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Model of Random Spatial Packing of Rigid Spheres with Controlled Macroscopic Homogenity

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Abstract: It has been shown that in particulate filled composites, a cross-property relationship exists between various transport properties (e.g., electrical conductivity, mechanical reinforcement, gas permeation) of a macroscale composite. Thus, knowledge of the effective mechanical properties of a composite immediately places bounds on its electrical conductivity or gas permeation behavior. Using these bounds allows us to predict the phase dispersion state that optimizes one or multiple properties of the composite and, thus, the knowledge of how spatial arrangement of filler particles at their given content affects physical properties of the composite can be valuable. In this paper, a new numerical model is presented capable of generating 3D random spatial distribution of rigid monodisperse spherical particles. The optimal number of particles inside a reference sphere and the macroscopically homogenous distribution of particles were the two main aspects investigated. The proposed model can be used to calculate inter particle distance, to predict particle agglomeration and, finally, to predict macroscopic properties of particulate composites. This can be of great interest, especially, when considering effects clustering or self-assembly of nanoparticles have on the properties of polymer nanocomposites.

Keywords: particle, composite, sphere, inclusion, Monte Carlo, distribution.

1 Introduction

It was suggested [Hyun and Torquato (2001); Torquato, Hyun, and Donev (2002); Torquato, Hyun, and Donev (2003); Bansal, Yang, Li, Cho, Benicewicz, Kumar, and Schadler (2005)], that there exist cross-property bounds between different transport properties (e.g., electrical conductivity, mechanical reinforcement, gas permeation) of a macroscale composite. Thus, knowledge of the effective mechanical properties of a composite immediately places bounds on its electrical conductivity or gas permeation behavior. Using these bounds allows us to predict the phase

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dispersion state that optimizes one or multiple properties of the composite. Thus, if one "phase", say *A*, of a binary composite is both mechanically reinforcing and electrically conducting (while the other, *B* phase, is not), then the macroscale mechanical and/or electrical conductivity is optimized if the *A* phase is percolating. In contrast, if only the *A* phase were mechanically reinforcing, while only the *B* phase were conducting, then, either property is optimized if the appropriate phase is percolating. However, to simultaneously optimize both the electrical and mechanical properties of the composite requires that the two "phases" are connected in a triply periodic fashion, i.e., both are simultaneously percolating. This immediately suggests that optimizing one *vs.* two properties of a composite can require very different morphologies. While this idea is new and unproven in the field of nanocomposites, it suggests that the creation of multifunctional composites requires exquisite control over nanoparticle spatial distribution [Wu, Hultman, O'Brien, and Koberstein (2008); Bansal, Yang, Li, Benicewicz, Kumar, and Schadler (2006); Harton and Kumar (2008); Akcora, Liu, Kumar, Moll, Li, Benicewicz, Schadler, Acehin, Panagiotopoulos, Pryamitsyn, Ganesan, Ilavsky, Thiyagarajan, Colby, and Douglas (2009); Tuteja, Duxbury, and Mackay (2007)]. Such understanding, which is currently only at a nascent stage, is crucial to the end use of these materials in a variety of ubiquitous contexts, e.g., in strong, flame retardant fabrics; mechanically sound gas and water purification membranes; and high refractive but transparent polymers which are wear resistant. Making such connections between nanoparticle dispersion and organization with macroscale properties is then a crucial aspect that is only now beginning to be considered.

This paper describes a basic model for generation of random set of spherical heterogeneities in a box of continuous second phase. The mathematical model can be built as a representation of different kinds of two-phase systems. The model was originally built for the composites where the continuous phase is a polymer matrix and spherical inclusions are some filler particles. But it can represent different examples of similar systems (for example foams where the continuum is a polymer material and the gas bubbles are spherical inclusions). Its application is not limited only to solid state science; it can be used also as a model of different types of suspensions, emulsions or aerosols.

Study of problems, which are related to presence of heterogeneous particles in continuum, has several levels. It can be demonstrated basic difference in the systems with particles ordered to crystalline-like lattice and systems where the particles are distributed irregularly and in an extreme case randomly. It was detected that even the random distribution shows variation of density and leads to formation of agglomerates. Nevertheless, the formation of agglomerates is observed in real heterogeneous particle structures and their study is a key factor for understanding of

structure properties relations and prediction of them. For example the influence of agglomeration is different in the case of nanocomposites and in the case of microcomposites. The agglomeration in nanocomposites decreases the stiffness of nanocomposites [Chen, Justice, Schaefer, and Baur (2008); Wang and Pyrz (2004) Part I; Wang and Pyrz (2004) Part II; Termonia Y 1994; Kashani and Padovan (2007)], agglomeration in microcomposites increases stiffness of them. The modulus is only one example of properties depending on agglomeration because the agglomeration can influence for example viscoelastic properties [Heinrich and Klüppel (2002)], light diffraction [Yanagioka and Frank (2008)] or electrical properties [Wu, Lin, Zheng, and Zhang (2006)].

The aim of this work, that is supposed to be our initial study of the problematic of heterogeneous systems, is application of the substantially improved procedure [Tovmasjan, Topolkarev, Berlin, Zhurablev, and Enikolopjan (1986)] to the building of a model of randomly distributed spheres, and filling the space with given volume fraction, where an analysis of space distribution and correction of macroscopic distribution was newly introduced.

2 Methods and model

The proposed model generates a finite set of particles of defined spheres that are randomly distributed in a given space having some prescribed volume fraction. In this section we introduce partly a basic idea of proposed model [Tovmasjan, Topolkarev, Berlin, Zhurablev, and Enikolopjan (1986)] and some information which seems to be necessary for justification of generated set of particles and which is necessary for correction of original model. The model of randomly distributed particles is limited by the situation when particles are ordered into the crystallographic lattice of the highest volume package φ_{max}.

2.1 Binomial and hypergeometric distribution

The binomial distribution gives the discrete probability distribution to obtain exactly successes out of trials, where the result of a trial is true with probability p and false with probability (1-p) [Mason, Gunst, and Hess (2003)]. The probability distribution function of cases when the number n of successful trials realized in the whole set of N trials is given by the equation:

$$P_p(n|N) = \binom{N}{n} p^n (1-p)^{N-n} \tag{1}$$

Frequently CDF, the cumulative distribution function $F_p(n|N)$, is defined:

$$F_p(n|N) = \sum_{i=0}^{n} \binom{N}{i} p^i (1-p)^{N-i} \tag{2}$$

where $n \leq N$.

The random distribution of particles leads to definition of the task based on binomial distribution. The limiting condition is that the volume fraction of particles is very low or their radii are very small, respectively. It could be considered some situation when N particles are randomly spaced in volume V_0 and the particles are only points. Then the binomial distribution exactly describes the probability of founding exactly n particles in selected sub volume $V \leq V_0$ that is given by an expression derived from binomial distribution.

$$P_p(n|N) = \binom{N}{n} \left(\frac{V}{V_0}\right)^n \left(1 - \frac{V}{V_0}\right)^{(N-n)} \tag{3}$$

In the case, when the volume fraction of N particles is not negligible, the situation is more complicated and it is possible to describe it with certain approximation. The approximation can be derived by the aid of hypergeometric distribution function. Generally, this distribution gives a probability of the realization of k selections of "success element" in n trials taken from the set of N elements where within the N elements is a part of M elements marked as (+ $\sim$ success) and complementary number $(N-M)$ elements is marked as (- $\sim$ fails).

The probability of such situation is:

$$P_p(k,M,n|N) = \frac{\binom{M}{k}\binom{N-M}{n-k}}{\binom{N}{n}} \tag{4}$$

The condition max(0,n-$(N-M)$) < k < min(M,n) has to be fulfilled, otherwise $P_p(k,M,n|N) = 0$.

Specifically in the case of particle set in a continuous phase the following mask to the discretization of volume should be applied. M spherical particles (marked as +) occupy in the reference space V_0 a volume V_S that constitutes a filling with volume fraction $\varphi = V_S/V_0$. The maximal number of equivalent particles, which can be placed into V_0, is equal:

$$N = M\frac{V_0}{V_S}\varphi_{\max} = M\frac{\varphi_{\max}}{\varphi}, \tag{5}$$

where φ_{max} is a volume fraction corresponding to closest packing of spheres (*see Section* 2.2). In other words, it is a finite number of N positions, which are at disposal in V_0. When the volume V, as a part of the space V_0, is investigated there are

$$n = M\frac{V}{V_s}\varphi_{\max} \tag{6}$$

disposal positions. The probability that in V can be find exactly k spheres is given by above stated relation (4). We remind that the volume fraction of spheres in V, where exactly k spheres were found, is equal to:

$$\varphi_K = \frac{k}{M}\frac{V_0}{V}\varphi \tag{7}$$

i.e. when $k/M = V/V_0$ then $\varphi_k = \varphi$ what is the average volume fraction of spheres in V_0.

It is must be also accented that the *Eqs. 5-7* do not give generally integer numbers, whereas the function of hypergeometric distribution (*Eq. 4*) requires integer numbers as input variables. Therefore, for the calculation of the distribution function, a specific definition function was applied.

$$x! = \Gamma(x+1) \tag{8}$$

where Γ is the gamma-function, which is from definition extension of factorials to the real or complex numbers.

2.2 Ordered Lattices

The original models of heterogeneous systems were based on ordered lattices. The closest packing is observed in two cases: the face-centered cubic lattice of spheres, hexagonal close spaced lattice. Both the lattices have the highest packing density equals to 0.7405 volume fraction. Topology, particle coordinates, volume fraction and interparticle surface-to-surface distances are well known and for some simple cases, often used in composites studies, are given in *Tab. 1*:

In reality the particles are not ordered into ideally packing geometry. The lower is the volume fraction the more particles are distributed randomly. With increasing volume fraction their random positions are more and more transformed to an ordered geometry up to the closest one. That means that at very low volume fractions the distribution of particles in a given volume can be described by the binomial distribution function and when the volume fraction is higher, that implies some interparticle interactions, more ordered situation, described by hypergeometric distribution, should be considered. The very high volume fractions lead to creation of ordered domains.

Table 1: Examples of often used model cubic lattices for calculation of the particle composite properties; a-length of cube side; d-particle diameter

Lattice type	**Num.of particles per unit a^3**	**Distance of closest particles 1. Centers 2. Surfaces**	**Volume Fraction**	**Max volume fraction**
Cubic	1	1. a 2. $a-d$	$\frac{\pi}{6}\left(\frac{d}{a}\right)^3$	0.524
Body Centered Cubic (BCC)	2	1. $a\frac{\sqrt{3}}{2}$, 2. $a\frac{\sqrt{3}}{2}$ - d	$\frac{\pi}{3}\left(\frac{d}{a}\right)^3$	0.680
Face Centered Cubic (FCC)	4	1. $a\frac{\sqrt{2}}{2}$, 2. $a\frac{\sqrt{2}}{2}$ - d	$\frac{2\pi}{3}\left(\frac{d}{a}\right)^3$	0.740

2.3 Radial distribution function

An appropriate function for description of space distribution of points or spheres is the radial distribution function (RDF). The value of RDF is the density $\rho_{points}(R)$ of point particles in arbitrary selected sphere of given coordinates center and radius R:

$$\rho_{\text{points}}(R) = \frac{N_p(R_i \leq R)}{V_S(R)}, \tag{9}$$

where $V_S \subset V_0$ is a volume of sphere with radius R surrounding the selected central point of RDF, N_p is number of particles in distance equal or and lower than R from the central point of RDF. ρ is used as a synonym of RDF in all equations and formulas. It is because RDF as a name of function can be easily confused with a power of some variables R•D•F.

RDF is constructed as a link between the model with finite number of particles and real systems with number of particles approaching infinity. For infinite, homogeneous and isotropic system the RDF must be independent on selected central point and converges to the average density of the system. The convergence is realized in an envelope given by the binomial distribution. The homogeneity and isotropy of a model system can be checked in the same way. It is necessary to show that the RDF of such system is center-independent and the deviation from mean density is

based on binomial distribution, too.

It is advantageous to define "relative RDF" (rRDF) related to the model mean points density because it is independent on volume fraction of particles. The synonym of rRDF - ρ_{rel} was used in equations again. The rRDF is defined by the following equation:

$$\rho_{\text{points,rel}}(R) = \frac{N_p(R_i \leq R)}{V_S(R)} \cdot \frac{V_0}{N}. \tag{10}$$

The situation with non-zero volume particles is slightly different, the RDF, or rRDF respectively, is defined for analysis of distribution of particles in a studied sphere. It is related to the average density of particles what is a volume of all particles related to volume of the sphere V_0. Function rRDF in case of non-zero volume particles is:

$$\rho_{rel}(R) = \frac{N_p(R_i \leq R) \cdot V_p}{V_S(R) \cdot \varphi}, \tag{11}$$

where V_p is volume of one particle and φ is the average volume fraction of the model.

For checking of the macroscopic homogeneity of our models were the limit envelope curves calculated for 95% reliability applied. The envelope curves were derived for the given reliability from binomial distribution (that means that 95% of random particle generations will generate RDF inside the interval delimited by envelope curves) or similarly from hypergeometric distribution for finite particle volume.

2.4 Modeling of composite structure

The main idea of the modeling was proposed by Tovmasjan [Tovmasjan, Topolkarev, Berlin, Zhurablev, and Enikolopjan (1986)]. The first step was a generation of given number of randomly distributed particle centers in a given sphere space. Two next operations were then performed. First, it was an inflation of particles. The inflation of particles led to an increase of the particles volume. It was simply possible at low volume fractions. When the volume fraction grew the intersections of particles occurred. The second operation then consisted in an elimination of particle intersections. The procedure was progressing from the center of the sphere to its boundary. In the case that the intersecting particles were detected, the outer particle (of greater distance R to the center of the sphere) was pushed out by the inner particle. The pushing was performed in the direction of a vector given by central points of both particles until the intersection was eliminated. However, the pushing out of one particle can lead to intersections with other particles not realized before pushing out of this particle. Hence, the procedure had to be repeated

until all the intersections are eliminated. The model was applied to the organization of structure of aluminum oxide composite in polypropylene [Topolkarev, Tovmasjan, Dubnikova, Petrosjan, Meshkova, Berlin, Gomza, and Shilov, (1987)]. The effect of Al_2O_3particle size and its volume fraction was investigated. The organization of particles was depended on the volume fraction and the agglomeration was found. Relation between structure and mechanical properties of composites was interpreted. The influence of agglomeration on creep and failure properties [Michler, Tovmasyan, Topolkaraev, Dubnikova, and Shmidt (1988)] was analyzed.

2.5 Random Mersenne twister

One aspect of successful model constitution is the quality of random generation of many numbers. Using of basic random generators, implemented for example in common programming languages, lead to slight inhomogeneity of a random number generation. The results derived from such non-random model can be disrupted and the effect of the random generator can be misinterpreted as a result of the inherent model property.

A pseudorandom number generator generally is an algorithm for generating a sequence of numbers that approximates the properties of random numbers. The sequence depends on a seed state which depends on time when the seed was generated. Therefore, each run of software in different series will produce unique sequence of random numbers. An example of well worked pseudo random number generator is a Mersenne Twister [Matsumoto and Nishimura (1998)] that was used in our present work. The new and more commonly used version of the Mersenne Twister MT19937 with 32-bit word length was applied.

3 Results and Discussion

The aim of the work was to generate a random system of particles in a reference sphere when the volume fraction of particles is prescribed. The solution must fulfill following conditions:

- The particles dispersion must provide the prescribed volume fraction in a predefined volume element (sphere, cubic box) of the composite
- The particles must not intersect each other
- The macroscopic distribution of particles must be homogenous
- The particles are taken in this paper to have uniform size (radii) and density. (Further versions of models will enable user-defined size distributions of particles.)

The set of particles was generated by in house software based on above described Tovmasjan approach [Tovmasjan, Topolkarev, Berlin, Zhurablev, and Enikolopjan (1986)]. In this paper a set of spherical particles placed in a reference sphere is always considered. Variable R in majuscules always marks a distance of the mentioned point from the center of the reference sphere. In most cases, the center of main rRDF is aligned with the center of the model. Rarely, the center of rRDF is placed in an arbitrary point (x,y,z) of the model and the distance is marked $R_{x,y,z}$.

3.1 Generation of randomly distributed particles

The generation of random distribution of points was tested for compliance with binomial distribution (the test of Mersenne twister). Random situated points were generated in unite cubic box. The sets of thousand independent generations of the same number of points were performed. Each set of generation consisted of 1, 5, 10, 50, 100, 500, 1000, 5000, 10000, 50000 points, respectively. Each generated box of points was divided into 2, 4, 8, 16, 32, 64, 128 equivolume layers. The distribution of points number in the layers should correspond to the binomial function that can be taken as an evidence of random numerical distribution. It was proved (*Fig. 1*) that the used random generation of particles is in compliance with the theoretical model.

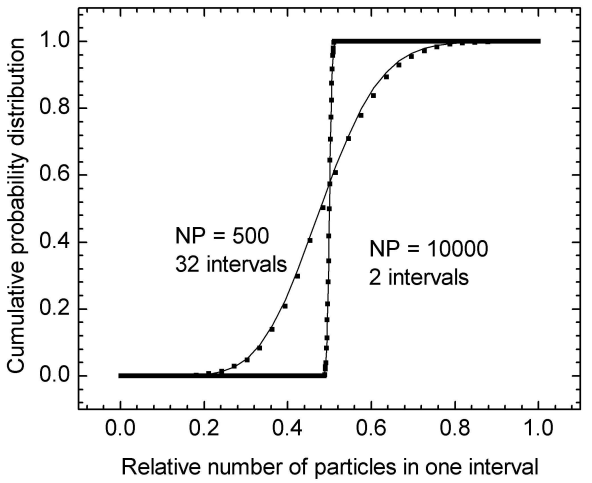

Figure 1: Cumulative probability distribution of total set of particles into sub-set of particles. x axis is a number of particles in subset related to maximum number of particles in subset; y-axis is a probability that x particles and less is present in interval. (□) - distribution as an output from random number generator; lines-analytical form of binomial distribution.

The binomial distribution function can also be applied to calculation of the optimal number of points. That is the crucial input value of our model. Low number of particles causes low reliability of the model and, on the other hand, high number of particles leads to an extreme consumption of the computer time. The criterion for optimum number of particles was defined in our case as follows. If it is considered a generation of N particles in the reference volume V_0 then the number of particles found in the volume $0.5 \cdot V_0$ with the probability of 95 % will be grater than N_{min} and less than N_{max}. And it is demanded to use such N for that the relative difference $(N_{max} - N_{min})/N$ (precision) is less than 2 % (± 1 %). The dependence of this value is given in *Tab. 2*. It was concluded that our condition is fulfilled for $N \geq 10000$ and then the number of particles taken into account in our model will be at least of 10000.

Table 2: Precision of random generation as a function of number of generated particles; N - number of all generated particles, N_{min}, N_{max} borders of tolerance interval with 95% reliability from binomial distribution.

N	N_{min}	N_{max}	**Precision**
10	2	8	0.600
100	40	60	0.200
1000	469	531	0.062
10000	4900	5100	0.020
100000	49700	50300	0.006
1000000	499000	501000	0.002
10000000	5000000	5000000	0.000

3.2 Model of particle distribution

The model whose properties are further described and investigated is built by following way. A unite cube was taken as a basic geometry. A sphere of unity diameter was inscribed into the basic box. Very small random particles (radius 10^{-6}, volume fraction $\varphi = 2.5 \cdot 10^{-4}$) were generated into the cube by the aid of Mersenne Random generator. Only the particles inside the inscribed sphere were taken as a relevant. Each generation ran until inside the sphere was required number of particles (N = 10000, see *Section 3.1*). The test of spheres intersection was then performed. If an intersection of particles was detected the generation was canceled and repeated. If the intersection was not detected the inflation procedure could be applied (see *Section 2.4*).

3.3 Borders of radial distribution fuction

The borders of the radial distribution function were calculated for two cases. The first case is the simple binomial distribution that can be applied for very small particles. There is supposed the purely random distribution. The second case is for particles when their volume cannot be neglected. Then the hypergeometric distribution is to be applied instead of binomial. As it was stated above all particles are placed in the reference sphere (radius R_{ref}). Inside the reference sphere a concentric sphere (radius $R \leq R_{ref}$) can be defined. The rRDF can be calculated as a function of R and it is possible to draw the borders between the 95 % of rRDF(R), calculated for randomly distributed particles, lie (see *Fig. 2*).

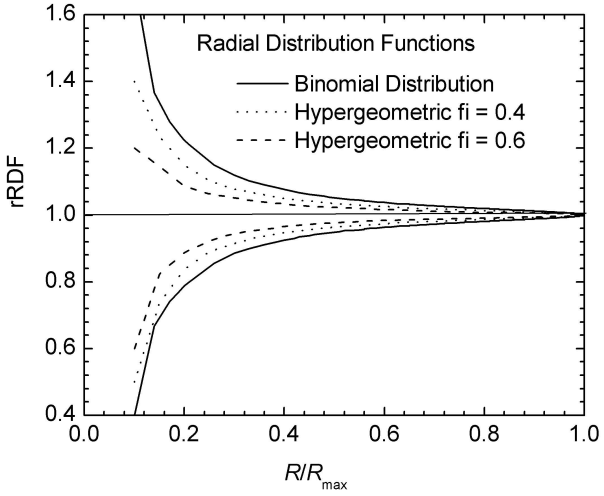

Figure 2: Borders of rRDF for 10000 particles and 95% probability level. Random distributed particles (Binomial and Hypergeometric distributions); Constant function rRDF = 1.0 is macroscopically homogenous rRDF; black solid - border curves for binomial distribution; dotted and dashed - border curves for hypergeometric distributions for different volume fractions of particles.

3.4 Filling of referencece sphere by particles with given volume fraction

A set of 10000 very small uniform particles according to the *Section 3.2* was generated. The generation was repeated 5 times. The rRDF was calculated and compared to limits given for binomial distribution (*Fig. 3*). The position of rRDF is used for checking the macroscopic homogeneity of the particle distribution and it is seen that all generations lie into the defined interval.

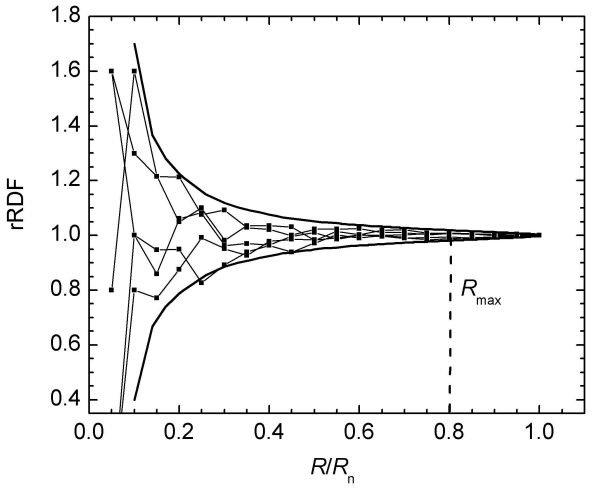

Figure 3: Relative Radial Distribution Functions (rRDFs) of randomly generated set of 10000 very small spherical particles; Thin lines + symbols 5 rRDFs calculated from the 5 sets of particles. Thick solid line - envelope function calculated analytically from binomial distribution; dashed - calculation of R_{max}.

The distortion is observed in the case of substantially inflated particles. At first the value of R_{ref} is lost and instead of this the value of R_n (the distance of the farthest particle of the set) is used. Secondly a problem of some surface effect was recognized after the inflation procedure. It is demonstrated at the example of rRDF computed for five particle sets inflated to the volume fraction 0.1 (*Fig. 4*). During the inflation procedure a big number of particle collisions were registered, it is generally strongly dependent on the required volume fraction of particles (see *Tab. 3*).

As a logical consequence of collisions the surface of system is surely not an ideal sphere (there can be slight cavities and hills at the surface) and some drop of rRDF

Table 3: Number of collisions N_c occurring in particle generation until reaching given volume fraction φ.

φ	0.001	0.002	0.005	0.01	0.02
N_c	71	160	374	797	10822
φ	0.05	0.1	0.2	0.3	-
N_c	46442	107470	269358	521681	-

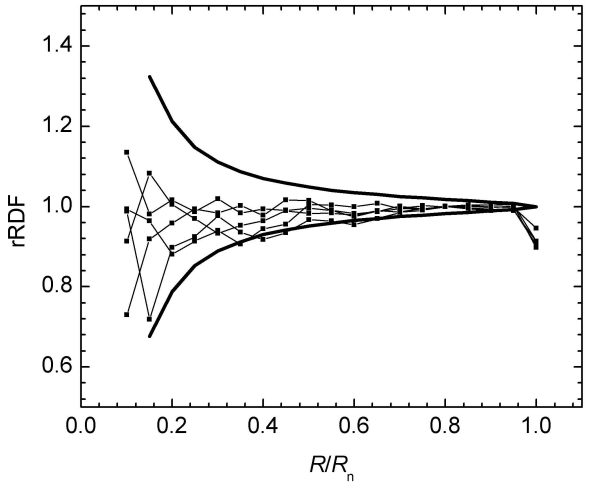

Figure 4: Relative Radial Distribution Functions (rRDFs) of spherical particles inflated to volume fraction 0.1; Thin lines + symbols 5 rRDFs calculated from the 5 sets of particles. Thick solid line - envelope function calculated analytically from hypergeometric distribution.

for R approaching R_n was registered.

Therefore the maximum limit R_{max} should be considered. From the course of rRDF can be seen that the value $R_{max} = 0.9 \cdot R_n$ is sufficiently correct to reach the homogenous space. However, because the model must show good functionality and safe results, we consider $R_{max} = 0.8 \cdot R_n$ as an optimal solution. Such sphere represents 0.51 volume of the original sphere. Hence, it contains approximately a set of 5100 valid particles from the set of 10000 initial particles.

Similarly the value of R_{min} was defined from the envelope of RDF. It is a radius when the rRDF is calculated with deviation $\pm$ 5% from central value. Under R_{min}, the rRDF has high deviation and it could lead to misinterpretation of macroscopic homogeneity.

The positions of rRDF functions were compared to the borders of corresponding hypergeometric distribution (*Fig. 4*). It is possible to conclude that they are inside of them and they can be considered as well randomly placed population of particles.

The third problem occurred when the volume fraction of particles became relative high. The number of collisions (*Tab. 3*) rapidly increased and the predominantly tangential directions with relatively only small radial shift of particle pushing outs

lead to an inappropriate shape of increase of rRDF (see *Fig. 5*). Therefore some correction procedure is necessary to apply. It is derived in following *Section 3.5*.

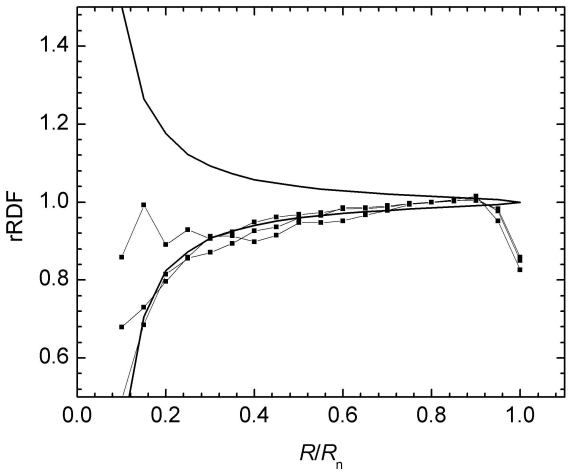

Figure 5: Relative Radial Distribution Functions (rRDFs) of spherical particles inflated to volume fraction 0.3; Thin lines + symbols three rRDFs calculated from the three sets of particles. Thick solid line - envelope function calculated analytically from hypergeometric distribution.

3.5 Correction procedure

The inappropriate increase of density can occur in the radial direction during the inflation procedure (see *Section 3.4*) and a correction function must be found. The idea of the correction procedure is to find an appropriate function of (R/R_n) for an increase of particle distances from the center of the sphere to receive homogenous density. The actual density $\rho_A(R)$ of particles is a density of particles in the shell between radii R and R+dR. The volume of the shell is $4\pi R^2 \mathrm{d}R$. The cumulative density corresponding to the rRDF can be defined:

$$\rho(R) = \frac{3}{4\pi R^3} \int_0^R 4\pi x^2 \rho_A(x)\, dx. \tag{12}$$

Then:

$$\rho_A(R) = \rho(R) + \frac{R}{3} \frac{d\rho(R)}{dR}. \tag{13}$$

The actual density was prerequisite to calculation of correction function $q(R)$. When the function is applied, arbitrary particle (i) with distance R_i from center of the system shifts to new position with distance $R_{f,i}$ from the center of system:

$$R_{\mathrm{f,i}} = R_{\mathrm{i}} \cdot q\,(R_{\mathrm{i}}) \tag{14}$$

The correction is realized by shift of layer boundaries. The mass of particles in the layer must be equal before and after the shift:

$$4\pi\rho_A\,(R)\,R^2 dR = 4\pi\rho_0 R_f^2 dR_f \tag{15}$$

where $\rho_0 = \rho(R_{min})$ is the desired homogenous density calculated in these step as the mean density inside R_{min}.

Substituting *Eqs.* (14) and (15) to (13) the equation for correction function can be derived:

$$q^3\,(R) \;+\; R\,q^2\,(R)\;q'\,(R) = \frac{\rho_A\,(R)}{\rho_0}. \tag{16}$$

This equation can be numerically solved by fourth order Runge Kutta method [Teukolsky, Vetterling, and Flannery (1992)] (*see Appendix B*).

The correction procedure was applied when the difference $[\rho(R_{max}) - \rho R_{min})]$ was greater than $0.05{\cdot}\rho(R_{min})$. It was applied to the particles in the interval $<R_{min}, R_n>$. When the $R \leq R_{min}$ the correction function $q(R) = 1$. The result of the calculation of $q(R)$ for rRDF dependence in *Fig. 5* is shown in *Fig. 6*.

And the example of the rRDF change before and after correction is shown in *Fig. 7*. It was noticed that after the described correction the volume fraction of particles in the whole system $\rho(R_{max})$ is changed and of course is decreased. Hence the particles should be inflated again to reach the final desired volume fraction. Thus, repeated series of inflations and corrections will lead to the homogenously filled space.

3.6 Some properties of final homogenously filled space by random set of particles

Five homogeneously filled spheres with uniform particles were built by repeated cycles inflation and correction. The positions of particles at volume fractions of ϕ = 0.01, 0.02, 0.05, 0.10, 0.20 and 0.30 were recorded. The corresponding rRDF functions were calculated, some examples are presented in *Figs. 3, 4 and 8.*

The homogeneity of some final set of particles can be tested by a modified calculation of rRDF. It is presumed that in the case of homogenous systems, the rRDF

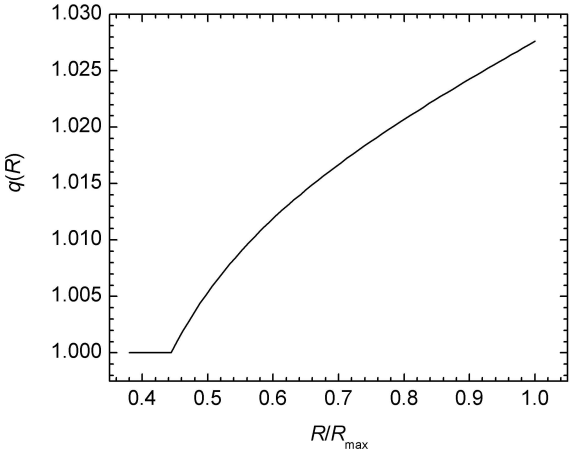

Figure 6: Correction function. Particle coordinates of all particles in interval $< R_{min}, R_n >$ are to be multiplied by the functional value of q.

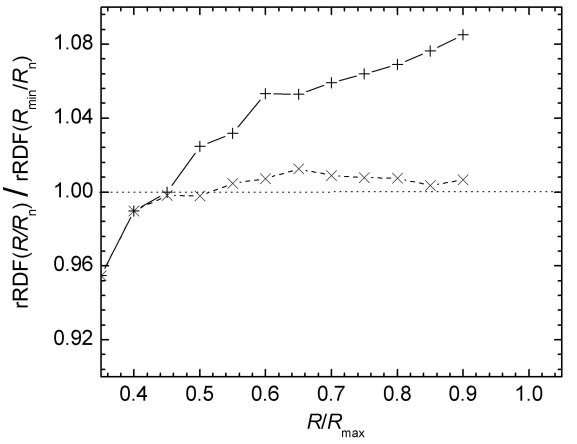

Figure 7: Relative Radial Distribution Function (rRDF) normalized to the value RDF (R_{min}/R_n) for volume fraction 0.3, Solid line, + symbols are example of RDF before correction; dashed line, x symbols: RDF after correction.

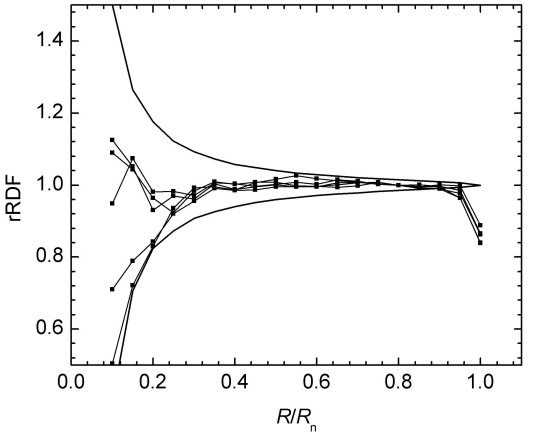

Figure 8: Relative Radial Distribution Functions (rRDFs) of spherical particles inflated to volume fraction 0.3, when the correction procedure is applied; Thin lines, + symbols: five rRDFs calculated from the five sets of particles. Thick solid line: envelope function calculated analytically from hypergeometric distribution.

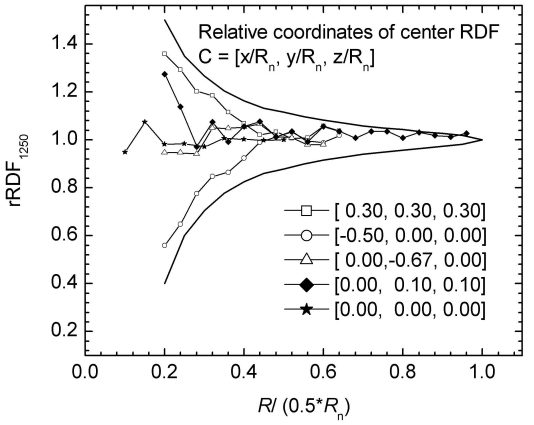

Figure 9: Testing of representativeness of different selections from one set of particles with volume fraction 0.3. Thin lines + symbols: 5 rRDFs of different sets selected from one set of 10000 central particles with center C in 5 different points in the system. Thick solid line - envelope function calculated analytically from hypergeometric distribution for 1250 particles.

functions are independent on the choice of RDF center. Until now it was presumed that the center of RDF and the center of the reference sphere were identical. The RDF having the center in a arbitrary deep point C in the reference sphere should be the same course. It was proved for the cases mentioned above and an example is presented in *Fig. 9*.

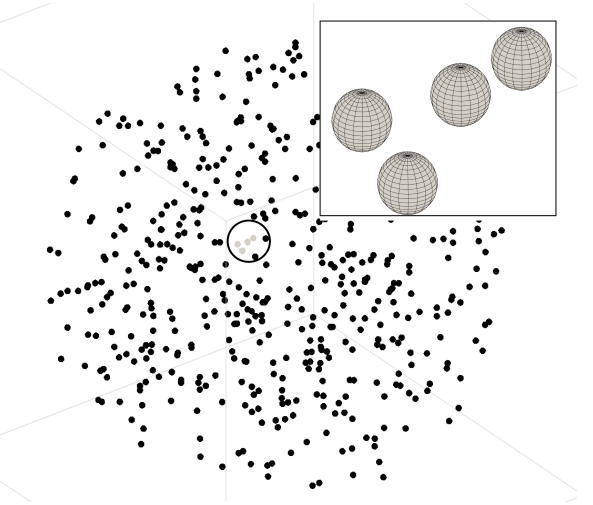

Figure 10: Randomly generated particles occupying 1% volume of spherical space; (Selected 500 particles from 10000 particle set).

Two examples of filled spheres of radius R_{max} are presented in 3D projection in *Figs. 10 and 11*. The first sphere is filled with the volume fraction 1% the second one up to the volume fraction 30%. A small selected part is enlarged to demonstrate more clear the density of the space filling.

4 Conclusions

The space distribution of spherical inclusions is frequently discussed problem. It can be applied to a prediction of properties of selected heterogeneous systems for example to the prediction of stiffness of polymer composites or for prediction of some viscoelastic properties of them. The Tovmasjan approach, based on random distribution, inflation and self-organization, was a starting point of the model presented here. The model described in this paper contains statistically significant set of particles for analysis of particles distribution. Thus, the resulting set is suitable for performing statistical processing of the result. When some large volume fraction of particles was approached, the original Tovmasjan model showed an inho-

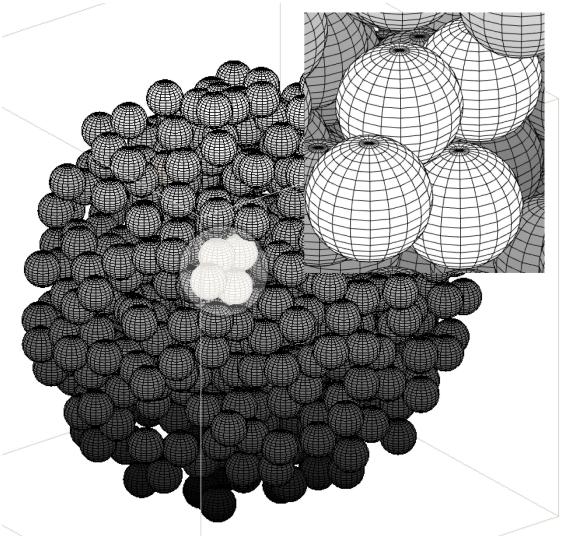

Figure 11: Randomly generated particles occupying 30 volume percent of spherical space; (500 particles selected from10000 particle set).

mogeneous mass distribution. Therefore some correction step was proposed in this paper. After application of this step, the mass distribution got homogenous. The particle coordinates and radii of statistically significant sets of particles were calculated. Such sets of particles can serve for a calculation of interparticle distances distribution or an agglomerate detection.

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Appendix A List of symbols

Lower case

a	Length of cube side in ordered lattices
d	Particle diameter
k	Number of successful trials from selection of n trials
m	Number of successful trials in the set of N all trials
n	Number of selected trials from the set N of all trials
n	Number of particles in a set
p	Probability of successful trial (presence particle in the selected volume V_s)
q	Correction function of particle homogenity

Upper case

F	Cumulative analytical probability distribution function of$P$
N	Number of trials of finding particle in selected volume V_s
N	Number of all particles
N_{min}	Minimum number of particles inside interval RDF
N_{max}	Maximum number of particles inside interval RDF
N_P	Number of particles inside interval RDF
N_c	Number of collisions
P	Analytical probability distribution function
R	Distance from center of RDF
R	General distance of arbitrary point from mass center of particles;
R_i	Distance of ith particle center
R_0, R_n	The nearest and farthest particle from the center of mass
R_{min}, R_{max}	Interval where the central RDF was considered reliable
$R_{x,y,z}$	Distance in the RDF whose center is not aligned with model center
RDF	Numerical value of radial distribution function
rRDF	RDF related to the macroscopic value of RDF
V	Volume
V_0	Volume of all particles set
V_s	Arbitrary volume selected inside volume of all particles model

Greek symbols

φ	Volume fraction of arbitrary subset, selected from main set
φ_{max}	Volume fraction corresponding to closest package volume
φ_P	Volume fraction of particles in the set
ρ	Symbol for RDF used in equations, where the using RDF could be confusing
Γ	Gamma function

Appendix B Runge Kutta method of Ordinary Differential Equations solutions

The method of homogenization is described in the *Section 3.5*. For the solution a method for ordinary differential equations (ODE) is necessary. The solution of ODE leads to the fourth order Runge Kutta ODE solution. A Runge Kutta is a method for the approximation of solutions of ordinary differential equations (ODE). A method was designed to solution of *Eq. 16* in form:

$$y' = f(t,\, y(t)\,) \tag{B1}$$

with boundary condition:

$$y(t_0) = y_0 \tag{B2}$$

where y_0 is a given numerical value. It is a constant which should be set as a parameter of the system.

The Fourth-order Runge-Kutta method is based on four estimations of tangents of functions in interval h. The t_n is variable in beginning of interval and t_n +h is a variable at the end of interval. One estimation of tangent function is in initial point (k_1) two in mid-points of interval (k_2 and k_3) and fourth in end point (k_4). The calculation of functions is given by a set of recurrent equations:

$$k_1 = f(t_n,\ y_n) \tag{B3}$$

$$k_2 = f(t_n + h/2,\ y_n + hk_1/2) \tag{B4}$$

$$k_3 = f(t_n + h/2,\ y_n + hk_2/2) \tag{B5}$$

$$k_4 = f(t_n + h,\ y_n + hk_2) \tag{B6}$$

The tangents are applied to estimation of slope. The result is calculated by recurrent function:

$$y_{n+1} = y(t_n + h) = y(t_n) + h(k_1 + 2k_2 + 2k_3 + k_4) \tag{B7}$$