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Observation of fivefold symmetry structures in computer models of dense packing of hard spheres

A.V. Anikeenko^a, N.N. Medvedev^{a,*}, A. Bezrukov^b, D. Stoyan^b

^a Institute of Chemical Kinetics and Combustion SB RAS, Str. Instutskaya 3, Novosibirsk 630090, Russia

^b Institut fuer Stochastik, TU Bergakademie, Freiberg, Germany

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Abstract

Structures of fivefold symmetry were obtained in computer models of dense packings of hard spheres containing crystalline regions ($\eta > 0.639$). Such structures are known to exist in small particles and thin films; however our models are specimens of a rather bulk phase (10000 spheres in a box with periodic boundary conditions). This observation indicates that the fivefold structures can also exist in real bulk systems and play a role in the process of homogeneous crystallization of simple liquids and ageing of amorphous solids. The Voronoi–Delaunay approach is used for disclosing these structures. The Delaunay simplexes are the basic geometrical elements for this analysis. Having a quantitative measure for the shape of the simplexes, one can mark (color) Voronoi sites according to a given physical criterion to reveal aggregates of atoms with a given structure. Aggregates consisting of good tetrahedral simplexes are studied in this work.

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1. Introduction

For the last 50 years, the phenomenon of fivefold symmetry has attracted the attention of physicists studying the structure of condensed matter. The intriguing issue here is that it is forbidden for space-filling crystals, while not infrequently it arises in cases without translation symmetry. The fivefold symmetry has been discussed for a long time for the case of simple liquids. Frank in 1952 proposed an icosahedral short-range order in the melt to explain the large undercoolings of pure metals [1]. This idea has been exploited till now for the structural interpretation of results of diffraction experiments in liquids [2–4]. Fivefold symmetry structures were also observed experimentally in small atomic clusters, metallic particles and thin films, see the reviews [5–7].

The direct experimental observation of such structures in bulk phases is difficult. Nevertheless, they were discovered in computer models, where tens thousands of atoms in a model box with periodic boundary conditions can be considered as a sample of bulk phase [8–10]. These structures may play a role in a mechanism of homogeneous crystallization of simple liquids as well as of ageing of amorphous solids, and therefore they should be investigated in detail. This is a nontrivial task, since traditional statistical methods for structure analysis of computer models of hard sphere packings (such as calculation of the radial distribution function, structure factor, using averaged characteristics of Voronoi polyhedra or orientation order parameters) are not sensitive enough for that purpose.

In the present paper the advanced Voronoi–Delaunay approach is used. We study the shape of the Delaunay simplexes and their mutual arrangement on the Voronoi network [9,11,12] with respect to packings of hard spheres. Such packings are good models for studying general

* Corresponding author. Tel.: +7 383 233 28 54; fax: +7 383 330 73 50.
E-mail address: nikmed@kinetics.nsc.ru (N.N. Medvedev).

principles of the structure of dense systems because their structure is determined mainly by the impenetrable core of atoms. A set of dense packings of hard spheres (with packing fraction η from 0.639 to 0.706) obtained in our earlier work [13] is investigated.

The nature of the phenomenon of fivefold symmetry has been investigated for a long time both in mechanical [14,15] and computer simulations, see e.g. [16,17]. From these studies it is known that the origin of fivefold local symmetry in dense liquids and non-crystalline packings of spheres is the occurrence of pentagonal bipyramids. Such a configuration consists of seven atoms forming a five-membered ring of 'good' tetrahedral configurations, i.e. of quadruplets of atoms the shape of which is close to a regular tetrahedron, Fig. 1(a, c). Five-membered rings arise because the dihedral angle of a regular tetrahedron (70.53°) is close to one-fifth of the round angle (72°); in addition, the tetrahedral configuration of four spherical atoms itself is the locally densest and energetically most favorable [1,14]. The difference in 1.5° between the mentioned angles is not important for non-crystalline systems, where atomic configurations are not obliged to have a rigorous shape.

In the physics of small clusters fivefold structures were studied in detail. It was shown that clusters of atoms of noble gases and metals can have an icosahedral structure demonstrating a sequence of stable structures with magic numbers (13, 29, 43, 55, 76, 147, ...) of atoms [6,7]. This means that the original idea of Frank [1] that the icosahedral local structure is more preferable in comparison with crystalline local arrangement is really justified for small clusters.

In thin films and small metal particles fivefold symmetry appears with pentagonal prisms [5–7]. The origin of these structures is also arranging five tetrahedra around a common edge. However, in this case the tetrahedral subunits of the fcc structure are organized in fivefold ring representing the pentagonal twinning. (The widely used term 'twinning' means an aggregation of crystalline units breaking translational order. In this case we have a multiple twinning, namely pentagonal twinning [5]). The crystalline subunits may contain many atoms, so the difference of the dihedral angle to one-fifth of the round angle becomes significant. However, this problem is solved by filling the gap with extra atoms, and slight deformation of the crystal structure nearby the fivefold axis [5,6]. If we deal with rather a small pentagonal structure, it is more natural to imply perfect pentagonal bipyramid as an inherent elements than fcc units. Such an ideal structure with one fivefold symmetry axis covering the all space homogeneously, was described Bagley in 1965 [18]. It can be understood as a succession of pentagonal atomic shells or be presented as a packing of alternating planes in which atoms are arranged in concentric pentagons, where the number of spheres in the pentagon edges is even in one plane and odd in the other [18]. The central part of this structure is the pile of pentagonal bipyramids, Fig. 1(f), and in each of the five sectors the crystal structure (a body centered

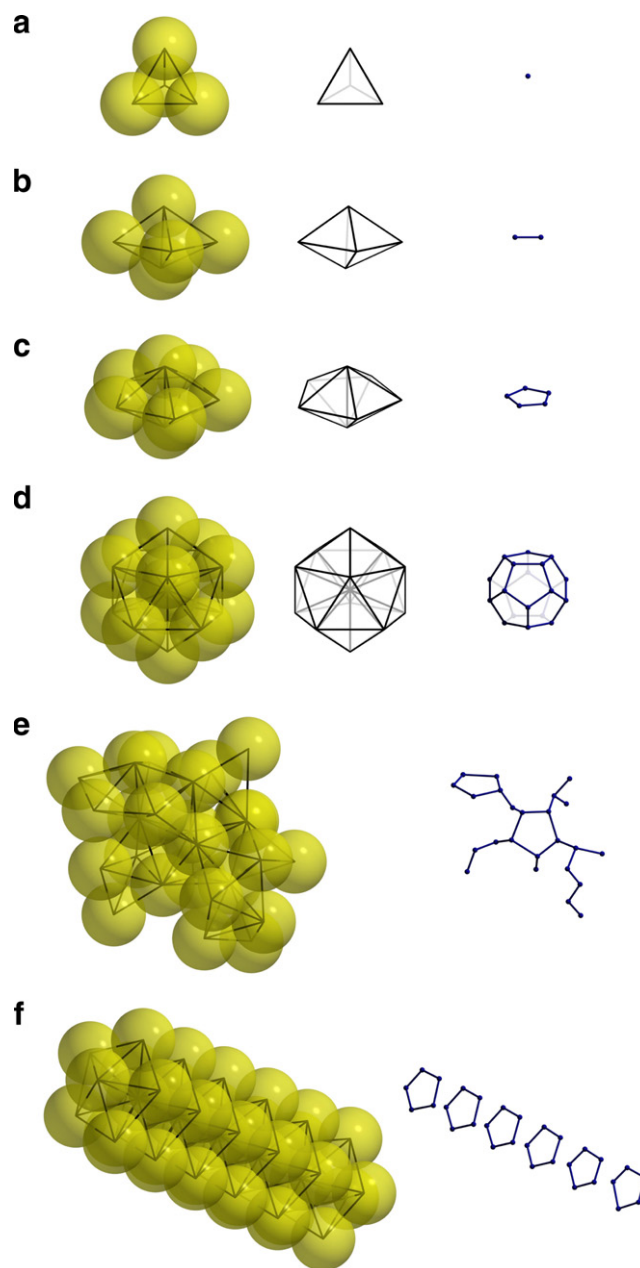


Fig. 1. Aggregates consisting of good (close to regular) tetrahedral configurations of spheres: (a) single tetrahedron, (b) trigonal bipyramid (pair of face-adjacent tetrahedra), (c) pentagonal bipyramid (decahedron, five tetrahedra organized in a ring), (d) icosahedron, (e) a complex aggregate typical for dense non-crystalline packings, see text, (f) an ordered pile of pentagonal bipyramids. On the right side of the figure the aggregates are represented according to the Voronoi–Delaunay method. Points denote centers of good tetrahedral configurations, lines connect the neighboring centers for which the tetrahedra have a common face. Consequently, an isolated tetrahedron is represented by a single point (a), a trigonal bipyramid by a short line (b), a pentagonal bipyramid by a five-member ring (c), icosahedron by a dodecahedron (d), a complex aggregate of face-connected tetrahedra by a complex cluster of lines (e), and a pile of pentagonal bipyramids by a pile of parallel five-membered rings (f).

orthorhombic cell) with density $\eta = 0.7236$ is realized. In this paper we use the Bagley structure as a reference construction for the analysis of pentagonal aggregates.

2. Models

The dense packings of hard spheres discussed below have been obtained in the paper [13] using algorithm, which belongs to the family of so-called ‘collective rearrangement’ algorithms [19–21]. It is based on the classical algorithm of Jodrey and Tory proposed in [19], but it is more efficient and able to simulate packings with arbitrary sphere diameter distributions [13]. We start with a set of spheres (10 000 in this case) of a given (rather large) radius uniformly distributed in a model box with periodic boundary conditions. Overlaps are permitted in the initial configuration. The algorithm attempts to reduce overlaps between spheres by pushing apart overlapping spheres and gradual shrinking of the radii. The choice of a ‘repulsion force’ between each pair of overlapping spheres is a nontrivial task but crucial to the efficiency of the algorithm. The paper [13] describes an expression for the calculation of the shift of overlapping spheres and gives a way in which the diameters are shrunk in the algorithm for general case of sphere of different radii. For the case of equal spheres, which is relevant for the present paper, the ‘potential function’ is chosen as simply proportional to the volume of intersection of the overlapping spheres. In every step of the algorithm the shifting and a shrinking operation are performed for all spheres until overlappings vanish. The speed of the algorithm decreases drastically with growing packing fraction. In this respect it is very difficult to get a packing with density close to ideal crystalline value 0.74. But this problem is general for all algorithms of family [19–21]. Indeed, to avoid a defect in uniform crystalline sample needs for a simultaneous rearrangement of a large amount of spheres what is unlikely event for such algorithms.

The critical value of $\eta = 0.64$ is well known in physics of liquids and glasses, and corresponds to a limiting density at which a non-crystalline (i.e. without containing any crystal nuclei) packing of hard spheres can exist [14]. Our packing at $\eta = 0.639$ just corresponds to such a system, in which we have observed aggregates of good tetrahedral configurations, which are impossible for a crystal; see Fig. 1(e) as one example. Increasing density leads inevitably to the occurrence of crystalline regions of the densest crystalline structures (f.c.c. and h.c.p.). At values of η about 0.65 there appear small isolated crystal nuclei; at values of about 0.66 there are distinct crystalline islands of different orientation (Fig. 2(a) shows a simulated packing with $\eta = 0.664$); and at values of η exceeding 0.68 a uniform crystalline structure with defects appears [10,13].

We use the Voronoi–Delaunay method, which is known in many areas of science [22] and is a powerful tool for structure investigation of atomic systems [12]. The statistical analysis of the Voronoi polyhedra is the most known approach for structure characterization. In particular, the finding of a high fraction of pentagonal faces on the Voronoi polyhedra revealed the importance of local fivefold symmetry in liquids years ago [14–16]. But here the structure investigation is based on shape analysis of the Delaunay

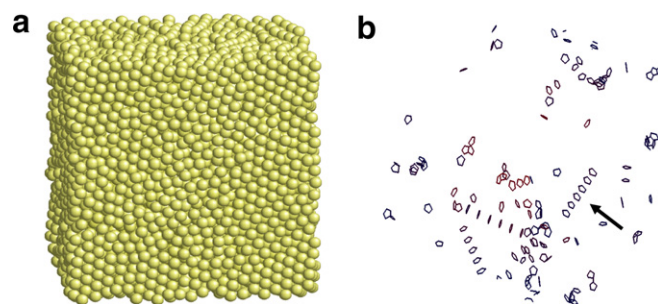


Fig. 2. A simulated dense packing of hard spheres ($\eta = 0.664$) with partial crystallization. (a) Atoms in the simulation box. (b) Clusters of good tetrahedral configurations resulting from T -coloring of the Voronoi network. Only cycles (backbones) of clusters are shown (see text). Piles of parallel five-membered rings are visible. The arrow points to a pile which is in the central part of the Bagley structure shown in Fig. 3.

unary simplex [11,12,22,23]. A Delaunay simplex is defined by the four ‘mutually-nearest’ atoms, and is a tetrahedron, in general of irregular shape. For our problem the simplexes similar to a regular tetrahedron are of particular interest. We characterize them by the shape measure T , called *tetrahedrality* [9,23], which is the variance of the lengths of edges of the simplex.

$$T = \sum_{i \neq j} (e_i - e_j)^2 / 15 \langle e \rangle^2. \quad (1)$$

Here e_i and e_j are the lengths of the i th and j th edges, and $\langle e \rangle$ is the mean edge length for a given simplex. When all T values are determined, the good tetrahedral configurations of atoms in a given packing can be found, which are defined as those Delaunay simplexes with T close to zero. In the framework of the Voronoi–Delaunay approach the location and connectivity of the simplexes are defined on the Voronoi network, in a result the spatial arrangement of distinguished Delaunay simplexes can be investigated easily. The procedure of selecting good tetrahedral configurations is called T -coloring of the Voronoi network [11,12].

At the right side of Fig. 1 aggregates of spheres consisting of Delaunay simplexes of good tetrahedral shape are shown in the spirit of the Voronoi–Delaunay method. Instead of atoms, only the centers of the corresponding Delaunay simplexes are drawn. If neighboring simplexes have a common face, the corresponding centers are joined by a line. (note that these lines are edges of the Voronoi network). An isolated tetrahedral configuration is thus represented by a point (Fig. 1(a)), a pentagonal bipyramid by a five-member ring (Fig. 1(c)), and a complex polytetrahedral configuration by a branched cluster of segments, which may contain also five-membered rings (Fig. 1(e)).

3. Results

Fig. 2(b) shows the spatial distribution the ‘backbones’ (cycles) of the T -colored clusters in the model of

$\eta = 0.664$. We selected Delaunay simplexes with values of the measure $T < 0.012$. In this case nearly one quarter of all simplexes are marked as good tetrahedra. It is difficult to draw all of them because the total number of Delaunay simplexes in the packing is over 60 000. Therefore, we kept only the backbones of these clusters to cut out ‘dead ends’ and remove linear clusters. In this way we got only about 600 good tetrahedral configurations. We are focused on piles of parallel five-membered rings in Fig. 2(b). There are three clear piles with five, six, and seven five-membered rings, and also a few shorter piles with three and two rings. In the model of density $\eta = 0.651$ a few short piles are also observed, but in the models of lower densities (disordered packings) there are no piles of pentagonal rings. Also, such piles are missing in models in which a uniform crystal is developed ($\eta \geq 0.68$).

In order to confirm that Bagley structures are present in our models we fitted the theoretical Bagley structure to the spheres surrounding the observed piles of pentagonal bipyramids. First, using the coordinates of the spheres in a pile, we estimated the optimum orientation of the fivefold axis and the mean distance between the planes forming the Bagley structure. Then we could calculate the coordinates of all sites of the theoretical Bagley structure. Having this theoretical structure we calculated the values of σ_i , i.e. the root-mean-square deviations of the sphere of the packing from the nearest site of the Bagley structure. The calculation was carried out separately for every i -th concentric shell of the Bagley structure averaged over all sites in the shell. The following values were obtained for the pile shown by the arrow in Fig. 2(b): $\sigma_0 = 0.03$, $\sigma_1 = 0.04$, $\sigma_2 = 0.05$, $\sigma_3 = 0.09$, $\sigma_4 = 0.22$, $\sigma_5 = 0.27$, $\sigma_6 = 0.37$, $\sigma_7 = 0.40$. The index 0 corresponds to the central line of spheres in the pile, index 1 to the first shell, and so on. One can see that up to the third shell the spheres of the packing are very well fitted by the sites of the theoretical Bagley structure. This structure extracted from the packing is shown in Fig. 3. Distortion becomes visible on the subsequent shells, especially at the butt-ends of the structure.

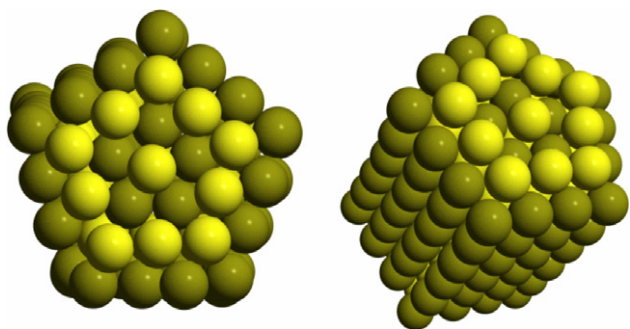


Fig. 3. Bagley structure with an axis of fivefold symmetry. The light and dark spheres belong to different planes of the structure. The central part of this structure forms a pile of pentagonal bipyramids (see Fig. 1(f)). The figure shows two different projections of the configuration taken from the packing shown in Fig. 2.

However, if the outermost pentagonal bipyramids of the pile are ignored (only five rings in the middle are used) the Bagley structure becomes clearly visible up to five concentric shells. So we can estimate that several hundred spheres belong to the Bagley structure.

4. Discussion

Analysis of the neighborhood of the other piles of five-membered rings, Fig. 2, showed that they also form Bagley structures of nearly the same quality. The piles of three and two parallel rings, which are also present in the model in a small amount, can be regarded as embryos of such structures. Note that a pair of parallel five-membered rings presents the simplest pentagonal prism (twisted icosahedron). This structure is observed in simple liquids at the beginning of crystallization [8,9], and we can also see a few of them in the densest non-crystalline phase in our model at $\eta = 0.639$.

On the contrary, we could never see icosahedra in *bulk* systems of hard spheres. In our approach they would be represented by decahedra in the Voronoi network, Fig. 1(d). We did not observe them even if we accepted tetrahedral configurations of lower quality (increasing the limiting value of T). Actually the same statement was made in the article [8], where the structure of crystallizing systems of hard spheres was studied. Using topology of the Voronoi polyhedra, only twisted icosahedra instead of the origin icosahedra were obtained in a small amount. Note that in the literature there are many papers where the authors report on icosahedra (icosahedral local order) in simple liquids, see e.g. [2–4] and references there. This contradiction has a terminological reason. We are looking for an icosahedron as a three-dimensional structure unit. Of course, it can be distorted but it should keep main features of the icosahedron. In contrary, the mentioned authors speak about icosahedra if they find any manifestation of icosahedral structure, i.e. five-membered faces on the Voronoi polyhedra, characteristic angles to neighbor atoms, characteristic pair distances or their manifestation in the structure factor. It is known that all non-crystalline packings contain many good tetrahedral configurations, but they are arranged in an irregular way. Fig. 1(f) shows a typical aggregate of face-connected tetrahedra extracted from our model with $\eta = 0.639$. Good tetrahedral configurations in liquids and glasses are arranged in various linear, branched or cyclic aggregates with five-membered rings as constituent parts. They demonstrate a rich variety of morphologies and irregular spatial distribution, at the same time all of them demonstrate a specific set of icosahedral pair distances and angles. In this respect discussing diffraction experiments data [2–4] it is more correctly to speak (following [24]) about ‘polytetrahedral’ structure of simple liquids than ‘icosahedral’.

On the other hand, recently we have demonstrated the existence of icosahedra and Mackay structures in a large volume of inhomogeneous packing of 100 000 Lennard-Jones atoms [25]. However, this model contains big pores

(up to ten atomic diameters), and regions of dense packing of atoms of the same scale. This model was made for modeling porous media, and was created by a long Monte-Carlo relaxation of the Lennard-Jones system with a given density at zero temperature. Obviously, the dense regions in that model cannot be considered as bulk structures. Rather, they should be considered as small atomic clusters because they are contiguous with the pores substantially, but the existence of icosahedral structures in small objects is a known fact [5–7,26].

The models with packing fraction $\eta > 0.68$ represent uniform crystals with numerous defects, but there are no separated nuclei independently oriented. We do not see any fivefold structure in these models.

There are different opinions about the origin of the fivefold symmetry structure in the crystallization of liquids. As it was discussed by Bagley [27], it is due to the growth of the pentagonal bipyramid, and it should not be regarded as a result of accidental crystal twinning. However, in a recent paper [8] an opposing opinion was proposed, which says that the fcc nuclei are joined through the hcp stacking fault with a ‘fivefold’ orientation and as a result the pentagonal twinning arises. We think that both of these mechanisms may work, depending on the hardness of the interatomic potential and on the density of the system. The method used in the paper [8] may miss some of the fine steps of structure reorganization, because it uses a rather complex structural unit: the atom with all of its neighbors. This is a rather rough characterization as compared with the Delaunay simplex, which contains only four atoms.

Note that in order to distinguish crystal nuclei we should use a more complex coloring of the Voronoi network. In this case we should take into account not only the good tetrahedral but also good octahedral configurations, which are typical for f.c.c. and h.c.p. crystals. More details about this procedure are given in [9,12].

5. Conclusion

The fact that we have obtained fivefold symmetry structures in dense packings of spheres suggests that they really can appear in real bulk systems. That means that they should be taken into consideration in the process of homogeneous crystallization. Additional investigations are needed to study the role of pentagonal bipyramids at the initial stage of nucleation of liquids, and pentagonal prisms (Bagley structures, pentagonal twinning) at the main stage of crystallization.

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