

A novel delaunay simplex technique for the detection of crystalline nuclei in dense packings of spheres

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The paper presents a new approach for revealing regions (nuclei) of crystalline structures in computer models of dense packings of spherical atoms using the Voronoi-Delaunay method. A Delaunay simplex, comprised of four atoms, is the simplest element of the structure. All atomic aggregates in an atomic structure consist of them. The shape of the Delaunay simplex and the shape of its neighbors are used to determine whether the Delaunay simplex belongs to a given crystalline structure. The characteristics of simplexes which define their relationship to FCC and HCP structures are studied. The possibility of using this approach for investigation of other structures is demonstrated. In particular, polytetrahedral aggregates of atoms atypical for crystals are discussed. The occurrence and growth of regions in FCC and HCP structures is studied on an example of homogeneous nucleation of a Lennard-Jones liquid. The volume fraction of these structures in the model during the process of crystallization is calculated.

Key words: Voronoi diagram, Delaunay simplex, crystallization, homogeneous nucleation.

Introduction

Investigation of structural transformations in liquid, amorphous and crystalline phases during crystallization, ageing or relaxation processes is an important problem of modern material science. A characteristic feature of such processes is the structural heterogeneity, which means that the sample may contain regions of different structures, both crystalline and disordered. It is not an easy task to investigate these structural features. While the simulation of large computer models of atomic systems is a rather routine problem, the analysis of regions of different structures requires development of special approaches. Recently, considerable progress in this direction was achieved through the utilization of the Voronoi-Delaunay method [1, 2]. An important aspect of implementation of the method is based on the Delaunay simplexes. The Delaunay simplex is described by four atoms and represents the simplest three-dimensional element (brick) of the structure. Any fragment of the structure can be presented as a cluster of Delaunay simplexes. Thus, one can determine regions of the required structure by obtaining simplexes of a given structural type [3–6]. The Delaunay simplexes can be used for more precise identification of regions of the given structure than methods based on Voronoi polyhedra [7–9], spherical harmonics [10, 11], or the

distribution of angles between geometrical neighbours [12, 13]. Voronoi polyhedra and spherical harmonics characterize the nearest environment of the atom, i.e. the structural unit that consists of large numbers of atoms (15 on average). This does not present a problem when relatively large heterogeneities are studied. However it is not suitable for studying small regions, such as nuclei (embryos) of a new phase, since characteristic features of structures are based on smaller groups of atoms. For instance, a difference between face centered cubic (FCC) and hexagonal close packing (HCP) crystalline structures is observable on groups of 6 atoms, and the main parts of an icosahedron (fragments with 5-fold symmetry) are detected on groups of 7 atoms [6].

The method based on using Delaunay simplexes cannot be applied directly. First of all, we must point out that an individual simplex, as a rule, does not characterize the structure uniquely. For example, a good tetrahedron can belong to both FCC and HCP structures, and can also be found in an amorphous phase. On the other hand, a crystalline structure is not always represented by one particular type of simplex. In practice, each mentioned crystalline structure consists of three types of Delaunay simplexes of a different shape: tetrahedron, quattoctahedron (a quarter of an octahedron), and, in a small proportion, simplexes close to a flat square. All differences between the crystals are defined by the mutual arrangement of the above types of simplexes.

In our previous investigations related to the identification of simplexes of a given shape, we have developed

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a methodology based on measures of simplex forms T , Q and K . These measures are defined as special variances (dispersions) of lengths of edges of the simplexes [5, 6, 14]. To extract regions of a given structure, we studied the arrangement of selected simplexes in the Voronoi network of the model. Clusters of such simplexes allow crystalline regions to be revealed as well as specific non-crystalline aggregates of atoms. However, the type of the structure can be established only after a cluster of the simplexes is constructed. Thus, cycles (rings) of tetrahedra and quattohedra arranged in the form of a rhombus are typical for FCC structure, and the trapezoid form is found in the HCP structure [5, 6]. Such an analysis is rather qualitative, as it demonstrates the presence of the above structures in the model of a crystal. However, an open problem is to determine the quantity of specific structures in a given sample. To address this problem, one needs a more specific, quantitative description of the simplexes to a given structure type.

In this paper, we suggest a method to characterize the relationship of the simplexes to a given structure considering the shape of both a given simplex and its neighbors. We refer to this problem as a problem of identification of a structural type of a Delaunay simplex. In the case of neighboring simplexes we propose considering simplexes with adjacent faces. The structural unit, which identifies a type of a given structure, is an aggregate of eight atoms: four atoms of a given simplex and four atoms of its faces. However, only the central simplex is used for subsequent structural analysis.

The Voronoi-Delaunay Method

Methods for the using geometrical ideas of Voronoi and Delaunay for the structural analysis of atomic systems is discussed in detail in many articles (see, for example, [3-7, 15]). A set of coordinates of all atoms of the model $\{A\}$ serves as the basic information for structural analysis of atomic models. At the first step, the Voronoi-Delaunay partitioning of the model studied is calculated. Actually, for our analysis we deal only with the Voronoi network, defined as a network of edges and vertices of a set of Voronoi polyhedra. The Voronoi network is represented by a set of coordinates of vertexes $\{D\}$ and a table of their connectivity $\{DD\}$. Every vertex of the Voronoi network is incident on four atoms of the system $\{A\}$, defining a Delaunay simplex. This means that every vertex of the Voronoi network determines the position of one of the Delaunay simplexes of the system. Using coordinates of atoms of a given simplex, one can calculate any geometrical characteristics of it (in particular measures of its shape). Next, using the connectivity of the Voronoi network, it is convenient to study their mutual arrangement, and to define clusters of simplexes with given structural characteristics [5, 16].

Simplex Shape Measures

T , Q and K measures

A choice of simplex characteristics depends on the problem being studied. In our case we study dense packings of spherical atoms. The main configuration for this study is the tetrahedral configuration of four atoms. It is the densest local configuration and is a preferable energy-wise configuration for spherical atoms. In FCC and HCP crystals there are also octahedral configurations, which together with tetrahedral configurations ensure translation symmetry of the crystal. An octahedral configuration is not a simplex, since it has six vertexes. An ideal (perfect) octahedral configuration provides an example of a degenerated configuration: all six vertices lie on a sphere. However, in a computer simulation of physical systems, atoms are typically shifted from their ideal positions. Thus, every octahedral configuration is represented through Delaunay simplexes unambiguously. Usually, there appear four similar simplexes (quattohedra [14]). A perfect quattohedron has five equal edges, and the sixth edge is $\sqrt{2}$ times longer than the five others.

However, at some specific displacements of atoms, the perfect octahedron can be divided into five instead of four simplexes. The fifth simplex springs up from the flat configuration of four atoms of octahedron. This simplex was found in the models of dense liquids and was called a simplex Kize [17]. It has two opposite edges (diagonals of a square) which are $\sqrt{2}$ times longer than the other four edges. These simplexes are rather rare, however they should also be taken into account when studying crystalline structures.

To extract a good tetrahedral configurations we use measure T , called *tetrahedrity* [6, 16]. It 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. The number 15 used as normalization factor is the number of possible pairs of six edges of the simplex. For a perfect tetrahedron, the value of T is equal to zero. A small value of T means unambiguously that the simplex is close to a perfect tetrahedron.

For the unambiguous extraction of a good quattohedron, we use the special measure Q called quattohedrisity [6, 16]:

$$Q = \left(\sum_{\substack{i < j \\ i, j \neq m}} (e_i - e_j)^2 + \sum_{i \neq m} (e_i - e_m / \sqrt{2})^2 \right) / 15 \langle e \rangle^2 \quad (2)$$

This measure is similar to the measure T , only now the computation of the variance of edge lengths takes into

account that one edge is $\sqrt{2}$ times longer than the others. To compute Q , the longest edge m of a simplex needs to be found first, and then the calculation is carried out according to equation (2). It is obvious, that for an almost perfect quattoctahedron, the value of the measure Q approaches zero. The inverse is also true. Note, the value of the measure T calculated according to equation (1) for simplexes of quattoctahedral shape is equal to 0.050. However, the same value can correspond to many simplexes of other shapes. Due to this fact, one needs to introduce a special measure for every different shape.

To extract Kizhe simplexes, a measure K was constructed following the same principle. Here we use the fact that two edges are $\sqrt{2}$ times longer than the others [6, 17]:

$$K = \left(\sum_{\substack{i < j \\ i, j \neq m, n}} (e_i - e_j)^2 + \sum_{i, j \neq m, n} (e_i - e_m / \sqrt{2})^2 + \sum_{i \neq m, n} (e_i - e_n / \sqrt{2})^2 + (e_m - e_n)^2 \right) / 15 \langle e \rangle^2 \quad (3)$$

The meaning of this expression is that when the value K approaches zero, a simplex degenerates into a square. To compute K , a pair of the longest opposite edges of the simplex needs to be found first as the edges m and n , and then the calculation is carried out according to equation (3).

Note, the equations (2) and (3) differ from formulae derived in [3, 6, 17]. In those references, every element of the expression was normalized based on the number of pairs of edges. In our work we introduce a common normalization factor equal to 15, which is the total number of different pairs. This method of normalization is not crucial for selection of simplexes with a good shape. However, below we introduce new characteristics of simplexes, for which the unified equations for measures of shape (1)-(3) are more convenient.

Calibration of the measures

In order to ascribe a Delaunay simplex to a given shape, one should indicate boundary values of measures, T_b , Q_b и K_b , i.e. to make a calibration of the measures (1)-(3). Following [16, 17], we calibrate our measures with the help of a known structure, namely an FCC crystal at a temperature below the melting point. Calibration models were generated by the Monte Carlo method, and consisted of 10000 Lennard-Jones atoms in a cube with periodic boundary conditions. Initially the atoms were settled on sites of a perfect FCC lattice, and then the model was relaxed at a given low temperature. Figure 1(a-c) demonstrate histograms for T , Q and K , calculated for all Delaunay simplexes in the model of a crystal at the temperatures of 0.32 and

0.48 (in reduced units). The peaks at small values of these variables can definitely be related to the good tetrahedra (a), quattoctahedra (b) and Kizhe simplexes (c).

Boundary values which separate simplexes with an appropriate shape from others can be chosen as locations of minima on the histograms. We have assigned:

$$T_b = 0.018, Q_b = 0.013 \text{ и } K_b = 0.007. \quad (4)$$

Thus, the simplexes having one of the measures of T , Q or K less than in (4) are of interest to our analysis of the structure. We will state that boundary values in (4) determine "a full set" of simplexes typical for a crystal structure. Indeed, all of them can be found in the model

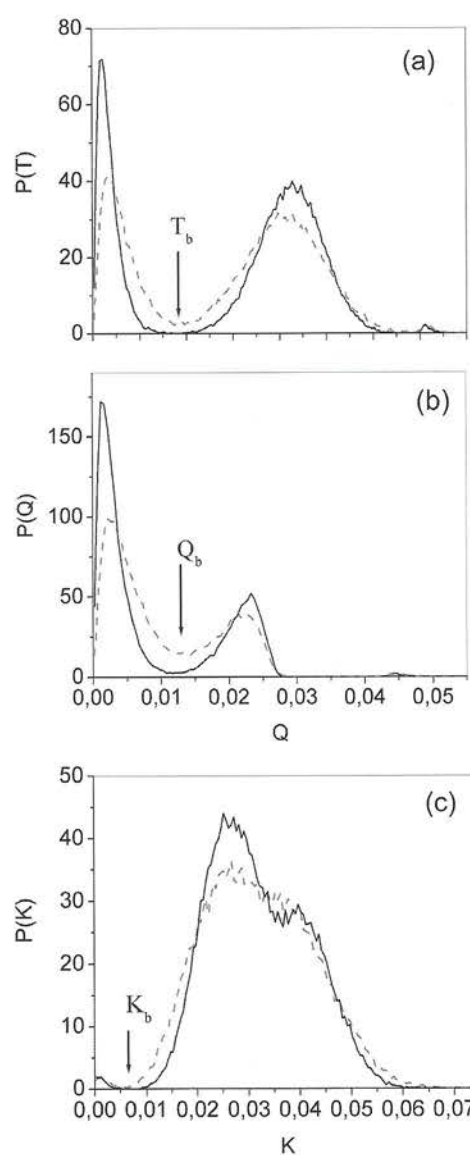


Fig. 1. Histograms of the distribution of the Delaunay simplexes over different shapes for the models of an FCC crystal: (a) tetrahedrality T , (b) quattoctahedrality Q , (c) measure for Kizhe simplex K , see formulae (1)-(3). Solid lines for the model with a temperature $T^* = 0.32$, dashed lines for $T^* = 0.48$. Arrows show boundary values for the extraction of proper simplexes for crystalline phase.

which is, from a physical point of view, a good crystal. Decreasing the boundary values gives us, obviously, higher-grade simplexes, but an excess of them introduces simplexes whose shape could not agree with the crystal structure.

Note, that variations of the boundary values (4) within 10-20% does not influence the results obtained, where we determine not only the shape, but also the environment of the Delaunay simplexes (see below).

Structural types of the Delaunay simplexes

Crystal types

The essence of our approach to ascribe a structure to a Delaunay simplex is a consideration of the environment of the simplexes together with their shape. In this study, the simplest step is realized in this direction: as an environment of the Delaunay simplex, only its neighbors on adjacent faces are taken into account.

In the FCC configuration every tetrahedral configuration is adjacent over faces only to octahedra, and every octahedral configuration is adjacent only to the tetrahedra. In terms of the Delaunay simplexes, this represents a possibility of the following combinations of neighboring simplexes for a simplex of a given shape:

- (I) $T: Q Q Q Q$
- (II) $Q: T T Q Q$
- (III) $Q: T T Q K$
- (IV) $K: Q Q Q Q$

Thus, a tetrahedral simplex may be adjacent to four quattohedra (I). Quattohedron can be adjacent to two tetrahedra and two quattohedra (II) or to two tetrahedra, one quattohedron and one simplex Kizhe (III). Simplex Kizhe can be adjacent only to four quattohedra (IV).

Based on the above, a given Delaunay simplex can identify the FCC structure if it satisfies one of the above conditions (5). Situations (III) and (IV) arise in the case when an octahedral configuration is divided into Kizhe simplexes (see above).

The HCP structure has pairs of adjacent tetrahedra (trigonal bipyramids), and the octahedra are organized in chains in which they are also adjacent by faces. Thus, we can formalize the neighborhoods of the Delaunay simplexes:

- (I) $T: T Q Q Q$
- (II) $Q: T Q Q Q$
- (III) $Q: T Q Q K$
- (IV) $Q: T T Q Q$
- (V) $Q: T T Q K$
- (VI) $K: Q Q Q Q$

Note, combinations (I)-(III) are new ones, but (IV)-(VI) are the same as for FCC (5). The similarity noted of some combinations is not surprising due to the

inherent genetic proximity of the densest crystalline structures. This also means that dissection of crystalline simplexes between FCC and HCP is not an unambiguous question in the general case. Further classification of such "disputed" Delaunay simplexes requires additional considerations. The number of such questionable Delaunay simplexes can be decreased by further analysis of the model. Indeed, if for instance the disputed quattohedron ($Q: T T Q Q$) is adjacent to tetrahedra, which belong to an FCC type, then it also can be classified as of FCC type. Therefore, after determination of the neighboring simplexes, we ascribe additional simplexes to crystalline types: if a disputed simplex is adjacent to an FCC type simplex (and does not have an HCP type) then we assign it to the FCC type. Analogously, a disputed simplex neighboring an HCP type and not of an FCC type is classified as HCP type. If a disputed simplex is adjacent both to FCC and HCP types, we keep it as disputed. Such cases take place at the regions bordering FCC and HCP structures. We keep simplexes as disputed also if they do not have neighbors of either FCC or HCP types. This case happens for small aggregates of simplexes with good crystalline shape in a disordered phase. Note, the residuary disputed simplexes, nevertheless, represent regions of crystalline structure.

Non-crystalline types

A proposed ideology to select Delaunay simplexes related to FCC and HCP may be extended to other structures, in particular, to non-crystalline ones. It is known that a dense amorphous phase contains aggregates of good tetrahedra adjacent by faces (polytetrahedral aggregates). Such an arrangement of more than two tetrahedra is extraneous for crystals, since they are incompatible with translational symmetry. For studying such aggregates, one should extract Delaunay simplexes with a good tetrahedral shape having also at least two good tetrahedra in its neighborhood:

$$T: T T * * \quad (7)$$

The other pair of neighboring simplexes can have, in a general case, an arbitrary shape. Polytetrahedral clusters, and particularly, five-membered rings of tetrahedra (pentagonal bipyramids), are identified by these simplexes.

Recently [6, 9, 18], a significant number of pentagonal prisms was detected in models of dense packings of hard spheres and in frozen Lennard-Jones liquids. The existence of such configurations is not trivial. They are not crystalline but also are unnatural for an amorphous phase. In this paper, we suggest a method to study them with the help of Delaunay simplexes of the following structure type:

$$T: T T Q Q \quad (8)$$

i.e. a good tetrahedron, with two tetrahedra and two quattohedra in their neighborhoods.

The Model

We studied a process of development of a crystalline phase on a model of a rapidly cooled Lennard Jones liquid. The model was generated by the Monte Carlo method in an NPT (isobaric-isothermal) ensemble. It contained 10000 atoms in a cube with periodic boundary conditions. The initial configuration corresponded to the liquid phase at a temperature $T^*=0.8$ and density $\rho^*=0.73$. At every 500-th Monte Carlo step, the temperature was decreased by $\Delta T^*=0.00075$. (500 steps are enough for energy relaxation of the model). Cooling was continued to zero temperature. The pressure was kept constant and equal to zero. During the process, the density increased to $\rho^*=1.037$. The total number of Monte Carlo steps was 533000. The result of such gradual cooling, was a halfway crystallization happened. For full crystallization a slower cooling process would be required.

Results

Figure 2 shows the volume fraction for different structural components of our model as a function of the temperature. Three upper curves belong to the crystalline phase. For extraction of the structural types, we used simplexes with shapes corresponding to a full set of crystalline shapes (4). First of all, we see that the HCP structure is predominant. It arises before the FCC structure appears and exists up to complete freezing of the sample. This structure represents 30% of the model volume. The total volume of the crystalline phase is more than 60%, where 11% belongs to the disputed simplexes representing cases bordering between the FCC and HCP regions.

The two lowest curves belong to structural types not typical for crystals (see formulas (7) and (8)). The

lowest curve shows the volume fraction occupied by polytetrahedral simplexes (7), except for the volume of simplexes that correspond to pentagonal prisms (8). One can also note that the largest volume occupied by non-crystalline simplexes is observed at the beginning of crystallization. This fact corresponds to the suggestion [6] that the existing polytetrahedral aggregates in liquids (together with embryos of pentagonal prisms) may initiate the appearance of crystalline nuclei. Simplexes of pentagonal prism type represent 3% of the volume when the model is completely frozen, which is more than the other polytetrahedral simplexes. They consist of central nuclei of five-fold twins of the FCC structure. However, they can also be found in other aggregates without 5-fold symmetry.

Approximately 30% of the model volume is not related to the structural types mentioned above, and represent a disordered structure in the model.

We calculate the volume of a phase as the sum of volumes of the Delaunay simplexes of the corresponding structural type. Note, that during the volume calculation we take into account all simplexes of a given type, single as well as in clusters. Of course, from a physical point of view, a separated simplex (four atoms) does not present a region of a given structure. Larger aggregates are usually treated as elements of an individual phase. However we do not discuss the size of aggregates in this paper. Our aim is to extract local configurations of a specific structural type. Detailed analysis of the structure, growth and stability of nuclei, are important topics for further investigation.

Figure 3 demonstrates the fractions of FCC and HCP structures in our model extracted with various criteria for the shape of the Delaunay simplexes. A pair of curves marked by the value 2 corresponds to boundary measures T , Q and K which are twice as small as the full set of crystalline simplexes (4). The pair of curves marked by the value 3 corresponds to boundary measures T , Q and K which are four times smaller. The curves from Fig. 2 for the full set of forms are also present (pair 1) for comparison. For more perfect shapes of simplexes, the volumes of extracted phases are obviously less. A nontrivial result that we obtained here is the fact that the ratio between FCC and HCP phases is changed. The pair of curves 1 demonstrate that HCP is identified significantly earlier than FCC. For the pair of curves 2 the HCP and FCC structures practically coincide over the whole interval from the moment when the crystalline phase originates to complete freezing. For the pair of curves 3 the structure FCC becomes predominant.

These results mean that the regions of the FCC structure are comprised of the more perfect simplexes than some aggregates of the HCP structure. This result can shed light on the fact that HCP nuclei are always present at the beginning stage of crystallization despite the FCC structure being more predominant in systems

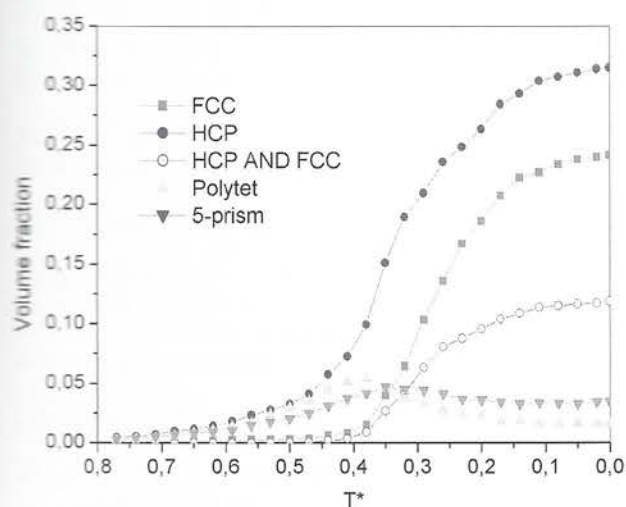


Fig. 2. Volume fraction occupied by Delaunay simplexes that belong to different structural types as a function of temperature of the model.

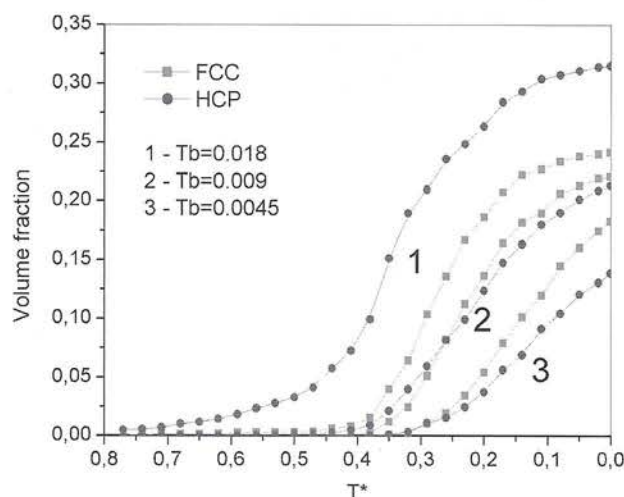


Fig. 3. Volume fraction of FCC and HCP structures for various criteria of shape quality of the Delaunay simplexes. 1) $T < 0.018$, $Q < 0.013$, $K < 0.007$. 2) $T < 0.009$, $Q < 0.0065$, $K < 0.0035$. 3) $T < 0.0045$, $Q < 0.00325$, $K < 0.00175$.

of spherical atoms. An interpretation of this is usually based on the suggestion that the appearance of FCC and HCP is equally probable at the first stage of crystallization. However, our analysis demonstrates that HCP is even more likely than FCC. This happens because the simplexes of HCP type are less affected by the quality of their shape than FCC simplexes, Fig. 3. Some polytetrahedral nuclei (aggregates of adjacent tetrahedral) may also correspond to an HCP structure, because HCP, in contrast to FCC, has pairs of tetrahedra adjacent by face. The detailed analysis of the spatial distribution of Delaunay simplexes of the HCP type demonstrates that at the first stage they exist as small nuclei uniformly distributed through the model.

Conclusions

A novel method for the extraction of crystalline nuclei for FCC and HCP structures using the shape and mutual arrangements of the Delaunay simplexes is proposed. Structural elements corresponding for each of the defined structural types are identified and described. The basis of such a structural element is a Delaunay simplex of a shape similar to one of three characteristic forms of dense crystalline structures: a tetrahedron, a quarter of an octahedron (quartoctahedron), and a flat square. The structural type of the simplex is determined by the shape of neighboring simplexes, adjacent by faces. Clusters of simplexes of a given structural type represent the nuclei of a corresponding structure. This approach can be also applied for extraction of other specific structures, in particular, for polytetrahedral

aggregates typical for an amorphous phase, and pentagonal prisms.

The structure of a Lennard-Jones liquid in the process of cooling has been studied as part of this research. The non-trivial result is that nuclei of the HCP structure appear earlier than FCC nuclei. This is justified by the fact that elements of HCP can be generated from simplexes whose shape is less perfect than the one needed to form elements of FCC.

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