smaller than 1.5, but the \( \tilde{S}_4 \) increases rapidly if \( p \) is larger than 2.0, which are demonstrated in Fig. 8(b). As shown in Fig. 8(c), when \( p \) firstly increases from 1.0 to 1.5, the packing density \( \varphi \) increases for all the solid volume fractions \( X_{\text{sb}} \). However, when \( p \) further increases from 1.5 to 5.0, the \( \varphi \) keeps constant for \( X_{\text{sb}} \leq 0.5 \) but increase continuously for \( X_{\text{sb}} \geq 0.7 \). Similar properties are observed for the \( \tilde{S}_4 \) in Fig. 8(d).

We also observed that the \( V - X_{\text{in}} \) curves at \( \alpha = \alpha_c \) are linear when \( p \leq 1.5 \) and concave upward when \( p \geq 2.0 \), as shown in Fig. 10 (a). Therefore, the linear properties of the specific volume curves are affected by the degrees of order in the mixtures. The linear relationship between the specific volume and solid volume fraction for the EPSR will arise if all the mixtures are highly disordered, such as the mixtures of spheres and superballs with \( p \leq 1.5 \), which are close to spheres. However, nonlinear relationship between the specific volume and solid volume fraction will be observed if the mixtures with a large solid volume fraction of non-spherical particles are highly ordered, i.e., the mixtures are not in the same random state, such as the mixtures of spheres and superballs with \( p \geq 2.0 \), which are much different from spheres. Meanwhile, we conject that the linear relationship between the specific volume and solid volume fraction for the EPSR

![Fig. 5.](image)

Fig. 5. The normalized cubatic order parameter \( \tilde{S}_4 \) of binary mixtures consisting of spheres and superballs versus the solid volume fraction of superballs \( X_{\text{sb}} \) for different size ratio \( \alpha \). The surface shape parameters \( p \) are (a) 1.5, and (b) 5.0, respectively.

![Fig. 6.](image)

Fig. 6. (a) The global packing density \( \varphi \) of binary mixtures consisting of spheres and superballs versus the size ratio \( \alpha \) for different surface shape parameter \( p \). The solid volume fraction of superballs is \( X_{\text{sb}} = 0.5 \). (b) The EPSR \( \alpha_c \) as a function of the surface shape parameter \( p \).

![Fig. 7.](image)

Fig. 7. The packing configurations of binary mixtures consisting of spheres and superballs for different solid volume fractions of superballs \( X_{\text{sb}} \) and surface shape parameter \( p \). The size ratio for every mixture is the EPSR \( \alpha_c \).
will always arise if all the mixtures are highly disordered and on the same random degree, regardless of whether the nonspherical particle is close to the sphere or not.

3.2.3. The local structure analysis

We analysis the average local specific volumes of superballs and spheres in the binary mixtures with different solid volume fraction $X_{sb}$ at $a = a_c$. The $v_{sb}$, which is the average local specific volume of superballs in the mixtures, is calculated as

$$v_{sb} = \frac{1}{N_{sb}} \left( \sum_{i=1}^{N_{sb}} v_{cell}^{sb}_{i} \right)$$

where $v_{cell}^{sb}_{i}$ is the local specific volume of the $i$th superball in the mixtures. The $v_{cell}^{sb}_{i}$ is the volume of the $i$th superball's Voronoi cell, which is obtained via the Voronoi tessellation. More details about the Voronoi tessellation we carry out can be found in Liu et al. (2018a) and Liu et al. (2018b). Similarly, the $v_{s}$, which is the average local specific volume of spheres in the mixtures, is calculated as

$$v_{s} = \frac{1}{N_{s}} \left( \sum_{i=1}^{N_{s}} v_{cell}^{s}_{i} \right)$$

where $v_{cell}^{s}_{i}$ is the volume of the $i$th sphere’s Voronoi cell.

Fig. 9 shows the average local specific volumes of superballs $v_{sb}$ and spheres $v_{s}$ as functions of the solid volume fraction of superballs $X_{sb}$ in binary mixtures at $a = a_c$ for different surface shape parameter $p$. For small values of surface shape parameters (1.0 ≤ $p$ ≤ 1.5), the $v_{sb}$ and $v_{s}$ maintain constant and are equal to the specific volume of mono-sized superball and sphere packings $V_{sb}$ and $V_{s}$, respectively. In other words, the average local specific volume of each constituent component does not change when the solid volume fraction of superballs is varying. The mixture is a linear superposition of mono-sized superball and sphere packings weighted by their solid volume fractions. Therefore, we further verify that the particles in the binary mixtures at $a = a_c$ will not produce any interaction if the superballs are close to spheres.

However, when the surface shape of superballs is closer to an ideal cube (2.0 ≤ $p$ ≤ 5.0), both the $v_{sb}$ and $v_{s}$ increase with the increase of $X_{sb}$, as can be seen in Fig. 9. For superballs in the mixtures, the average local specific volume $v_{sb}$ decreases if the superballs are surrounded by more spheres, i.e., the superballs are packed closer and the packing space is saved. For spheres in the mixtures, the average local specific volume $v_{s}$ increases if the spheres are surrounded by more superballs, i.e., the spheres are packed looser and more packing space is needed. Meanwhile, the global specific volume variation $D \nu$ mentioned above is smaller than zero, meaning that more packing space is needed for the mixtures. Therefore, mixing makes the mixtures packed looser as a whole but makes the superballs packed closer and spheres packed looser if the superballs are much different from spheres.

3.3. The linear fitting method

Fig. 8(b) and (d) shows that all the mixtures with $X_{sb} ≤ 0.5$ are highly disordered with infinitesimal values of $S_4$, regardless of
which surface shape parameter \( p \) is used. The \( V - X_{sb} \) curves with small solid volume fractions of superballs \( 0.0 \leq X_{sb} \leq 0.5 \) demonstrate good linear properties for all the surface shape parameters \( p \) we studied. The nonlinear parts of \( V - X_{sb} \) curves in Fig. 10(a) only arise for large solid volume fractions of superballs \( (X_{sb} > 0.5) \). Considering these properties, we fit the \( V - X_{sb} \) plots with \( X_{sb} = 0.0, 0.1, 0.2, 0.3 \) in Fig. 10(a) via linear functions

\[
V = mX_{sb} + n
\]  

(15)

The fitted lines represent the ideal specific volume curves for the binary mixtures which are all highly disordered at the same random level.

Via Eq. (15), the packing density of the mixture with \( X_{sb} = 1.0 \), i.e., the mono-sized superball packing, can be estimated as

\[
\tilde{\varphi}_{sb} = \frac{1}{V_{sb}} = \frac{1}{m + n}
\]

(16)

which means the ideal random packing density of mono-sized superball packing. For the superballs with a small value of surface shape parameter \((p \leq 1.5)\), the estimated packing density \( \tilde{\varphi}_{sb} \) will be equal to the real packing density of mono-sized superball packing \( \varphi_{sb} \), i.e., the real packing density of mixtures with \( X_{sb} = 1.0 \).

However, the \( \tilde{\varphi}_{sb} \) will be smaller than \( \varphi_{sb} \) for the superballs with a large value of surface shape parameter \((p \geq 2.0)\), as also shown in Fig. 10(b). The \( \varphi_{sb} \) is marked as “MRJ” and the \( \tilde{\varphi}_{sb} \) is marked as “Estimated”. The results of Zhao (Zhao et al., 2017), Delaney (Delaney and Cleary, 2010), Jiao (Jiao et al., 2010) and Liu (Liu et al., 2018a) are also demonstrated for comparison. The packing densities of the “MRJ” packings are close to those of Jiao (Jiao et al., 2010) which further validate the ASC algorithm we use. The “Estimated” packing densities are close to those of the MDRPs which are the densest packings among all random packings at the same random state. Therefore, we further verify the meaning of the MDRP state. The MDRPs of non-spherical particles correspond to the ideal random packings whose degrees of order are at the same level with that of the random close packing of spheres.

Moreover, the linear fitting method can be used to determine whether the generated packing of mono-dispersed non-spherical particles is random or not. It can be used to determine whether the packing is at the same random degree with the random close packing of spheres, which is a stable and well-accepted state, but cannot evaluate the degree of randomness. For a given mono-dispersed non-spherical particle packing obtained under a specific random packing protocol, the following approaches are carried out.

Firstly, we determined the EPSR of the non-spherical particle
which corresponds to the minimum packing density when mixed with spheres at a given solid volume fraction under the same packing protocol. Then the curve of the specific volume versus the solid volume fraction of non-spherical particles in the binary mixtures is obtained, and the linear fitting method mentioned above is used to estimate the ideal random packing density of non-spherical particles. If the curve is linear and the estimated ideal random packing density is close to the real packing density of the mono-sized non-spherical particle packing, the generated mono-sized non-spherical particle packing will be at the same random degree with the random close packing of spheres, such as the packings of superballs with a small value of surface shape parameter \( p \leq 1.5 \) in Fig. 10(a). Otherwise, some global or local ordered structures will arise in the packing and special order parameters are needed to evaluate the degrees of order in this packing, such as the packings of superballs with a large value of surface shape parameter \( p \geq 2.0 \) in Fig. 10(a).

Meanwhile, the linear fitting method also provides a new way to obtain the ideal random packing density, i.e., the packing density of the MDRP state, for non-spherical particles which are easy to crystallize. This method does not need any particular order parameter to evaluate and constrain the degrees of order in the packings, thus avoids choosing or constructing appropriate order parameters which effectively identify the main order forms in the packings of non-spherical particles, which is still a challenging problem (Torquato, 2018). The linear fitting method is a universal method and could be used to estimate the random packing density of other shaped particles besides superballs. We also conjecture that the linear relationship between the specific volume and solid volume fraction for the EPSR will always arise in the MDRP state, regardless of whether the non-spherical particle is close to the sphere or not, demonstrating another advantage of the MDRP state.

4. Conclusions

In this work, we propose a new approach to determining the random packing densities of superballs. The main idea of the approach is to suppress order formations in non-spherical particle packings via the polydispersity of particle shapes, which avoids using order metrics. The packing density of superballs in a mixture can be segregated using the linear fitting method with the concept of equivalent packing diameter. Firstly, we systematically study the packing properties of binary mixtures consisting of spheres and superballs with different size ratios and verify the properties of the equivalent packing sizes of superballs. For the superballs we concerned in this work, whether they are close to the spheres or not, the EPSR always corresponds to the size ratio for which the minimum packing density or the minimal specific volume variation is obtained, and is independent of the solid volume fraction of superballs. The specific volumes of mixtures with the EPSR are also the upper bound for all solid volume factions.

Then we obtain the equivalent packing sizes of all the superballs we concern and investigate the packing properties of binary mixtures under the equivalent packing sizes for different solid volume fractions. In the mixtures of spheres and superballs with small surface shape parameter, the specific volume variations are almost equal to zero and a linear relationship between the specific volume and the solid volume fraction of superballs is observed. There is no volume variation between unmixing and mixing states, and the particles in the mixtures will not produce any interaction. However, in the mixtures of spheres and superballs with large surface shape parameter, the specific volume variations are smaller than zero and the specific volume curve are nonlinear. The binary mixtures are packed looser than unmixed particles and a larger container is needed to pack the mixed particles. Mixing results in more space to pack the particles, which is against our common sense. Moreover, these differences between the mixtures with various surface shape parameters are further verified via the local Voronoi analysis and are related with the order degree of superballs in the mixtures.

Finally, we use the linear fitting method to determine the random packing densities of mono-sized superball packings. The estimated packing densities are surprisingly close to those of the MDRPs, further verifying that the MDRPs of non-spherical particles correspond to the ideal random packings whose degrees of order are at the same level with that of the random close packing of spheres. Therefore, the linear fitting method is a new approach to obtain the packing density of the MDRP state for the non-spherical particles without any particular order metric, and thus avoids choosing or constructing appropriate order parameters which effectively identify the main order forms in the packings of non-spherical particles, which is still a challenging problem so far. The linear fitting method can also be used to determine whether the generated packing of mono-sized non-spherical particles is random or not.

Moreover, we conjecture that the linear relationship between the specific volume and solid volume fraction for the EPSR will always arise if all the mixtures are in the MDRP states, regardless of whether the non-spherical particle is close to the sphere or not, demonstrating another advantage of the MDRP state. More work will be carried out to verify this conjecture. The linear fitting method is a universal method and could be used to estimate the random packing density of other shaped particles besides superballs. We also note that for the non-spherical particles which are much easier to crystallize, such as cubes, the binary mixtures with spheres are not sufficient to suppress crystallization. In these cases, the polydisperse mixtures with more shapes besides spheres will be used to suppress the order structures, which will be carried out in our future work. Our work leads to a better understanding towards the random and binary packings and sheds new light on the meaning of MDRP. Our work also provides a guide for the optimal particle size distributions of powders in the chemical engineering process.

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Appendix A. The normalized cubic order parameter \( \hat{S}_4 \)

The cubic order parameter is often used to evaluate the degree of orientational order in the packings of symmetrical particles with three axes (Liu et al., 2017; Batten et al., 2010; John et al., 2008). In this study, the cubic order parameter \( S_4 \) is defined as

\[
S_4 = \max_{\mathbf{N}} \frac{1}{14N} \sum_{i=1}^{N} \sum_{j=1}^{3} (35 \cos^4 \theta_{ij} - 30 \cos^2 \theta_{ij} + 3),
\]

where \( N = N_{a} \) is the number of superballs in the mixtures studied in this work, \( i = 1, 2, 3 \ldots N \) is the \( i \)-th particle, \( j = 1, 2, 3 \) are the three main axes \( x, y, z \) of a particle. \( \cos \theta_{ij} = \frac{\mathbf{u}_i \cdot \mathbf{u}_j}{} \) with \( \mathbf{u}_i \) the \( i \)-th particle’s \( j \)-th axis. \( \mathbf{N} \) is the unit vector for which \( S_4 \) is maximized. An approximate solution described in Batten et al. (2010) is applied to get \( \mathbf{N} \) and \( S_4 \). All particle axes \( \mathbf{u}_i \) are chosen as trial directors to get \( \mathbf{N} \) for the maximum \( S_4 \).

We note that the particle amounts \( N = N_{a} \) in the binary mixtures studied are not the same, and the values of \( S_4 \) in a random
system with limited particle amount cannot accurately be zero due to the limited particle amount \( N \). The Monte Carlo test (Liu et al., 2017) is carried out to investigate the influences of particle amount \( N \) on the values of \( S_b \). In the three-dimensional coordinate system, \( N \) particles are generated with random orientations and their centers fixed at the coordinate origin. Then the \( S_b \) is calculated according to Eq. (A.1). This procedure is carried out 10,000 times for each value of \( N \) and the probability distributions of \( S_b \) are investigated. Fig. A1(a) and (b) show the histograms of the relative frequency of \( S_b \) over 10,000 samples with \( N = 27 \) and 1000, respectively. The distributions are almost in Gaussian distributions and are fitted with the correlation factor \( R^2 = 0.98797, 0.99102 \), respectively. The means and standard deviations are \( S_b^\text{a} = 0.18140, S_b^\text{b} = 0.05142 \) for \( N = 27 \), and \( S_b^\text{a} = 0.03050, S_b^\text{b} = 0.00821 \) for \( N = 1000 \). Moreover, as shown in Fig. A1(c) and (d), the \( S_b^\text{a} \) and \( S_b^\text{b} \) are proportional to \( 1/\sqrt{N} \) with

\[
S_b^\text{a} = 0.97980/\sqrt{N} \tag{A.2}
\]

\[
S_b^\text{b} = 0.27048/\sqrt{N} \tag{A.3}
\]

In an infinite system with \( N \to +\infty \), the \( S_b^\text{a} \) and \( S_b^\text{b} \) are zero, meaning that the value of \( S_b \) in the random state are zero. However, in a finite system, the value of \( S_b \) in the random state is in a Gaussian distribution. In order to eliminate the effects of particle amount, the global cubic order parameter is normalized as

\[
\hat{S}_b = \frac{S_b - S_b^\text{a}}{S_b^\text{b}}
\]

\[
\hat{S}_b = \frac{S_b}{S_b^\text{b}}
\]

In an ideal random system with finite particle amount, the \( \hat{S}_b \) will be zero. The \( \hat{S}_b \) reflects how far the system is away from the ideal random system. The smaller the \( \hat{S}_b \) is, the more random the system will be. Two systems with different particle amount \( N \) are on the same random degree if the values of \( \hat{S}_b \) are equal. In an ordered system with all the particles in the same direction, the \( S_b = 1.0 \) and \( \hat{S}_b \) is related to the particle amount \( N \) with

\[
\hat{S}_b = \frac{1.0 - 0.97980/\sqrt{N}}{0.27048/\sqrt{N}}
\]

Especially, \( \hat{S}_b \approx 72.15 \) for \( N = 420 \), which is the total amount of particles in the mixtures we studied.

References


