

# Multi-Sized Sphere Packings: Models and Recent Approaches

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**Abstract:** This paper summarizes theoretical and applied studies of the structure of mixtures, formulated as the packing of spheres with different sizes. The effects of the particle size and the shape (fine or coarse) on the packing density are described. We discuss the relationships between the particle size distribution and the packing properties. We also sketch the major approaches, which can be usefully applied in nanotechnologies for the modeling of a material structure. Such a kind of analysis can be used both in the theoretical consideration of material engineering problems and in the chemical industry. Potential applications of these results include a synthesis of nanomaterials, adsorbents, catalyst carriers and packings for chromatographic columns.

**Keywords:** packing; sphere; sphere size distribution; density; simulation; Voronoy tessellation; Laguerre geometry.

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## 1 Introduction

Macroscopic properties of a material such as elasticity, hardness, thermal conductivity or permeability are highly affected by its structure on the particle level. In many cases the three-dimensional (3D) structural model of a matter can be represented as spheres packed in the available space. The cases when the packing space is limited by a predetermined region, such as different types of matrices, filling of a porous structure (channels) with atoms and molecules of different diameters (spheres), are commonly investigated by means of packing models. The first characteristic studied is the packing density  $\varphi$  (in the literature, often the term ‘porosity’,  $1 - \varphi$ , is used instead of  $\varphi$ ), in particular the relationship between the radius distribution and the maximum value of  $\varphi$ . The second one of main interest is the coordination number,  $\langle C \rangle$  which is the average number of contacts on a sphere. The mono-sized case has  $\langle C \rangle = 5.812$ . The densest packings are of a special interest due to numerous applications related to those problems, where a maximal fraction of the filled space is required. The densest packings of mono-sized spheres are achieved on ordered structures. Packing of mono-sized spheres in an N-dimensional space, being a part of the 18<sup>th</sup> problem in the Hilbert’s list, belongs to the most-studied models. It was conjectured by Johannes Kepler in 1611 and recently proved by Hales [1] that the face-centered cubic close packing and hexagonal close packing give the greatest density, equal to  $\pi/(3\sqrt{2}) \approx 0.74048$ , in a volume filled by identical spheres. A detailed review of known packing densities can be found in [2].

When a multi-component composition is studied, the main influence factors are: the (dimensionless) particle size distribution, the particle shape (fine or coarse), and the absolute particle size, where the particle size distribution is considered as more significant, see, e.g., [3, 4].

It is still difficult to measure the structural properties experimentally or by theoretical models. A computer simulation provides an effective alternative to the study of the packing structure of the particles. Rigorous and accurate models for the packing of multi-component particle systems are yet to be developed due to the complexity of geometry. Wang [5], studying an optimization problem modeled by a packing of unequal spheres in a three-dimensional (3D) bounded region in connection with a medical application, showed that this optimization problem and several related problems are NP-hard. Hence, some forms of approximation are needed. However, in the recent decade, a growing interest for this subject of research is noted due to forthcoming potent computational means and

algorithms. To the best of our knowledge, this work is the first intent to summarize the researches dedicated to multi-sized sphere packings.

The rest of the paper is organized as follows. The known packing methods for multi-sized spheres are classified in Section 2 with different viewpoints. The particle size and shape (fine or coarse) effect on the packing density is explained in Section 3. Section 4 is dedicated to the modeling of the packing structure with tessellation diagrams. Some useful algorithms based on original ideas are discussed in Section 5. Section 6 is dedicated to the distributions used for the simulation of multi-sized packings. Some concluding remarks complete the paper.

## **2 Classification of multi-sized sphere packing methods**

Since random sphere packings are useful models for the representation of many types of porous media, the main reason for their use as a model for particle systems is that the highly complex topology associated with randomness and polydispersity can be fully described in primary geometric terms like the radius and the position of each sphere, meanwhile obtaining complete descriptions of real packings is difficult. Computer algorithms are an important alternative to laborious and expensive experiments for creating packings of desired porosity, sphere size distribution, and spatial characteristics. These algorithms and methods to create a random packing should be classified from different points of view although the utility of each one depends mostly on its flexibility, accuracy, and speed.

Concentrating on geometric approaches, the diversity of the developed algorithms may be grouped into two general categories: sequential-deposition and collective rearrangement methods.

Sequential-deposition algorithms begin with an initial sphere or cluster. The position of each newly generated element is defined by its placement in contact with three other spheres that are already in place, using drop and roll type algorithms, which are derived from a similar physical process, where a sphere would be firstly dropped and then rolled till hitting another preexisting sphere or the floor, moving until a gravitationally stable position. Finally, the stability of the sphere is checked to see whether the rolling must continue or a new sphere should be generated [2, 6, 7]. This technique is comprehensible when the effect of the gravitation force is considered. However, it is difficult to program multi-sized systems by drop-and-roll techniques due to the migration of small spheres into the packing as well as high computational recourse consumptions.

The initial condition of collective rearrangement or dynamics methods is a loose packing/random overlapping [2, 8, 9]. Then the spheres are moved randomly in an effort to either decrease the porosity or to remove overlaps. A rearrangement algorithm consists of the random placement of spheres within a prescribed domain. Collective rearrangement is a process, where the overlapping spheres are eliminated with small displacements in order to remove all overlaps in the domain. Useful methods to simulate an initial packing are Monte Carlo and Discrete Element (molecular dynamics) methods. Monte Carlo simulations explore the physical optimization landscape using stochastic moves [8, 10]. The dynamics of forming a packing is properly of the discrete element method (DEM) [11, 12]. The validity and advantage of the simulation techniques have been demonstrated by various investigators, see, e.g., [13]. In the dynamic methods, such as the moving–shrinking method [14], gravitational methods [15] or the compression forces method [16], the particles usually change their position and/or their size during the filling process. Dynamic factors such as the deposition intensity, the friction, and the restitution coefficients can be readily studied by this method. These techniques allow the incorporation of short-range forces such as van der Waals, electrostatic and capillary (for dry systems) into models. So, the packing of fine particles by incorporating the van der Waals force into a DEM model was proposed in [12].

The most effective algorithms combine attributes of collective-rearrangement and drop-and-roll algorithms [6, 7, 17].

Considering the particle size distribution, modeling of packing falls into two main categories: discrete methods and continuous ones. In discrete models, originally developed by Furnas [18] and Westman [19], large or coarse particles are packed densely first, forming the skeleton (or interstices), where the smaller particles are introduced and placed. As a result, the packing density of the mixture increases. When particles of different sizes are mixed, there exists a maximum dense packing at some combinations of fractions of these particles.

A continuous approach was developed by Andreasen and Andersen [20] in the late 1920s and then continued by Ortega et al. [21]. Ouchiyama and Tanaka [22] developed an approach to estimate the packing porosity of particle mixtures from the particle size distribution. This model assumes that each particle of the mixture is surrounded by hypothetical spherical particles with a diameter equal to the number average diameter of the mixture particles and assumes that there is a void volume shared between the core particle and the hypothetical particles that surround it. The volume shared is partially

assigned to each packing particle and added to the physical volume of the packing particle. Their continuous approach was first applied to the packing of binary, ternary and quaternary spherical particles. Li and Ha [4], referring to this approach and basing on previous investigations, wrote that the uniformity assumption made in their model leads to lower predicted packing densities than the experimental data, and since the continuous theory is based on the analysis of the defined simple geometric unit, it cannot depict accurately the particle arrangement in a real particulate system. However, this model is nowadays considered as a basic one.

The third viewpoint of the classification of packing approaches can be found in the paper of Prior [23] who distinguishes analytical models, geometric ones and models of spatial distribution. In analytical models, a linear packing is the most popular approach. In these models, the specific volume is considered. It is the sum of the contributions of the specific volumes of each component in the mixture. The individual contribution depends on the abundance and the size of the component when compared to the others [3, 4, 23, 24]. A geometrical model to estimate the packing porosity of a mixed bed from the size distribution function of the solid particles was developed by Ouchiyama and Tanaka [22] which was mentioned above. The recently developed models of spatial distribution are distinct from the other two forms of modeling by making intensive use of the numerical calculation capacity of computers [25].

### **3 Particle size and shape effect**

Varying the absolute size and shape of the particles, different complex particle systems may be modeled, considering fine (cohesive) and coarse (non-cohesive) ones. These characteristics are a research subject for several years, progressing from simple spherical particles to complicated cohesive and non-spherical particle systems [24, 26, 27].

When the particle diameter is less than 100  $\mu\text{m}$ , the gravity is not the dominant force. It implicates that the ratio of the interparticle force to the weight of the particles is greater than the unity and the collective outcome of weak forces such as the van der Waals one, electrostatic or capillary forces, becomes more important than the gravity effect. Due to this, fine particles form aggregates or agglomerates because of the relatively strong cohesive forces. Therefore, packing behavior of fine cohesive particles is different from that of coarse particles. In recent years, various simulation studies

have been made to understand the influence of the particle size and inter-particle forces on the packing porosity, see, e.g., [3, 24].

It has been noticed that the absolute particle size of a component, as well as its shape, affects the porosity of a particle mixture mainly by its initial porosity, which is defined as the porosity of a component in the mixture [3]. For non-cohesive spheres, it has been well established that their initial porosity is 0.36 for random dense packing and 0.4 for a random loose packing [28], meanwhile nanoparticles, can give a porosity until 0.99 [24, 29]. In such approaches, nanoparticles should be considered as ultra-fine particles [24].

For mono-sized particles, the relationship between the porosity and the particle size has been established [3, 30], meanwhile for mixtures of cohesive or fine particles, only limited efforts have been made up to now in the formulation of predictive models or equations [3, 24, 31-33]. The porosity of such a system should be a function of the initial porosity, the nominal diameter of a particle or any measurable particle size, and the volume fraction [3, 24]. Zou et al. [24] presented a mathematical framework and a supportive experimental test to model the packing mixtures for both fine and coarse particles with a wide size range.

#### **4 Tessellation diagrams**

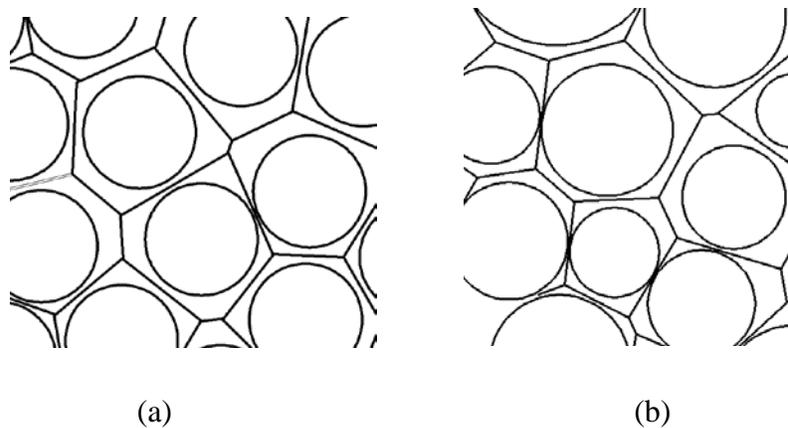
The tessellation approach in a sphere packing modeling has been extensively studied over a long period of time because of the predictability and high applicability of the method. A tessellation of the  $d$ -dimensional Euclidian space  $\mathbf{R}^d$  is a subdivision of the space  $\mathbf{R}^d$  into  $d$ -dimensional subsets called cells. The main idea is to construct a system of space-filling convex cells, where each cell contains exactly one sphere. The geometry of the packing can then be described by geometrical characteristics of the cells. The tessellation techniques are able to predict the metric and topological properties of a structure and its statistical analysis. This approach is based on the Voronoi-Delaunay tessellation technique to model packing structures. Below we review the variants of this technique found in the literature.

For each sphere of an arbitrary arrangement, the Voronoi region, is a polyhedron defined as the portion of space surrounding that sphere and closer to that sphere than to any other one [34]. A partitioning of a space into such regions is called Voronoi diagrams. It is assumed that the Delaunay

empty sphere moves inside the Voronoi region so that it touches at least three objects at any moment of time (Figure 1(a)). The interstices within a packing form a continuous network of interconnecting pores or voids.

In 1998, Mac Laughin has demonstrated that the smallest Voronoi cell is the regular dodecahedron circumscribing the sphere [34]. For mono-sized spheres, the ratio of the volumes of these two figures is 0.754697, which is very close to the 0.74048 Kepler's limit and thus, it is a perfect upper bound on the largest possible coefficient of the occupation of space and an excellent method to model a dense heap of particles.

Two Delaunay cells are considered to be adjacent if they have one face in common. The connectivity between pores is restricted by the void area in the face of two adjacent Delaunay cells. Therefore, it can be characterized by the pore throat size and the pore channel length. The channel length can be obtained from the radial distribution function and corresponds to the edge length of the Voronoi polyhedron.



**Figure 1.** 2D representation of the tessellation technique: (a) Voronoi-Delaunay tessellation; (b) Voronoi diagram in Laguerre geometry.

In the case of nonequal spheres, the Voronoi tessellation with respect to the sphere centers is not appropriate because then the cells can cut spheres or the cells of touching spheres are not necessarily in contact (Figure 1(b)). Therefore, another tessellation concept is necessary. One possible approach is the radical tessellation or also referred to as Voronoi diagram in Laguerre geometry (LV), which

represents a weighted form of the Voronoi tessellations constructed by means of Power diagrams [9, 11, 35-37]. The radical tessellation is an extension of the Voronoi tessellation to a multi-sized particle system. Similar to the Voronoi tessellation, the radical tessellation divides the whole packing space into a set of non-overlapping convex polyhedra and each polyhedron contains exactly one particle. The plane used in the radical tessellation to separate two close particles is the assembly of points with equal tangential distance to the two spheres, different from the bisecting plane. The touching spheres have a common face; larger spheres tend to have larger cells than smaller ones. If the radii of all spheres in the set are equal (or all weights are equal), the Voronoi tessellation is obtained. For mathematical aspects of the Voronoi-Delaunay diagrams as well as LV diagrams, the reader is referred to e.g., [9, 38].

The Delaunay cell is the topological dual to the Voronoi polyhedron and vice versa as well as the Laguerre diagram is dual to regular triangulations. So, the Voronoi polyhedron is directly related to the connectivity of particles, like the thermal conductivity or interparticle forces, while the Delaunay cell is related to the connectivity of pores in a packing, e.g., permeability [12]. The vertices of the regular triangulation are the spheres (germs) of the corresponding Power diagram, the edges correspond to faces and the vertices of the Power diagram are the orthogonal centers of the triangulation. The weight is similar to a distance and it enables some control of the size of grains. The larger the weight is, the bigger is the grain.

The original Voronoi tessellation method is mainly used for the packing of uniform or mono-sized spheres in early studies since the works of Bernal [39] and Finney [40]. However, it has been extended to handle the packing of multi-sized particles, giving the so-called radical tessellation and Johnson–Mehl tessellation [41]. The studies so far were mainly focused on binary mixtures of particles. These past studies were based on the results generated by the sequential addition or collective rearrangement.

Yang et al. [12] described the size distribution of the Delaunay cells by the lognormal distribution, where the majority of Delaunay cells in the packing with higher density are regular tetrahedrons, generated in such a way that each particle is supported by three particles underneath, and it also provides a support to the other three particles above. However, as the particle size decreases and the interparticle force such as the van der Waals force becomes dominant, more Delaunay cells are formed by ‘untouching’ particles and become more irregular, generating more disordered packing and pore

structures. Consequently, a packing with small density gives a scattered correlation between the cell size and the cell sphericity.

The Delaunay triangulation method was further extended to generate valid finite element meshes for practical engineering problems. Finite element mesh generation methods have been given recently, and different methods and their variations have been developed for an unstructured mesh generation. In most Delaunay triangulation processes, before interior nodes are inserted, a tessellation of the nodes on the domain boundary is produced. However, in this process there is no guarantee that boundary segments will all be present in the triangulation. In the paper by Lo and Wang [42], the idea to connect centers of tightly packed spheres of variable size by the Delaunay point insertion technique is used. Starting from an arbitrary point in the space (defined as the origin) and guided by the concept of an advancing front, spheres of a size compatible with the specified element size are packed tightly together one by one to form a cluster of spheres of different sizes. Three criteria for a sphere packing were applied: nearest, densest, and tangent and no overlapping. The algorithm is fast and robust, and the time complexity for a mesh generation was expected to be almost linear.

In the paper by Yi et al. [13], a radical tessellation analysis on the packing of ternary mixtures is performed, in connection with previous studies of the authors. The metric and topological properties of each polyhedron are studied as a function of the volume fractions of constituent components, for a better understanding of the complicated packing structures of particle mixtures. The polyhedron face as part of the plane is guaranteed to be outside the particles and will not intersect with any particle. The radical tessellation retains most of the features of the Voronoi tessellation, and it recovers the Voronoi bisecting plane for monosized particles. The authors concluded that the radical tessellation can be used successfully to model different properties of multi-sized packings and the development of a predictive method to describe the effect of the particle size distribution on the structural properties of the packing of particles.

The Poisson–Voronoi diagram (PV) has been extensively used to simulate the microstructure (see, e.g., [13]). The PV diagram is a kind of a Voronoi diagram with the set of points generated through a homogeneous Poisson point process. A PV diagram is composed of an array of convex, space-filling and non-overlapping polyhedrons, which represent the grains of the polycrystalline material. The polyhedrons of the PV diagram possess the properties that four edges share a vertex and three faces share an edge, which are also observed in real material.

In the paper by Fan et al. [38], some inadequate features of the PV diagram are considered using LV diagrams. The authors suppose that the proposed model, called the RCPLV diagram, is probably better than the PV diagram in the simulation of the microstructure of real polycrystalline materials because it is based on real material characteristics instead of inadequate ones used in the PV diagram: the average number of faces per polyhedron, the range of the coefficient of variation of the grain volumes, and the polyhedron volumes obeyed a lognormal distribution instead of a gamma distribution.

A powerful tessellation approach was used in the paper by Lochmann [11] in the analysis with different statistical methods of the geometrical organization of disordered packings of spheres. Four different structures were considered: mono-sized, binary, power-law and Gaussian size distributions. The comparison of basic geometrical characteristics such as the packing fraction, the two-point probability function, the pair correlation function and the coordination number has shown that these characteristics can have quite different forms, which are closely related to the radius distribution. The description was refined by means of tessellation-related characteristics, which enable a quantitative description of the different local arrangements by means of the number of cell faces and edges per face. A depth analysis of the coordination number, which is the fundamental topological parameter, is given for different radii distributions. In this paper, the tessellation employed was the radical (or LV) tessellation.

In [37], Laguerre tessellations generated by random sphere packings were employed as models for the microstructure of cellular or polycrystalline materials, using lognormal or gamma distributions of the volumes. The authors studied the dependence of the geometric characteristics of the Laguerre cells on the volume fraction in a sphere packing and the coefficient of variation of the volume distribution. The moments of certain cell characteristics were described by polynomials, which allows one to fit tessellation models to real materials, like open polymer and aluminum foams, without further simulations. The author considered relatively dense packings with 66.7%, where the cell volumes, like the sphere volumes, were approximately lognormally distributed. The topology parameters, the number of facets per cell and the number of edges per facet as well as the tessellation characteristics were analyzed.

LV based on a random close packing of spheres was considered by [9] as a successful method for modeling and characterizing two-phase composites. First, it was generated with two groups of spheres and each group has its own volume distribution, basically lognormal, by using a modified

rearrangement algorithm. Then an LV diagram was performed basing on the sphere packing to generate the grains of the two phases, thus the model of a two-phase composite was obtained. Various geometrical and topological characterizations were conducted, yielding useful information about this kind of composite. Three groups of representative parameters were selected to characterize the particle shape, the local and the overall geometrical distributing patterns: 1) the form factor; 2) the nearest neighbor distance, and 3) the second order intensity function and the pair distribution function. Three aspects were selected as general descriptions of the composite models: 1) the volume fraction of constituent phases; 2) the mean and standard deviation of grain volume; 3) the grain volume distribution. Several topological parameters were computed. The authors concluded that the model and the characterization based on a random close packing of spheres using an LV diagram are effective for analyzing composite microstructure.

In the paper [43], the LV diagrams were used for performing a numerical approach to study the effects of a grain size distribution and the stress heterogeneity on yield stress of polycrystals. Firstly, the numerical scheme was used for the generation of polycrystalline microstructures. It combines the Lubachevsky-Stillinger algorithm for a dense sphere packing [14] with Power diagrams. It has been shown that the combination of a dense-sphere packing and LV diagrams provides a convenient way to produce microstructures with a prescribed grain size distribution.

## 5 Algorithms

In this section, we discuss some basic algorithms containing original ideas which are extensively used for poly-sized sphere packings.

The extended Lubachevsky–Stillinger (L–S) algorithm [9, 43, 44] is a nonequilibrium molecular dynamics simulation, in which the spheres grow over time. Originally, it was developed for mono-sized sphere packings [14]. Once the initial conditions are fixed, the system evolves deterministically. This algorithm has a single parameter which represents the sphere growth rate relative to the mean sphere speed. If the algorithm is run with a high compression rate, however, the packing fraction of the resulting configurations reaches a density equal to approximately 0.645 (in the mono-sized sphere packing case). As the spheres grow larger, the collision frequency increases and the maximum packing fraction were asymptotically approached. An extension of the L-S algorithm was used for the concurrent generation of dense poly-sized sphere systems considering the packing of a sphere mixture

over a wide range of sphere volume ratios. The resulting algorithm runs significantly more slowly than the mono-sized version.

With the Monte Carlo simulation model, developed by [8], the unequal spherical particle with radii obeying a given (lognormal) distribution are generated and randomly placed within a cubic packing domain with high packing density and many overlaps. Then a relaxation iteration is applied to reduce or eliminate the overlaps. As the overlap approaches a stable value but is still higher than a specified tolerance, the particle sizes are reduced. The simulation is completed once when the mean overlap value falls below a preset value. To simulate a random close packing, a ‘vibration’ process is simulated within the relaxation procedure to randomly disturb the positions of those particles, which have a coordination number less than 4 since the particles that form bridges have fewer contacts with others.

The mechanical contraction method [25] was developed at the University of Utrecht, The Netherlands, for packing spheres and spherocylinders. It makes a direct simulation of a rapid densification (by sedimentation), where the pressure on the particles dominates over their thermal fluctuations. If a thermal system is to be quenched, the quench rate must be extremely high such that the particles are forced into a permanent contact with each other on a time scale, and the system cannot move towards a more thermodynamically favored phase as this would affect the final structure and density. Mechanical contraction extended method [16] is a geometric-based approach, a compression algorithm for a random filling of the geometric domains with spheres of various sizes. It employs several existing numerical techniques, such as a very highly efficient contact search algorithm.

The Monte Carlo ballistic deposition algorithm [45] is an extension of an earlier approach by the authors, called the ‘central string’ algorithm, which allows the analysis of a multi-modal hard-sphere with broad particle size distributions. Each particle of a different size or density (a mode) is represented in the pack by its own cylinder, scaled appropriately to the particle size. As the pack is built, each particle mode remains within its own cylinder. The smallest mode particle resides in the smallest cylinder, and it is closest to the axis of symmetry. Larger particles may lie within the inner cylinders, but also extend into outer cylinders; each mode is always constrained to remain within its own cylinder. The largest particle in the pack may lodge in any of the cylinders, and in the outermost cylinder it resides alone. It should be clear that setting all cylinders to have the same size (the size of the largest particle’s cylinder) produces a three-dimensional simulation. The implementation allows one to build simulated packs with both reduced and tridimensional approaches by simply choosing

each particle's cylinder size appropriately. The concentric-cylinder approach introduces the complexity into the calculation of the pack microstructure and the packing statistics.

In [13], DEM was used to generate the packing of a ternary mixture of spheres. The translational and rotational motions of each particle were described by Newton's second law of motion, where the gravity and interparticle forces as well as the torques were explicitly considered. The interparticle forces including the contact and noncontact forces, such as the van der Waals and electrostatic forces, were ignored because the authors only dealt with coarse and dry particles.

## 6 Particle size distributions

For multi-sized mixtures of components, the particle size distribution is the key issue of any investigation of the composition structure. Therefore, the methodology, the parameters measured and the simulation algorithms are subjected to the distribution type. In this section, we give a brief review of the works studying the distributions in the context of multi-sized packings. The main focus is on the application area, specific parameters and interesting details.

One of basic works was given by Stovall et al. [46]. Stovall's model for the calculation of the packing density of multi-sized grains employed a continuous particle size distribution. It was established on the principle that each particle in the packing system is in contact with the neighboring ones. The packing density was expressed as a function of the fractional solid volume of each grain size. The model was used for predictions with binary, ternary and higher-order mixtures.

One of the first in-depth researches in this area was made by He et al. [8]. They focused the attention on bimodal and lognormal distributions for a computer simulation of a random packing of unequal particles. For lognormal distributed particles, the effect of the particle size standard deviation and the fraction of large particles, on the packing density and the coordination number were investigated. It has been observed that for a random close packing, the trend of the effect of the standard deviation  $\sigma$  of the particle radii on the random close packing density  $\varphi_c$  is similar to previous studies: As  $\sigma$  was smaller than 0.15, its influence on  $\varphi_c$  was insignificant; when  $\sigma$  was greater than 0.15,  $\varphi_c$  gradually increased with  $\sigma$ . It can be estimated that, for  $\sigma = 0.1$ , the radii of more than 95% of the particles are expected to fall into a range between (0.8, 1.2), where the mean radius of the lognormal distributed particles is normalized to be 1.0. For such a narrow distribution, the ratio of the

radii of any two contact particles was close to 1.0. Therefore, a small standard deviation  $\sigma < 0.1$  will not cause a significant increase in the packing density. The randomness, homogeneity, and isotropy, which were firstly evaluated for packing of distributed particles, were examined using statistical measures.

Zou et al. [47] employed ternary and continuous distributions of the particle sizes studying wet coarse mixtures. Glass beads with sphere diameters of 6, 2 and 0.67 mm were used for the experiments in the first case, and 12 glass beads with diameters ranging from 1 to 12 mm, for the second one. The results were used to examine the similarity between mono-sized and multi-sized, and between dry and wet packing systems.

A simulation of polycrystalline structure with a Voronoi diagram in Laguerre geometry was realized in [38]. The volumes of the spheres were set to serve a lognormal distribution, which was strongly inherited by the distribution of the cell volumes in the LV diagram of a random closed packing of spheres. The authors noted that grain volumes usually follow a lognormal distribution in a real material with a coefficient of variation, which is the reason for the resultant standard deviation of the gain volumes and their mean, ranging from 1.09 to 2.13. In the experiment, the volume distribution was lognormal with the coefficient of variation of grain volumes varying from 0.6 to 3.0 in intervals of a length of 0.2, so 13 types of the random close packing of spheres with different coefficient values were obtained.

The spheres of the random size distribution or of the size specified by a node spacing function were used for the finite element mesh generation over an unbounded 3D domain packing algorithm in the work by Lo and Wang [42].

A statistical analysis of random sphere packings with variable radius distribution was given in the paper by Lochmann et al. [11]. The sphere systems considered in this paper obeyed a binary distribution or had a Gaussian or power-law distribution of the radii. Formulas were given to calculate the probability density function for the distributions used. The ratio of the maximal value of the radii to the minimal one  $R_{\max}/R_{\min}$ , was considered as the parameter of main interest for a power-law radius distribution. Indeed, it had a considerable influence on the packing density. If the interval  $[R_{\min}, R_{\max}]$  was small, the spheres were almost equal and the packing density was close to the packing density of a mono-sized sphere system; if it was large, a higher maximum packing fraction was expected. In

practical applications, usually certain limits for  $R_{\min}$  and  $R_{\max}$  have to be respected, like e.g. the maximum pore size or given maximum and minimum particle radii. With the Gaussian distribution of the sizes, it was observed that an increase of the variability of the coefficient of variation has led to an increase of the packing density. Moreover, the authors noted that, if the packings of spheres were obtained numerically by a simple deposition, the contact points were exactly known. However, in packings simulated with DEMs (e.g. molecular dynamics), the determination of the contact number was difficult. The spheres in such systems were usually not in exact contact; there were smallish overlaps or gaps. This problem was handled by introducing a tolerance parameter  $\varepsilon$ : All spheres with a surface-surface distance less than  $\varepsilon$  were considered as in direct contact. In this work,  $\varepsilon = 1\%$  of the mean radius was chosen.

In the work by Yang et al. [12], which was dedicated to the pore structure of the packing of fine particles, the size distribution of the Delaunay cells was described by the lognormal distribution. A formula for the probability function was given.

A continuous particle size distribution was investigated in the paper by Ye et al. [48], where cement mixtures were considered for seeking the optimum particle size distribution. The idea of the authors was that a higher packing density needs a wider particle size distribution, while a faster hydration rate needed a narrower particle size distribution. The packing density and the hydrates quantity could be perfectly matched and the densest hardened cement paste could be formed.

In the paper by Redenbach [37], the case of hard sphere packings with lognormal or gamma distributed volumes was investigated for the modeling of the microstructure of cellular or polycrystalline materials, because these distributions were often suggested for the size distributions of grains (cells) in granular (cellular) materials. The Laguerre cells on the volume fraction in the sphere packing and the coefficient of variation of the volume distribution were studied in detail. The moments of certain cell characteristics were described by polynomials, which allow fitting tessellation models to real materials without further simulations. The procedure was illustrated by the examples of open polymer and aluminium foams.

Wu et al. [9] used two groups of spheres and each group had its own volume distribution for modeling and characterizing the two-phase composites. The volume distributions in each group of grains were lognormal-like, and each phase had a different degree of dispersion, measured by the

coefficient of variation. The mean of the grain volume and the coefficient of variation of each phase were controlled by changing the volume distributions of two groups of spheres in a random close packing. Therefore, the method can be utilized to predict the real material performance for two-phase composites with a certain mixture ratio. After an analysis performed on microstructures obeying lognormal distributions, the authors concluded that such a distribution would give good indications for practical researches when generating a random close packing.

Zou et al. [24] presented an experimental and theoretical study of a packing of mixtures of cohesive (fine) and non-cohesive (coarse) particles. Initially, the experimental results were used to depict the similarity between packings of fine and coarse particles. On this basis, the so-called linear packing model was extended to estimate the porosity of mixtures of fine and coarse particles with a wide size range. The packing of particles with a lognormal distribution, involving both cohesive and non-cohesive particles, were investigated in detail. An illustrative example demonstrated the application of the proposed packing to a real electrode system.

The uniform, normal, and lognormal distributions were considered in [49] to study several basic microstructure features and electrochemical properties of composite electrodes of solid oxide fuel cells, such as the coordination numbers and the percolation probability, among others. A simple and clear figure illustrated the distributions studied and a comparison between uniform, normal, and lognormal distributions vs. individual lognormal-type distribution of yttria-stabilized zirconia (YSZ) – particles.

In the paper by Yi et al. [13], the packing of ternary mixtures of spheres with size ratios 24.4/11.6/6.4 was simulated by means of DEM. The packing structure was analyzed with a radical tessellation. The properties of each component of a mixture were shown to be strongly dependent on the volume fractions. Their average values can be quantified by a cubic polynomial equation.

Farr [50] applied his previous one-dimensional algorithm for predicting the random close packing fractions of multi-sized hard spheres to the case of lognormal distributions of sphere sizes and mixtures of such populations for modeling colloidal and granular systems. Moreover, it was mentioned that in studies of emulsions, it was frequently found that the volume-weighted size distribution of droplets was lognormal, and this can also be a good approximation for granular materials, such as sediments. Formulas for calculating the distribution of the number-weighted diameters and volumes

were given. The author noted that one should alternatively define a lognormal distribution with the particle volume, rather than with the diameter, as the independent variable. In this case, for the same physical distribution, the volume-based lognormal ‘width’  $\sigma_v$  will be  $3\sigma$ .

## 7 Conclusions

Random sphere packings are useful models for different types of porous media considering a particle of a matter as a sphere. When it is necessary to attain a packing density greater than 0.9, as, e.g., in clinical applications [9], spheres of unequal diameters should be used. The main interests of researchers are to find the relationship between the packing density and the particle size distribution and to predict the optimum particle composition that would yield the maximum packing density.

When we consider mathematical aspects of the packing density, the particle size and distribution are probably the most significant assumptions in the modeling. Indeed, it strictly depends on the particle size, which kind of forces interact in a particle system, whether the gravitational field, or short-range forces such as the van der Waals, electrostatic and capillary ones are relevant.

The particle size distribution defines the contribution of each constituent of the mixture to the resultant density. The selection of a distribution depends directly on the real matter characteristic or on the modeling objectives to be reached. For modeling multi-sized packings, there were employed discrete distributions, for packing of binary, ternary, quaternary, etc., spherical particles [13, 46, 47, 51] as well as continuous ones, for packing particles with continuously distributed sizes of the particles.

One can see that random packings obtained by models with a lognormal size distribution are more frequent in the research because they represent the structures of a variety of materials, like polycrystalline materials, open polymer and aluminium foams [37], two-phase composites [9], electrodes of a solid oxide fuel cell [49], colloidal, and granular systems, sediments [50], zeolite crystals [51], as well as amorphous metals, simple liquids, and isostatically compressed components of ceramic and metal powders [8]. The Gaussian distribution of the particle size is also suggested to be modeled, e.g., with commercial powders in [7, 11]. On the other hand, Shi and Zhang [7] mentioned that particles with a uniform size distribution are impossible to be manufactured based on the current technologies. Nevertheless, the uniform distribution is one of the principal ones, and the studies of

multi-sized packings, which involve it into the consideration, attract the attention of researchers. The LV tessellation supports the majority of the investigations in modeling and studying multi-sized packing structures. So, it is a more general approach to model such structures.

The present review shows a significant progress, which has been made in the recent decades in the modeling of the relationship between the density (porosity) and the particle size distribution for spherical particles. However, rigorous and accurate models for the packing of multi-component particle systems are yet to be developed. We have also sketched the major approaches, which can be usefully applied in nanotechnologies for modeling the structures of materials.

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