THE DISTRIBUTION FUNCTION OF MASS DENSITY — A TOOL FOR THE ANALYSIS OF SPHERE PARTICLE SYSTEMS

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Abstract

A method for characterizing sphere particle systems based on the calculation of the distribution of the average mass density in concentric spherical layers surrounding an arbitrary center has been developed. The effectiveness of the method has been tested on several variants of polydisperse system models obtained in two different ways and one system obtained by full-scale modeling. The distribution of the mass density for both methods of generating model systems allows you to choose the better option. For a system obtained by the field simulation method, a difference in properties is shown depending on the position of the observation center. This paper introduces the MaDiS program which implements the developed method.

Keywords: *characteristics of a system of spherical particles, distribution of mass density, program for the analysis of polydisperse systems, methods for generating a system of spherical particles.*

1. INTRODUCTION

Direct modeling of natural and artificial materials by systems of spherical particles of the same size (monodisperse systems) or of different sizes (polydisperse systems) has a long history and has been successfully used to study the mechanical properties and structure of powder, porous and composite materials (alloys) [1, 2]. Such modeling can also be successfully used to study structures with dimensions in the micro- and nanometer ranges based on the analysis of optical and X-ray scattering indicatrixes (see examples [3, 4]). It is noted that in the study of scattering, the diversity of model systems can be much wider than in the study of mechanical properties. Mechanical model systems are mostly densely packed and almost uniform. Whereas in X-ray scattering, modeling of fractal systems [5] can be of undoubted interest, and interference contributions appear even for rarefied systems with a volume fraction of matter in units of percent [4].

If characteristics of the system such as the paired correlation function of particle centers, the distribution of coordination numbers, etc. are important in the study of mechanical properties [3, 6], then the distribution of mass (electronic) density in the system comes to the fore in

the simulation of scattering. In this paper, a method for characterizing a system of spherical particles using a graph of the radial distribution of the scattering mass (electron density) has been developed. Using this graph, it is possible to check both the homogeneity of the mass distribution and find possible patterns in such a distribution. The method makes sense regardless of the packing density of particles and is especially interesting for polydisperse systems, in which, in contrast to monodisperse systems, the spatial density centers may not correlate with the density of spatial mass distribution.

2. METHOD DESCRIPTION

In the first step of the method, the center O and radius R_{gl} of the bounding spherical region, in which the desired distribution function will be constructed, must be specified in the tested particle system. It is observed that in one of the effective methods of direct simulation of X-ray scattering [4], such a region is determined naturally. In the next step, N particles, that can get at least part of their volume into the bounding area, are selected. Then the bounding area is divided into M spherical layers with centers at the point O, and for each layer the ratio of the total mass of particles entering the layer to the volume of the layer is calculated:

$$\eta_k = \frac{\sum\limits_{i=1}^{N} \rho_i \cdot v\left(p_i, r_i, R_k, R_{k+1}\right)}{V(R_{k+1}) - V(R_k)}, \quad k = 1, 2, ..., M. \tag{1}$$

In which,
R_k, R_{k+1} — inner and outer radii of layer with number k ($R_1 = 0$, $R_{M+1} = R_{gl}$);
p_i, r_i and ρ_i — radius vector module i-particles relative to the center O, its radius, and its density respectively;
$v\left(p_i, r_i, R_k, R_{k+1}\right)$ — volume for i-particles falling into a layer with boundary radii R_k, R_{k+1};
$V(R)$ — volume of sphere radius R. Value k matched to the average layer radius: $L_k = \frac{1}{2}(R_k + R_{k+1})$.

When calculating the function $v\left(p_i, r_i, R_k, R_{k+1}\right)$, the formula (see [7]) is used for the volume of the area of intersection of two spheres with radii x and y and incenter distance p for the case $|x - y| \le p \le x + y$:

$$V_{inter}(x, y, p) = \pi \left[\frac{2}{3}(x^3 + y^3) - \frac{(x^2 - y^2)^2}{4p} - \frac{p}{2}(x^2 + y^2) + \frac{p^3}{12} \right]. \tag{2}$$

Calculating the volume of $v\left(p_i, r_i, R_k, R_{k+1}\right)$ comes down to a number of cases presented in table 1.

The developed method is implemented as the MaDis program. It is necessary to upload a table of coordinates, radii, and particle densities of the tested system at the program input. In the proposed software implementation of the method, the coordinates of the center of the studied area, the maximum radius of the R_{gl} area, and the number of m spherical layers (intervals of radii) must be specified. The intermediate radii of the layers are determined from the condition that the volumes of the layers are equal to each other. Changing Ì allows to change the resolution with which the mass density distribution function is calculated.

3. METHOD TESTING

The effectiveness of the developed method for characterizing the system was tested on several variants of model polydisperse systems of spherical particles with a density equal to 1, ob-

Table 1. Calculation formulas for a spherical particle of radius r with modulus of radius vectors p of the volume $v(p, r, R_{\mathrm{in}}, R_{\mathrm{ex}})$ part, falling into the spherical layer with internal R_{in} and external R_{ex} radii. Here the notation used are as follows $a = |p - r|$, $b = p + r$ for the minimum and the maximum distances of the particle points from the center O layer

Correlation of particle and layer parameters	Location of the intersection points of the particle and layer boundaries with the axis passing through the center of the O layers and the center of the C particles. The bold segment highlights the particle diameter	Formulas for calculating the volume of a particle entering a spherical layer
$\begin{cases} a \le R_{\mathrm{in}}, \\ b \le R_{\mathrm{in}} \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	0
$\begin{cases} a \le R_{\mathrm{in}}, \\ R_{\mathrm{in}} < b \le R_{\mathrm{ex}} \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	$V(r) - V_{\mathrm{inter}}(r, R_{\mathrm{in}}, p)$
$\begin{cases} a \le R_{\mathrm{in}}, \\ R_{\mathrm{ex}} < b \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	$V_{\mathrm{inter}}(r, R_{\mathrm{ex}}, p) - V_{\mathrm{inter}}(r, R_{\mathrm{in}}, p)$
$\begin{cases} R_{\mathrm{in}} < a \le R_{\mathrm{ex}}, \\ R_{\mathrm{in}} < b \le R_{\mathrm{ex}} \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{ex}}$, $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	$V(r)$ when $r \le p$, $V(r) - V(R_{\mathrm{in}})$ when $p < r$
$\begin{cases} R_{\mathrm{in}} < a \le R_{\mathrm{ex}}, \\ R_{\mathrm{ex}} < b \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{ex}}$, $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	$V_{\mathrm{inter}}(r, R_{\mathrm{ex}}, p)$ when $r \le p$, $V_{\mathrm{inter}}(r, R_{\mathrm{ex}}, p) - V(R_{\mathrm{in}})$ when $p < r$
$\begin{cases} R_{\mathrm{in}} < a, \\ R_{\mathrm{ex}} < b \end{cases}$	(diagram: a, C, b; O, R_{in}, R_{ex} / $-a$, C, b; $-R_{\mathrm{ex}}$, $-R_{\mathrm{in}}$, O, R_{in}, R_{ex})	0 when $r \le p$, $V(R_{\mathrm{ex}}) - V(R_{\mathrm{in}})$ when $p < r$

tained by two different methods, and one system of homogeneous particles obtained by full-scale modeling.

The first method (method A) of generating a model system consisted of the following steps:

1. Generation of a set of radii r_i $(i = 1, 2, \ldots, N)$ particles in accordance with a given law $f(r)$ of the radius distribution. Subsequently, the value $N = 5 \cdot 10^4$ was selected. Radii are measured in arbitrary units. A variant of the Schultz-Zimm distribution [8], which is often used in describing particle size distributions in nanosystems, was chosen as the $f(r)$ distribution. To test the reproducibility of the mass density function, 10 samples of the system were generated with an expected value of the radius of one particle of about 8 and a square root of the dispersion of about 4. An example of a histogram of the particle size distribution is shown in Fig. 1.
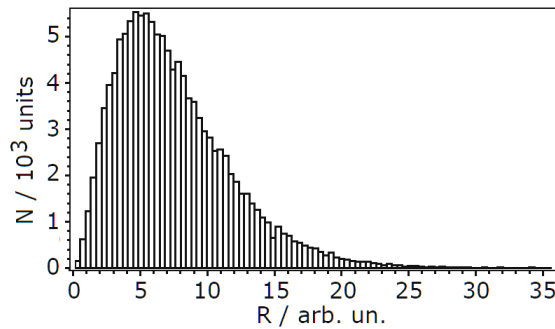
Figure 1. Histogram of the particle size distribution in one of the model system samples. The total number of particles is $5 \cdot 10^4$

2. Based on the set value of the volume fraction Φ of the space filling and particle radii obtained in paragraph 1, the radius R_{gl} is calculated such that the total volume of particles is the fraction of Φ of the volume of a sphere of radius R_{gl}:

$$R_{\mathrm{gl}} = \sqrt[3]{\frac{\sum_i^N r_i^3}{\Phi}}. \tag{3}$$

3. Sequential generation of the coordinates of the particle centers. Each of the Cartesian coordinates x, y, z of the center of the next particle was generated in accordance with the law of uniform distribution in the interval $[-R_{\mathrm{gl}}, R_{\mathrm{gl}}]$. Coordinates x, y, z we assigned to the center of the particle number i under the following conditions:

a) the center i-th particle is inside a sphere of radius R_{gl}:

$$\sqrt{x_i^2 + y_i^2 + z_i^2} \le R_{\mathrm{gl}}; \tag{4}$$

b) the i-th particle has no intersections in space with all previous particles:

$$\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \le r_i + r_j, \ \text{ for } \ j = 1, 2, \ldots i - 1. \tag{5}$$

To optimize the coordinate generation process, the set of particle radii was preliminarily sorted in descending order. When adding the coordinates of the next particle, the number of attempts were limited by the number 10^{12}.

In the second method (method B) of generating the system, particles were initially filled in a certain cube with an edge A. Then, the particles that fall inside the sphere, with a radius slightly less than half the edge of the cube, were selected: $R_{\mathrm{gl}} = \dfrac{A}{2(1 + c)}$. The parameter c was conventionally set to 0.01.

In this method of generating the system, the following steps were performed:

1. Generation of a set of radii r_i ($i = 1, 2, \ldots, N_{\mathrm{src}}$) of particles in accordance with the given law $f(r)$ of the radius distribution. The amount of N_{src} particles filling the cube was selected

$$N_{\mathrm{src}} = \frac{6}{\pi} N \varepsilon (1 + c)^3. \tag{6}$$

so that the number of particles falling inside a sphere with a radius R_{gl}, also turned out to be close to $N = 5 \cdot 10^4$. The fraction in the right part of the formula (6) is the ratio of the volumes of the cube and the sphere inscribed in the cube. The parameter ε was added in order to compensate for the edge effects, which are discussed below.

2. The calculation of the cube edge value based on the volume fraction Φ of the space filling and the particle radii obtained in the step 1:

$$A = \sqrt[3]{\frac{4\pi \sum_i^N r_i^3}{3\Phi\varepsilon}} \tag{7}$$

3. Sequential generation of the coordinates of the centers of particles. Each from the coordinates x, y, z of the center of the next particle was generated in accordance with the law of uniform distribution in the interval $[-A, A]$. Coordinates x, y, z were attributed to the center of the particle number i when the condition (5) was met.

4. After generating the coordinates of all N_{src} particles, those whose centers fell inside the sphere with a radius were selected from them

$$R_{\mathrm{gl}} = \frac{A}{2(1 + c)}, \tag{8}$$

that is, those particles for which the condition (4) with the radius (8) was met.

5. The parameter ε was selected as a result of several repetitions of the steps 1–4 so that the volume of particles selected in the step 4 was the fraction Φ of the volume of the sphere of radius R_{gl}, accurate to three significant digits.

Both methods of testing systems described above have been tested on model systems with volume fractions $\Phi = 0.1; 0.2; 0.3; 0.4$.

A dense system of spherical particles obtained experimentally in the work [3] was chosen as another type of system to be tested. In this work, only a table of coordinates of the centers of particles is shown. In the authors' work, this coordinate table was supplemented by a column of the radii of particles. The radii of the particles were selected sequentially using the following algorithm. For the given particle, the "nearest" particle was determined such that the distance l_{nb} of its center from the center of a given particle was the minimum possible. If the radius r_{nb} "nearest" was already determined in the previous steps, then the next particle was assigned a radius equal to $l_{\mathrm{nb}} - r_{\mathrm{nb}}$. Otherwise, the next particle was assigned a radius equal to half l_{nb}. Since the density of the particle material in [3] is the same, the relative distribution of mass density does not depend on the absolute density value. In the future, it will be assumed that this value is also equal to 1.

4. METHOD APPLICATION RESULTS

To illustrate the informativeness of the proposed testing method, Fig. 1 shows the graphs of the distribution of mass density for the model system $5 \cdot 10^4$ rigid spherical particles with a density of 1. Figure 2a shows the combined distributions for ten instances of the system, which show the degree of uncertainty of the mass density value in the ensemble of systems.
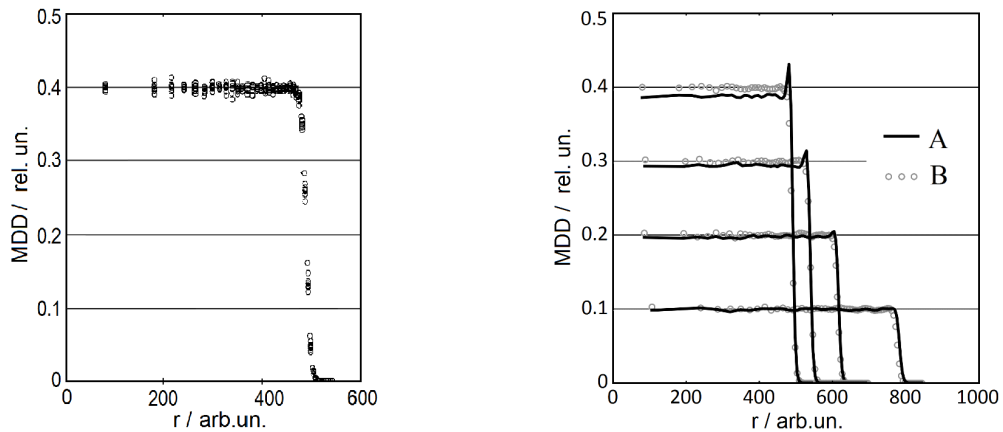
(a) for ten instances of the system using the B generation method and the volume fraction of the volume $\Phi = 0.4$

(b) averaged across ten instances of the system for two generation methods (A and B) and values of $\Phi = 0.1, 0.2, 0.3, 0.4$

Figure 2. The results of the MaDiS program for model systems $5 \cdot 10^4$ solid spherical particles with a density of 1. Mass density distribution (MDD) in relation to distance r to the center of the system

The graphs in Fig. 2b show the difference in the mass density distributions for the two generation methods described above and for a different volume fill rate. These graphs are obtained by averaging the graphs calculated by the MaDiS program for ten separate model systems for each Φ value and each of the generation methods. This averaging smooths out random density fluctuations and emphasizes the essential properties of the generated system. From the graphs of Fig. 2b it is clearly seen that for $\Phi = 0.3, 0.4$ and generation method A, the average density inside the system differs less from the expected value, and a density spike occurs at the system boundary. With the generation method B, both defects are absent.
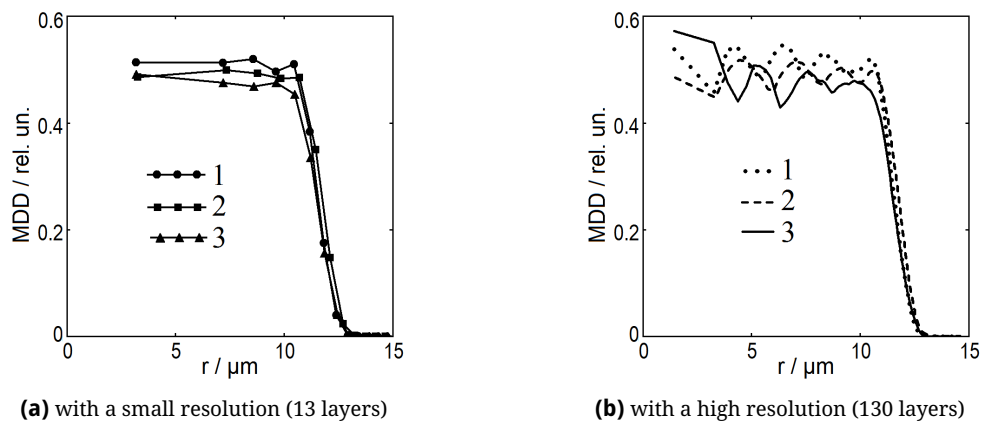

(a) with a small resolution (13 layers)

(b) with a high resolution (130 layers)

Figure 3. The results of the MaDiS program for the actual system: The distribution of mass density inside spherical regions cut from the system of particles [3], r — distance from the center of the cut-out area: 1 — the area near the system boundary; 2 — the intermediate area; 3 — the area near the center of the system

Testing the effectiveness of the proposed method for the actual system (see Fig. 3) was carried out as follows: From the general array of particles from [3], located in a parallelepiped measuring 492 µm × 513 µm × 28 µm, three subsystems of particles were cut, the centers of which fall into spherical regions with a diameter of 23 µm. The first region was located close to the boundaries of the system, with the center coordinates (23.5 µm, 23.5 µm, 11.7 µm), the second — in some

intermediate position with the center coordinates (70 μm, 70 μm, 11.7 μm), the third — near the center of the system with the center coordinates (250 μm, 250 μm, 11.7 μm).

Figure 3a (low density mass distribution) shows that as the observation focus shifts toward the center of the system, the average mass density inside the cut out area (the first three points) decreases. The density distribution in the same areas constructed with a high resolution (Fig. 3b) has clearly visible maxima, 4 μm ... 11 μm. Moreover, the abscissae of the density maxima in this range (the conditional radii of the coordination spheres) increase when the observation area is shifted to the center of the entire system. The decrease in mass density to zero at $L \geq 11$ μm is due to the out-flow of the cut-out area. The graphs in Fig. 3 show that the particle system in [3] becomes less dense when it moves from the boundaries to the center of the filled volume.

5. TECHNICAL IMPLEMENTATION

The MaDiS program is implemented in C# language [9] based on the .NET Framework 4.7.2 [10] using the WPF system [11] for building the user interface, as well as the *Helixtoolkit* libraries [12] for building the 3D model of the nanoparticle system, and *oxyplot* [13] to display 2d graphs of additional metrics (particle size distribution function). The calculations were implemented using the Mathnet library [14].

In addition, a script was developed in Python 3.4 [15], using the scipy [16], numpy [17], and matplotlib [18] libraries.

Both the program and the script accept data on the Cartesian coordinates, radii, and particle densities in matrix format as a set of columns: x, y, z, r, ρ. If there is no density column, the densities are assumed to be equal to one.

The results of the work of both programs are a text file with the calculated values of the mass density distribution function and a file with a graph of the function. The source code of the programs is available at the GitHub [19].

6. CONCLUSION

A method for characterizing systems of spherical particles with an arbitrary distribution of centers, radii, and densities has been developed. The method is based on calculating the distribution of average mass density in concentric spherical layers in the vicinity of a given arbitrary center. The effectiveness of the method was tested on variants of model polydisperse systems with a value of the volume filling fraction $\Phi = 0.1, 0.2, 0.3, 0.4$ obtained in two different ways. The mass density distribution allows you to detect defects in one of the generation methods. For the system obtained by the field modeling method, the presence of periodicity in the mass distribution, as well as a de-crease in the density of the system when the center of observation is shifted from the edge of the system to its center, is demonstrated.

There are many methods for producing model systems of spherical particles [6, 20–24]. The developed method for calculating the radial distribution of the scattering mass (electron density) will be useful for studying the properties and structure of such systems. Thus, for instance, the mass distribution homogeneity has a strong influence on SAXS-intensity when calculated for model systems generated with the method described in [4] and a given value of Φ. It is obvious that the density spike at the system boundary and the discrepancy between the expected and actual values of the average density inside the system, detected for one of the generation methods (see Fig. 2b), lead to a distortion of the calculated intensity. In work [3] it is presumed that the experimentally prepared system is homogeneous can be considered to be mostly homogeneous. However, as is shown above, when shifting from the edge to the center of the system a decrease in the average mass density distribution can be observed.

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Функция распределения плотности массы — инструмент для анализа систем сферических частиц

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Аннотация

Разработан метод характеристики систем сферических частиц, основанный на расчете распределения средней плотности массы в концентрических сферических слоях, окружающих произвольный центр. Эффективность метода проверена на нескольких вариантах моделей полидисперсных систем, полученных двумя разными способами, и на одной системе, полученной натурным моделированием. Распределение массовой плотности для обоих способов построения модельных систем позволяет выбрать лучший вариант. Для системы, полученной методом моделирования поля, показано различие свойств в зависимости от положения центра наблюдения. В данной статье представлена программа MaDiS, реализующая разработанный метод.

Ключевые слова: *характеристики системы сферических частиц, распределение плотности массы, программа для анализа полидисперсных систем, методы генерации системы сферических частиц.*

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