Delaunay simplex analysis of the structure of equal sized sphere packings

A.V. Anikeenko and N.N. Medvedev
Institute of Chemical Kinetics and Combustion SB RAS, Russia

T. Di Matteo, G.W. Delaney, and T. Aste
The Australian National University, Australia

Abstract

Delaunay simplexes decompositions of equal sphere packings obtained both experimentally and by numerical simulations are investigated in order to understand the origin of the Bernal's limiting density of 64% in volume faction associated with the densest non-crystalline phase (random close packing limit). We show that the fraction of 'quasi-perfect tetrahedra' grows with the packing fraction up to a saturation fraction of $\sim 1/3$ reached at the Bernal's limit. Aggregate 'polytetrahedral' structures, made of quasi-perfect tetrahedra which share a common triangular face, reveal a clear sharp transition occurring at the density 0.646. These results are consistent with previous findings [13] concerning numerical investigations only.

I. INTRODUCTION

Sphere packings have been used for centuries to model natural structures both at the atomic level and at macroscopic level [1]. One of the main quests in these studies is to understand the nature of the transition between disordered and ordered-crystalline packings. It is known that for the densest packing of equal spheres, the fraction of volume occupied by the balls with respect to the total volume (packing fraction or density) is equal to $\frac{\rho}{\sqrt{18}} \approx 0.74$ [1]. Such maximal density can be realized in infinitely many ways, with two common examples being the face centered cubic lattice (fcc) and the hexagonal closed packed structure (hcp). All the maximally-dense packings are based on stacking close-packed 2-dimensional hexagonal layers of spheres. After the first and the second layers (a) and (b), there are two possibilities for the relative location of the third layer: it can be placed with the spheres in vertical correspondence with the ones of the first layer (a) or in an other position (c) that differs both from (a) and (b). A layered structure with maximal density can be built by stacking such layers in positions a, b or c with the only restriction that repetitions of two consecutive 'letters' (aa, bb, cc) must be avoided. The class of such maximally dense layered packings are known as Barlow packings; named after the mid 19th Century scientist who

explored several possible stackings of spheres in an attempt to explain the atomic origin of crystal shapes. In terms of this 'alphabet' the hcp and fcc structures are the two simplest sequences being respectively: hcp = ababab... and fcc = abcabcabc... . They are the most common crystalline structures in atomic systems, like heavy metals, solid noble gases, and they are also commonly observed in colloids. However, these systems can also have non-crystalline phases. These are in general metastable states, and the atomic system will eventually relax into the crystalline phase, which is more stable from the thermodynamic point of view. On the other hand, particles of non-microscopic sizes (a-thermal systems with typical sizes above 50 μm, called under the general name of 'granular materials') reveal a strong tendency to avoid crystallization despite the fact that this is the most favorable state. To describe the nature of such non-crystalline packings and to understand the mechanisms that prevent crystallization is one of the major challenges in present days research on packings and granular materials. Empirical studies [1–6] show that such packings can be produced at different packing fractions in the rather broad range between the two limiting packing fractions 0.55 (called random loose packing) and 0.64 (called random close packing). The fact that non-crystalline packings of equal spheres cannot be packed tighter than the limiting density of 0.64 was observed by J.D. Bernal in his experiments with steel balls [10]. The microscopic origin of such bounding packing fractions is still unexplained. It is surprising that we still lack of a clear understanding of the structure of this disordered phase despite the relevance of non-crystalline packing problems to a broad range of applied and fundamental issues of scientific importance. Indeed, disorder is hard to classify as an equivalent to the 'order parameter' associated with the structural properties is hard to identify. In disordered packings, each configuration is different from the others and the overall structure is an assembly made up of a very large number of different configurations that precisely match together as in a sort of jigsaw puzzle with a unique solution. On the other hand, these disordered packing are not completely random. Indeed, they present a very large number of repetitions: local configurations with very similar properties are found all over the packing, but such local 'motifs' are not identical and they are not positioned regularly. In these systems, traditional methods such as pair correlation function or the structure factor fail to give a clear characterization of the three-dimensional structural organization. Indeed, these are essentially one-dimensional measures that quantify the occurrence of characteristic lengths. Conversely, to study these three-dimensional structures we must identify the three-dimensional 'motifs' in the atomic arrangements. To achieve this we employ a description of the packing based on Delaunay simplexes. These simplexes are unambiguously and uniquely defined for any (regular or disordered) set of points in space. They define configurations of quadruples of 'atoms', and they are the simplest elements to which a three-dimensional packing can be reduced. Delaunay simplexes represent a mosaic covered space of a sample,

FIG. 1: Simplexes typical for dense packings of hard spheres: (a) perfect tetrahedron, it has T=0, $d_t = 0$, $\delta = 0$; (b) an example of 'a boundary' tetrahedral shape, T 0.018, $d_t \sim d_q$, $\delta \sim 0.25$; (c) perfect quartoctahedron (a quarter of octahedron), one edge is $\sqrt{2}$ longer than the others, $T = 0.05$, $d_q = 0$, $d_t = 0.179$, $\delta = 0.41$, see text.

so if we select simplexes with a given structural substance, the clusters of such simplexes give a design on the mosaic to reveal a structural motif [11, 12].

Recently Delaunay simplexes were applied in studying the structure of a large set of hard sphere packings at different densities [13]. The paper considered the structure in terms of the content of the tetrahedral units (Delaunay simplexes of tetrahedral shape) and their local arrangements. Using a tetrahedrality criterion, derived from that used in Hales' recent solution of the Kepler conjecture, it was observed that the volume fraction occupied by the tetrahedra increased with increasing density of the overall packing up to the Bernal limit. At this stage it was observed that the volume fraction occupied by clusters of tetrahedra (polytetrahedra) passes through a sharp maximum while the fraction of spheres involved in tetrahedra saturates. Position of this maximum was estimated at 0.646. In this work we discuss in some further detail such transition by comparing the numerical data with experimental observation. We confirm the polytetrahedral structure of disordered packings and we retrieve the drastic behavior of the clusters of tetrahedra at the limiting density. We demonstrate that the structure of packings in physical experiments is very similar to the structure observed in ideal hard spheres packings.

Delaunay simplexes

The first step in the quest for a structural characterization is to identify local configurations and quantify their similarities and occurrence. There exists a general approach, used in geometry, which allows us to unambiguously select the closest quadruples for an arbitrary system of discrete points. Such an approach is the Voronoi - Delaunay tessellation (decomposition), well known both in physics [14] and mathematics [15]. This method exploits an evident geometrical fact that for each point in a set of points embedded in a given metric space it is always possible to distinguish the portion of space closest to such a point with respect to any other point in the set. This region is called the Voronoi polyhedron (cell, region) and the space-partition built from the assembly of all Voronoi cells is called the Voronoi tessellation or Voronoi diagram [15]. For any Voronoi tessellation, there exists a dual tessellation called the Delaunay tessellation, which consists of Delaunay simplexes (irregular tetrahedra, in the general case) whose vertices are the quadruples of closest points in the set. The names of these constructions derive from the mathematicians that posed the mathematical foundations of the methods: G.F. Voronoi (1868-1908) explored in detail the properties of these tessellations by using analytical methods for lattice systems; whereas B.N. Delaunay (1890-1980) proved the correctness of Voronoi's main theorems for points positioned at random in space [16–18].

Shape characterization of simplexes

In order to characterize the packing structure we first need to build a simple instrument to measure quantitatively the shape of each simplex. Several approaches have been suggested to characterize the proximity of a simplex to a perfect tetrahedron [11, 19–22]. In this paper we will discuss three different methods that embrace a significant range of possibilities.

Edge differences, T-measure

Let us start with a rather old and simple method in which the irregularity of the tetrahedron is quantified by summing over the average square of the simplex edge length differences [11]

$$T = \frac{1}{15\bar{l}^2} \sum_{i<j} (l_i - l_j)^2 \tag{1}$$

where l_i, l_j are the lengths of the simplex edges, and $\bar{l}$ is the mean edge length. In a perfect tetrahedron all edges have equal length and T is equal to zero. More generally, small values of T correspond to simplexes which are close to a perfect tetrahedron. Conversely, large values of T indicate significant deviations from regularity. We now want to identify

a bound on the value of T which differentiates between a class of tetrahedra that are regular enough and therefore can be considered 'quasi-perfect tetrahedra'. In Refs. [12, 23] this measure was calibrated using the models of a fcc crystal at different temperatures (at different degrees of perturbation). It is known that this crystal structure (as any Barlow packing) can be reduced to a tiling with elementary tiles made of two perfect tetrahedra and one octahedron. At finite temperatures they are distorted, but as long as the crystal structure is retained the two main classes of Delaunay simplexes, tetrahedra and quartoctahedra (quarters of octahedra), are present (see Fig. 1). As a boundary value which identifies simplexes that are closer to perfect tetrahedra we choose $T_b = 0.018$; a value which divides the two classes of simplexes in the calibrating models. This can be compared to studies with a more physical viewpoint (see Refs. [12, 23]), where the Delaunay simplexes, whose shape varies within the limits $0 \leq T \leq T_b$, are associated to the tetrahedral configurations of atoms in heated fcc crystal.

Procrustean distance, d-measure

From the perspective of mathematical shape theory [24, 25], the proximity of an arbitrary simplex to a given reference shape is estimated by the degree of coincidence upon their superposition. To this end, the total mean square deviation d^2 between the corresponding vertices of the optimally superimposed simplexes can be calculated. The magnitude d is called the Procrustean distance between the two simplexes. Let $\{x_1, x_2, x_3, x_4\}$ and $\{y_1, y_2, y_3, y_4\}$ be the coordinates of the vertices of two simplexes. The square of Procrustes distance between such simplexes is:

$$d^2 = \min_{\mathbf{R},\mathbf{t},P} \left\{ \frac{1}{4} \sum_{i=1}^{4} ||y_i - (\mathbf{R}\mathbf{x_i} + \mathbf{t})||^{\mathbf{2}} \right\}, \tag{2}$$

where the minimum is calculated over all three-dimensional rotations $\mathbf{R}$, the translations $\mathbf{t}$, and all possible mappings between vertices of simplexes P. The measure d allows us to compare a simplex to any reference shape. For instance, it is possible to calculate the distance from a given simplex to both the perfect tetrahedron d_t and to perfect quartoctahedron d_q. According to this classification, a simplex can be considered as a 'quasi-perfect tetrahedron' if its Procrustean distance to a perfect tetrahedron is less than its distance to a perfect quartoctahedron, i.e. if the following condition is satisfied

$$d_t < d_q. \tag{3}$$

For a given correspondence (mapping) between vertices, it is possible to calculate analytically the Procrustean distance and there are several algorithms to solve such least squares problems. For instance, one of the most efficient methods is based on computing the

singular value decomposition of the derived matrix (see Ref. [26] for details). Note that the Procrustean distances are a mathematically well defined distance measure, i.e. distance between equivalent simplexes is equal to zero, and the distance measured from simplex 1 to simplex 2 is the same as from 2 to 1. Thus the simplex with perfect tetrahedral shape has $d_t = 0$, and the distance between perfect tetrahedron and quartoctahedron is equal to 0.17936 [21].

Maximal edge length, δ-measure

A very simple but effective way to determine how close an irregular simplex is to a perfect tetrahedron consists of calculating the length of the maximal edge e_{max}. This method of selecting tetrahedral simplexes was used by Hales in his proof of the Kepler conjecture [22]. This approach seems especially suitable for identical hard spheres of unit diameters, where the minimal possible length of the simplex edge is 1. In this case, a value of e_{max} close to 1, unequivocally indicates that all edges are close to 1 and therefore the simplex is close to a regular tetrahedron. A convenient measure of the simplex shape is therefore the difference between the lengths of the maximal and the minimal edges: $\delta = e_{max} - 1$ [13]. Small values of δ unambiguously indicate that the shape of the simplex is close to a perfect tetrahedron, while large values correspond to substantially distorted shapes. In the proof of the Kepler conjecture, Hales chose the maximal edge length 1.255 as the upper boundary for 'quasi-perfect tetrahedra'. In our notation this corresponds to $\delta = 0.255$. It is important to remark that the δ-measure is strictly related to the two previous measures. One can verify that for dense packings of hard spheres all these measures pick practically the same tetrahedral simplexes. For disordered packing at density 0.64 we estimated that the conditions $T < 0.018$ and $\delta < 0.255$ select the same simplexes with an overlap of 95%, and the coincidence rate increases with the onset of crystallization. Thus each of the measures reliably picks tetrahedra with shapes close to perfection. Some ambiguity is observed only for simplexes with boundary shapes, which are not critical for our analysis.

II. MODELS

Computer simulations of sphere packings

We study a large series of hard sphere packings with packing densities ranging from 0.53 to 0.71. Each packing contains 10000 hard spheres of equal radii in a box with periodic boundary conditions. The majority of the packings (more than 200) were obtained using a modified Jodrey-Torey algorithm that employs "repulsion" of overlapping spheres with gradual reduction of their radii [27–29]. The initial configuration is a set of identical spheres uniformly distributed in the box. Overlapping of spheres is permitted at this stage. The

algorithm attempts to reduce overlaps between spheres by shifting overlapping spheres and gradually shrinking of the radii. This is continued until all overlaps vanish. This algorithm can easily produce not only disordered packings with densities up to the limiting value, but also more dense systems containing crystalline structures. It can lead easily to packings of a density of around 0.66. For higher densities, the result of an earlier run is used as a starting configuration, where the diameters are enlarged. This procedure can be repeated several times. In order to test the independence of structure on the algorithms used for packing generation we also computed a series of packings (about 70) in the range of densities from 0.54 to 0.67 by using the Lubachevsky-Stillenger algorithm [30]. This algorithm employs a different procedure for densification of the packing: Newtonian dynamics of perfectly elastic hard spheres with gradually increasing radii. The initial configuration of spheres in this case is also random, however no sphere overlaps are permitted. A principal parameter of this algorithm is the growth rate for sphere radii. Small values of growth rates will result in crystallization as it is well-known for "physical" simulations of hard spheres [31, 32]. To avoid crystallization the growth rate should be rather large, forcing the packing into "jammed" non-crystalline structures [33].

Physical experiments with sphere packings

We tested the numerical results over a set of 6 experiments from a database of sphere packings obtained by X-ray Computed Tomography of large samples of disorderly packed mono-sized spheres. The experimental technique and some results were presented in detail in [6–8]. These studies are the largest and the most accurate empirical analysis of disordered packings ever performed. At present, the entire database collects the coordinates (with precision better than 1% of the sphere diameters) of more than three million spheres from 18 samples of monosized acrylic and glass spheres prepared in air and in fluidized beds. The sample densities range from 0.56 to 0.64. In this work we will refer to sample A, B, C, D, E and F which are made of acrylic beads in air [6–8]. The geometrical investigation of the packing structure was performed over a central region at 4 sphere-diameters away from the sample boundaries.

III. RESULTS

Fraction of quasi-perfect tetrahedra

For each packing from our set of models and experiments we calculate all the Delaunay simplexes and selected the quasi-perfect tetrahedra shapes. Fig. 2 shows how the fraction of such tetrahedra depends on the packing density. One can verify that the general behaviors are comparable for all three measures of shape described above. Only the Procrustean

FIG. 2: Fraction of Delaunay simplexes with tetrahedral shape as a function of packing density. Different curves correspond to different methods for selecting tetrahedra. From top to bottom: $d_t < d_q$, $\delta < 0.255$, $T < 0.018$. Large symbols corresponds to experiments (for simplification of the picture, only two methods are shown: $d_t < d_q$ and $\delta < 0.255$). Vertical line marks the limiting density $\eta = 0.646$. Horizontal line marks the value of 1/3 that corresponds to the fraction of tetrahedra in the densest crystals.

distance ($d_t < d_q$) tends to overestimate the fraction of tetrahedra at low densities. Indeed, this criterion can pick rather distorted simplexes that are far away from perfect tetrahedron, but are even farther from perfect quartoctahedron. Note each point on a curve represents an independent packing. The good coincidence of points at similar densities illustrates the representativeness of our computer models and highlights the agreement between experimental and numerical results.

The fraction of tetrahedra rapidly grows with increasing density, reaching about 30% when approaching the critical value $\rho \sim 0.646$. Interestingly, further increase in density has little effect on the fraction of tetrahedra. Note that the fraction of quasi-perfect tetrahedra at $\rho \sim 0.646$ is close to 1/3, which corresponds to the fraction of perfect tetrahedra in the Barlow packings. Such a coincidence of the fraction of quasi-perfect tetrahedra with the ones in the densest crystalline structure deserves special attention, as this can shed light on the physical meaning of the class of quasi-regular tetrahedra. However the problem is not simple: the question is what is the maximum fraction of tetrahedra which can be present in dense disordered packing of equal spheres. It seems reasonable to conjecture that the fraction of 1/3 is an upper bound. However, a recent work [9] seems to suggest that disordered tetrahedral packings might reach larger fractions. Note also the body centered cubic (bcc) crystal consists of Delaunay simplexes which are all quasi-regular tetrahedra

according to our criteria ($T_{bcc} = 0.011, \delta_{bcc} = 0.15$). The fraction of tetrahedra depends also on softness of spheres. For instance, LennardJones glasses can contain up to 40% of tetrahedrons of the concerned quality.

Fraction of polytetrahedral aggregates

We have established that in disordered packings of equal sized spheres there is a rather large fraction of quasi-perfect tetrahedra which increases during densification and reaches a plateau around 30% when the limiting density is overcome. We now want to understand how these quasi-perfect tetrahedra can aggregate in more complex structures. We consider clusters built from three or more face-adjacent quasi-perfect tetrahedra and we call such structures polytetrahedra [13, 35]. Isolated tetrahedra and pairs of tetrahedra (bipyramids) are omitted as they are found in fcc and hcp structures. We can associate a graph to such polytetrahedra aggregates. In such a graph a vertex represents the centre of a quasi-perfect tetrahedron and a segment between two vertices is inserted when two quasi-perfect tetrahedra are sharing a face. Fig. 3 shows some of these graphs for local sphere packings configurations. In general, such graphs have the form of branching chains and five-edges cycles which combine in various "animals" [12, 35]. Mathematically speaking such a presentation of clusters of the selected Delaunay simplexes is called site coloring on the Voronoi network. Indeed, because of the duality of the Delaunay and Voronoi tessellations, the center of any Delaunay simplex is a vertex of the Voronoi network, and a common segment is a Voronoi edge connecting the neighboring vertexes [11, 14].

For disordered packings at low density a rapid growth is observed. Upon approaching the Bernal's critical density, the fraction of polytetrahedral aggregates also account for about 30% of all Delaunay simplexes (Fig.4). However, after the critical density the fraction of the tetrahedra belonging to polytetrahedral aggregates sharply decreases. This is a consequence of the formation of crystalline nuclei.

Fig. 4 clearly demonstrates the polytetrahedral nature of disordered hard sphere packings. Thus we can say the transition from a lower density to higher density packing occurs via increasing the fraction of quasi-perfect tetrahedral configuration and their coalescence into polytetrahedral aggregates. At the limiting density $\rho \sim 0.646$ the fraction of quasi-perfect tetrahedra reaches its maximum. Above this point the polytetrahedral aggregates get gradually disassembled. This is a result of changing of the densification mechanism, i.e. crystalline nuclei where only single tetrahedra and bipyramids begin to appear. A reason why the mechanism of densification can be changed was explained in [13]. At this density all spheres in the packing have been involved into the formation of tetrahedra. So a process of densification by means of formation of polytetrahedral nuclei becomes exhausted.

Fig. 5 demonstrates spatial distribution of polytetrahedral clusters inside our samples at

FIG. 3: Examples of polytetrahedral aggregates (clusters of face-adjacent tetrahedra). (a) three tetrahedra, b) a ring of five tetrahedra, c) a typical cluster for a dense disordered packing. The lower row shows the motives of the tetrahedra in clusters: the points mark the centers of tetrahedra and the lines indicate that they are adjacent through a common face. For cluster c) a skeleton of the graphs is also shown (dead ends are cut off).

FIG. 4: Fraction of tetrahedra involved in polytetrahedra as a function of the packing density. The behavior of these curves is quite different from the curves in Fig. 2.

density 0.64. For simplification of the pictures only skeletons of the clusters (see Fig.3) are shown. Thus, after elimination of lineal clusters and cutting off all dead ends of the clusters, we see mainly aggregates of five-member rings. This picture reveals a "5-symmetry nature" of the disordered packings discussed by Bernal in his work [10]. Visual analysis of these clusters

FIG. 5: Illustration of spatial distribution of the polytetrahedral clusters in packings of hard spheres at 0.64 in computer (left) and mechanical models (right). To simplify pictures only skeletons of the polytetrahedra are shown, see Fig.3. Tetrahedral simplexes are selected according the measure $T < 0.018$.

shows that they are rather irregular. Note there are no clusters like dodecahedron (twelve 5-member faces) which could correspond to icosahedral local configurations of spheres. This fact is an additional argument that "icosahedral local order" is not typical for disordered packings of identical atoms [36–38]. Note that we do not observe practically any 6-member rings, although our class of tetrahedra allow distortions of shape to organize such rings (e.g. a part of the Delaunay simplexes in the bcc structure can be arranged in such rings). In disordered packings, 6-member rings of tetrahedra seem not to be preferable.

IV. CONCLUSION

We performed shape analysis of Delaunay simplexes for dense packings of identical hard spheres in a wide range of densities. Particular attention was focused on tetrahedral configurations of spheres, which are the characteristic feature of all dense disordered packings of spherical particles. We confirm the polytetrahedral structure of disordered packings and drastic behavior of clusters of tetrahedra at Bernal's limiting density (0.646). In disordered packings the tetrahedra prefer to coalesce via their faces to form locally dense aggregates (polytetrahedra) of various morphology. The important properties of such aggregates are, on one hand, their rather high local density, and on the other hand their incompatibility with crystalline structures. (In crystal they are contacting with edges or organized in bipyramids). The fraction of polytetrahedral aggregates grows with the density of the disordered

packing. Upon reaching the limiting density all spheres of the packing become involved in construction of the tetrahedra. Any further increase in density within this "polytetrahedral" principle of packing at this point becomes impossible. To reach higher density the "crystalline" principle has to be engaged. To observe this sharp structural transition it is important that the basic tetrahedra are not perfect, i.e. not all spheres of the considered tetrahedral configurations contact each other, and the gaps between the neighboring spheres may be as large as $\delta \sim 25\%$ of the diameter of the sphere. These tetrahedra coincide with the class of quasi-perfect tetrahedra introduced by Hales. He selected tetrahedra with the help of criterion based on the maximal edge length. We also compared other measures used in selecting tetrahedra. Specifically, we used the rather old measure thetrahedrisity (summing over the average square of the simplex edge length differences) and the Procrustian distance from mathematical shape theory. All measures demonstrate similar efficiency, i.e. all of them select the same simplexes. The class of selected tetrahedra, from the physical viewpoint, is those Delaunay simplexes whose shape varies within the limits as the tetrahedral configurations in heated fcc crystal. We demonstrate that the structure of packings in experiments is very similar to the structure of ideal hard spheres with no friction. This seems to indicate that the structure of dense matter is determined first of all by impenetrability of atoms, and ultimately comes from geometric properties of the packings of non-overlapping spheres in thee-dimensional space.

Acknowledgements

This work was supported by RFFI grants no.05-03-032647, no.06_03-43028 and partly from YS INTAS no. 04-83-3865 (to A.A.). TA and TDM acknowledge the partial support by the ARC discovery project DP0450292.

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[1] T. Aste and D. Weaire, "The Pursuit of Perfect Packing", (Institute Of Physics Publishing London 2000).

[2] J. D. Bernal, A geometrical approach to the structure of liquids, Nature 183 (1959) 141-7.

[3] J. D. Bernal and J. Mason, Co-ordination of Randomly Packed Spheres, Nature 188 (1960) 910-911.

[4] G. D. Scott, Radial Distribution of Random Close Packing of Equal Spheres, Nature 194 (1962) 956-957.

[5] G. Y. Onoda and E. G. Liniger, Random loose packings of uniform spheres and the dilatancy onset, Phys. Rev. Lett. 64 (1990) 2727-2730.

[6] T. Aste, M. Saadatfar ,T.J. Senden, Geometrical structure of disordered sphere packings, Phys. Rev. E. 71 (2005) 061302 1-15.

[7] Aste, M. Saadatfar , A. Sakellariou, T.J. Senden, Investigating the Geometrical Structure of Disordered Sphere Packings Physica A 339 (2004) 16-23.

[8] T. Aste, Variations around disordered closed packings, Journal of Physics Condensed Matter 17 (2005) S2361–S2390.

[9] J. H. Conway, and S. Torquato, Packing, tiling, and covering with tetrahedra PNAS 103 (2006) 1061210617.

[10] Bernal, J.D. The Bakerian lecture, 1962.The structure of liquids. Proc. R.Soc. Lond. A280, 299-322 (1964).

[11] Medvedev, N.N., Naberukhin Yu.I. Structure of simple liquids as a percolation problem on the Voronoi network. J.Phys.A:Math.Gen. 21 L247-L252 (1988).

[12] Y. I. Naberukhin and V. P. Voloshin and N. N. Medvedev. Geometrical analysis of the structure of simple liquids: percolation approach, Molecular Physics. 73 (4) 917-936 (1991).

[13] A.V. Anikeenko, N.N. Medvedev, Polytetrahedral nature of the dense disordered packings of hard spheres. Phys.Rev.Lett. in press, 2007.

[14] N. N. Medvedev. Voronoi-Delaunay method for non-crystalline structures. SB Russian Academy of Science, Novosibirsk. 2000 (in Russian).

[15] Okabe A. Boots B., Sugihara K., Chiu, S. Spatial tessellations - concepts and applications of Voronoi diagrams, Wiley 2000.

[16] Voronoi, G. F. Nouvelles applications des parametres continus a la theorie des formes quadratiques. Deuxieme Memorie: Recherches sur les paralleloedres primitifs. J. Reine Angew. Math. vol. 134, 1908, pp. 198-287; vol.136, 1909, pp. 67-181.

[17] Delaunay, B. N. Sur la sphere vide. Proc. Math. Congr. Toronto Aug 11-16 1924. Univ. of Toronto press, Toronto, 1928, pp. 695-700.

[18] Delaunay, B.N. Sur la sph‘ere vide. A la memoire de Georges Voronoi. Izv. Akad. Nauk SSSR, Otd. Mat. i Estestv. nauk, No 7, pp. 793-800, 1934. (in Russian).

[19] Kimura M., Yonezawa F., Nature of amorphous and liquid stryctyre computer simulation and statistical geometry. J.Non-Cryst.Solids, V.61-62, p.535, 1984.

[20] R. M. Lynden-Bell and P. Debenedetti, Computational Investigation of Order, Structure, and Dynamics in Modified Water Models, J. Phys. Chem. B, 109 (14), 6527 -6534, 2005.

[21] A.V. Anikeenko, N.N. Medvedev and M.L. Gavrilova. Application of Procrustes Distance to Shape Analysis of Delaunay Simplexes. Proceedings of the 3rd International Symposium on Voronoi Diagrams in Science and Engineering 2006. Ed. B.Werner, IEEE Computer Society, 148-152, (2006).

[22] Hales, T.C. Sphere packings, I. Discrete Comput. Geom. 17, 151 (1997).

[23] Anikeenko A.V., Gavrilova M.L., Medvedev N.N. A Novel Delaunay Simplex Technique for Detection of Crystalline Nuclei in Dense Packings of Spheres. Lecture Notes in Computer Science (LNCS), 3480, 816 826 (2005).

[24] Dryden, I.L., Mardia, K., Statistical Shape Analysis. John Wiley & Sons, New York, 1998.

[25] Kendall, D.G.; Barden, D.; Carne, T.K.; Le, Huiling: Shape and shape theory, Wiley, Chichester, 1999.

[26] Umeyama S., Least-squares estimation of transformation parameters between two point patterns, IEEE Transactions on Pattern Analysis and Machine Intelligence, vol. 13, NO. 4, April 1991, pp. 378-380.

[27] Jodrey, W.S., Tory, E.M. Computer simulation of close random packing of equal spheres. Phys.Rev.A. 32, 2347-2351 (1985).

[28] Bezrukov, A., Bargiel, M. , Stoyan. D., Statistical Analysis of Simulated Random Packings of Spheres.Part. Past. Syst. Char. 19, 111-118, (2002).

[29] Lochmann, K., Anikeenko, A., Elsner, A., Medvedev, N., Stoyan, D. Statistical verification of crystallization in hard sphere packings under densification. Eur. Phys. J. B 53, 67-76 (2006).

[30] Skoge, M., Donev, A., Stillinger, F.H., Torquato, S. Packing hyperspheres in high-dimensional Euclidean spaces. Physical Review E 74, 041127 (2006).

[31] W. G. Hoover and F. H. Ree. Melting transition and communal entropy for hard spheres. J. Chem. Phys.", 49, 3609-3617 (1968).

[32] Auer, S., Frenkel, D. Numerical prediction of absolute crystallization rates in hard-sphere colloids. J.Chem.Phys. 120 (6) 3015-3029 (2004)

[33] Rintoul, M.D., Torquato, S. Hard-sphere statistics along the metastable amorphous branch. Phys.Rev.E. 58, 532-537 (1998).

[34] Torquato S., Truskett T.M., and Debenedetti P.G. Is random close packing of spheres well defined?, Phys.Rev.Lett, 84, 2064-2067 (2000).

[35] Finney, J.L., Wallace, J. Interstice correlation functions: a new, sensitive characterization of non-crystalline packed structures J.Non-Cryst.Solids. 43, 165-187 (1981).

[36] Frank, F.C., Supercooling of liquids. Proc. R. Soc. London. A215, 43-46 (1952).

[37] Spaepen, F. Five-fold symmetry in liquids. Nature 408, 781-782 (2000).

[38] Ganesh, P. and Widom, M. Signature of nearly icosahedral structures in liquid and supercooled liquid copper. Physical Review B. 74, 134205(2006).