

HOMOGENEOUS CRYSTALLIZATION OF THE LENNARD-JONES LIQUID. STRUCTURAL ANALYSIS BASED ON DELAUNAY SIMPLICES METHOD

A. V. Anikeenko and N. N. Medvedev

UDC 541.3+536.421.4+548.51

The crystallization process of a simple liquid upon slow cooling has been modeled by the Monte-Carlo method. The model contains 10,000 Lennard–Jones atoms in the model box with periodic boundary conditions. The model structure is investigated at different stages of crystallization using Delaunay simplices. The simplex belonging to one or another particular crystal structure was determined by the shape of the given simplex taking into account the shape of its neighboring simplices. Simplices typical of the fcc and hcp crystal structures, as well as of polytetrahedral aggregates, not typical of crystals, were studied. The analysis has shown that the “precursors” of a hcp structure are strongly dominating over the “precursors” of a fcc structure in liquid phase before the beginning of crystallization. When crystallization starts, small embryos of the fcc structure are observed; the simplices peculiar to hcp are present at that in great amount, but they are distributed over the sample more uniformly. As crystallization proceeds, the portion of the fcc phase grows faster than hcp. However, no unified crystal appears in our case of slow cooling of the model. A complex polycrystalline structure containing crystalline regions with multiple twinning, pentagonal prisms and elements of icosahedral structures arises instead.

Keywords: structure of simple liquids, homogeneous nucleation, Voronoi–Delaunay method, Delaunay simplices.

INTRODUCTION

Investigations of structural transformations in liquid, amorphous, and crystal phases are an important problem of modern materials science. A characteristic feature of such processes is their structural heterogeneity, i.e. there are coexisting areas of various structures both disordered and crystalline in one sample. The investigation of such systems is a rather complex problem. If the generation of computer models is restricted only by available computing facilities, their analysis, revealing and examination of areas with different structures demands the development of special approaches. Last years have brought an essential promotion in this direction being related to the Voronoi–Delaunay method [1-3]. The essential aspect of this method consists in using Delaunay simplices. The Delaunay simplex is defined by a quadruple of atoms and represents the simplest three-dimensional element of the structure. Any atomic system is represented as a mosaic of the Delaunay simplices. Thus, the areas of the required structure can be distinguished by analyzing the arrangement of simplices of a given specific type [3, 4].

Institute of Chemical Kinetics and Combustion, Siberian Division, Russian Academy of Sciences, Novosibirsk; nikmed@kinetics.nsc.ru. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 47, No.2, pp. 273-282, March-April, 2006. Original article submitted April 27, 2005.

The use of Delaunay simplices for studying the local structure has an advantage in comparison with the use of Voronoi polyhedrons [5, 6] or spherical harmonics [7, 8]. The Voronoi polyhedrons and spherical harmonics reflect a property of the nearest atom surrounding, i.e. the structural unit in this case includes approximately 15 atoms. It is not of much importance, if rather large areas of different structures are investigated, or if the characteristics of the nearest surroundings of atoms average in the model are under study. However, when small units are analyzed, ambiguities arise since some important structural features can manifest themselves at smaller number of atoms. Indeed, the differences between fcc (face-centered cubic) and hcp (hexagonal close packing) can be seen already in the six atom cluster. Another example: a pentagonal bipyramid (the ring of five tetrahedra adjacent by their faces), which is characteristic for any dense disordered packings of spherical particles, consists of seven atoms. It does not make an atom environment; therefore it cannot be revealed by means of spherical harmonics; and it also is problematic to be found out by Voronoi polyhedra analysis. Nevertheless, this bipyramid is important for understanding the nature of the dense disordered packing [9, 10]. The research of such structures, and also of more complex polytetrahedral units has been made exclusively with the help of Delaunay simplices [3, 4, 11].

When dealing with Delaunay simplices, one has to keep in mind the following moments. First, a separate (single) simplex does not characterize the structure unambiguously, as a rule. For example, “good” tetrahedron (close by its shape to the regular one) enters into both the densest crystal structures (fcc and hcp), and it is also present in a large amount in a dense amorphous phase. On the other hand, the crystal structure is not always represented by one type of simplices. Thus, three types of simplices of different shapes, tetrahedron, quattoctahedron (the quarter of an octahedron), and a small part of simplices with the shape close to a flat square, enter into the composition of the fcc and hcp structures, and all distinction between the crystals consists in a mutual arrangement of these simplices.

In our recent works we have used the shape measures, T, Q, and K, defined as dispersions of edge lengths of simplices in order to discriminate the specified simplices (see below and papers [4, 12, 13]). To reveal the areas of a specific structure we investigated the mutual arrangement of simplices of a given shape. Clusters consisting of such simplices allow one to find out both crystalline and specific noncrystalline aggregates of atoms. However, to reveal the structure of the separated unit is possible only after analyzing the mutual arrangement of the constituent simplices [13, 14]. This analysis allows the presence of various structures in the model to be demonstrated; however, it does not quantitatively answer the question about the portions of different phases in the sample. More certain assignment of simplices to the structure of the desired type is required for this purpose.

In the present work, we propose to characterize a structural belonging (structural type) of a Delaunay simplex by considering both the shape of the given simplex and the shape of its neighbors. As neighboring, we intend to consider only the simplices adjacent by faces. In this case, the atomic unit defining the structural type is an aggregate of eight atoms: 4 atoms of the given simplex and 4 atoms nearby its faces. However, we employ only the central simplex assuming it to be a “building block” of the given structure in the structural analysis of clusters.

STRUCTURAL TYPES OF DELAUNAY SIMPLICES

The application of Voronoi and Delaunay geometrical ideas for the structure analysis of atomic systems is described in the literature in details (see, for example, [3, 5, 15]). The first step of such a work is the computation of Voronoi–Delaunay decomposition of the whole system. It gives us the total information necessary for the further structure analysis. First of all, we calculate Voronoi network of the system (network of vertices and edges of all Voronoi polyhedrons). Each vertex of the Voronoi network is incident to four atoms of the system defining the Delaunay simplex. Thus we know all Delaunay simplices of the system, and now we can calculate their any geometrical characteristics. First, we calculate the measures of the simplex shapes. Further, using the network connectivity, a mutual arrangement of simplices is ascertained easily. This information allows us to easily state the structural type of each simplex. After the structural type of each simplex is assigned,

it becomes possible to investigate clusters of the simplices of a given structural type. Formally this problem is reduced to the analysis of clusters from the colored sites on the Voronoi network [3, 4].

Measures of the shapes of simplices. The choice of simplices under study depends on the particular problem. In the present case, we work with dense packings of spherical atoms. The basic local structure for them is the tetrahedral configuration of the four atoms, as it is energetically most favorable and locally the densest one. Moreover, octahedral configurations are present in the densest crystals. The perfect octahedron represents an example of a degenerate configuration: all six vertices (centers of atoms) lay on the same circumference. However, the atoms are always displaced from ideal positions in computer simulations; therefore every octahedral configuration is divided into simplices. So, there usually appear 4 similar simplices (quarters of an octahedron) which are called *quartoctahedra* [3, 16]. A perfect quartoctahedron has obviously one edge $\sqrt{2}$ times longer than the others. Note that the octahedron can be partitioned at some specific displacements of atoms to five simplices instead of four. The fifth simplex corresponds to a flat configuration of four atoms of an octahedron. This simplex has been discovered in the analysis of models of simple liquids in [12] and named as the *Kije simplex*. Its two opposite edges (the diagonals of the square) are $\sqrt{2}$ times longer than the others. Notwithstanding that such simplices arise infrequently, they also should be considered in the analysis of dense systems.

To separate good tetrahedral configurations we use the measure T, i.e. *tetrahedrity* [3, 16]. It is a variation of edge lengths of a 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 lengths of the i -th and j -th edges; $\langle e \rangle$ is the average length of edges in the given simplex. Factor 15 is used for normalization and is equal to the number of all possible pairs of edges of a simplex. For the perfect tetrahedron, the value of T equals zero. Small value of a measure T definitely shows that the shape of the given simplex is close to the perfect tetrahedron.

For the unambiguous separation of quartoctahedra, we use a special measure Q, *quartoctahedrity* [3, 16]

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

The sense of this measure is similar to that of the measure T. However, when calculating the variation of edge lengths, it is taken into account that one edge is $\sqrt{2}$ times longer than the others. For the calculation of Q, the longest edge of a simplex m has to be found first, and then the calculation by formula (2) follows. For the quartoctahedron close to the perfect one, the value of this measure tends to zero, and vice versa, a small value of Q specifies that the shape of a simplex is close to the perfect quartoctahedron.

To determine Kije simplices we have offered the measure K. It is designed on the same principle as the measure Q, apart from the fact that for a simplex close in shape to a flat square, two opposite edges are $\sqrt{2}$ times longer than four other ones [3]

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

The sense of this expression is that the value of measure K for a simplex degenerating to a flat square equals zero, and for weak distortions it will remain small. Here, in the calculation of the measure, the pair of the longest opposite edges of a simplex is chosen as the edges m and n .

Note that expressions (2) and (3) differ from the corresponding formulae used in [12, 13, 16] by the normalization factor. This choice is not critical for the determination of simplices of the required shape, however, the present way seems to be more unified.

Calibration of measures. In order to assign a simplex to a given shape it is necessary to carry out a calibration of the offered measures (1)-(3), i.e. to specify the boundary values T_b , Q_b , and K_b up to which we can consider the simplex belonging to this particular shape. The calibration based on the model for a known structure, namely a fcc crystal at temperature below melting temperature, has been offered and made in [4, 16, 17]. For a good crystal, the distribution of each measure, T, Q, and K, shows, of course, a peak at zero values of a corresponding measure that unambiguously refers to perfect simplices. Except this peak, there is another one at large values of a measure which simplices of another shape correspond to. The position of the minimum between these peaks weakly depends on temperature of a crystal; therefore it has been offered to choose this point as the boundary separating “good” simplices of a given shape from the others [4, 16]. It has been found in [17] that the boundary values for the shape measures defined according to formulae (1)-(3) are:

$$T_b = 0.018, \quad Q_b = 0.014, \quad K_b = 0.006. \quad (4)$$

We state that the simplices whose values of measures T, Q or K do not exceed the corresponding boundary values from (4) define a total set of simplices inherent to the crystal. In other words, all of them can be present in the aggregate, which, from the physical viewpoint, represents an area of a crystalline phase with the quality not worse than of a bulk crystal that is perturbed, though, by thermal vibrations, but is still far from melting. By reducing the boundary values of the measures we will, certainly, separate the simplices of a higher quality. However, if a simplex goes beyond the borders specified in (4), it can not be considered as a crystalline one.

It is important to note that the variation of the boundary values (4) within the limits of 10-20% practically does not affect the physical results obtained, if we define the structural type of a simplex allowing for its environment.

Crystalline types. The basic point of our approach consists in that to structurally assign a Delaunay simplex we take into account its environment. In the present work, the simplest step is done in this direction. Only the simplices adjacent by faces are considered as the environment of a given simplex. The shape of the simplices is used at that as the structural parameter.

The fcc structure is characterized by that each tetrahedral configuration in it is surrounded (on each face) by octahedral ones, and each octahedral configuration is surrounded by tetrahedral. It is easy to prove that in terms of the Delaunay simplices it means an opportunity for the existence of only the following four combinations:

$$\begin{array}{ll} \text{(I)} & T: \quad Q \quad Q \quad Q \quad Q \\ \text{(II)} & Q: \quad T \quad T \quad Q \quad Q \\ \text{(III)} & Q: \quad T \quad T \quad Q \quad K \\ \text{(IV)} & K: \quad Q \quad Q \quad Q \quad Q. \end{array} \quad (5)$$

(I): A tetrahedron adjacent to four quartoctahedra. (II): A quartoctahedron adjacent to two tetrahedra and two quartoctahedra. (III): A quartoctahedron adjacent to two tetrahedra, one quartoctahedron, and one Kije simplex. (IV): the Kije simplex adjacent to four quartoctahedra [17]. Note that situations (III) and (IV) arise in the case if the Kije simplex appeared due to the octahedron splitting (see above). Thus, a Delaunay simplex represents the fcc structure if, first, it has an appropriate crystalline shape (tetrahedral, quartoctahedral, or Kije), and, secondly, satisfies one of the conditions (5).

In the hcp structure there are pairs of face-adjacent tetrahedra (trigonal pyramids), while octahedra form chains in which they also contact with each other by their faces. It leads to the following theoretically possible variants of the environment of simplices:

$$\begin{array}{l}
\text{(I)} \quad T: T \quad Q \quad Q \quad Q \\
\text{(II)} \quad Q: T \quad Q \quad Q \quad Q \\
\text{(III)} \quad Q: T \quad Q \quad Q \quad K \\
\text{(IV)} \quad Q: T \quad T \quad Q \quad Q \\
\text{(V)} \quad Q: T \quad T \quad Q \quad K \\
\text{(VI)} \quad K \quad Q \quad Q \quad Q \quad Q.
\end{array} \tag{6}$$

Note that only combinations (I)-(III) are new here, (IV)-(VI) completely coinciding with (II)-(IV) found for fcc (5). This situation is not unexpected in view of the genetic affinity of the densest crystal structures. For the structural assignment of such disputable simplices, some additional reasons are required. Thus, it is possible to unambiguously attribute the fcc type to the simplices T: Q Q Q Q, and the hcp type to the simplices T: T Q Q Q, Q: T Q Q Q, and Q: T Q Q K. Other combinations singled out in (5) and (6), can represent both crystal structures. However, the quantity of such disputable simplices allocated in the analysis of the model, can be reduced essentially. For example, if a quartoctahedron at issue (Q: T Q Q) contacts with tetrahedra which belong to the fcc type, the given quartoctahedron should be assigned to fcc type too (because it is situated in the fcc environment). Therefore we make an additional assignment of simplices after defining the adjacent simplices. If the disputable simplex is adjacent to a simplex of the fcc type (but not adjacent to the hcp type), then the fcc type is to be attributed to it. Similarly, the disputable simplex adjacent to a simplex of the hcp type we assign to the hcp type too. But if the simplex is simultaneously adjacent both to the simplices of the fcc and hcp types, we leave this simplex as disputable. It occurs on a phase boundary. Furthermore, the simplices which do not adjoin neither to fcc, nor to the hcp types remain also disputable. It sometimes happens for small aggregates of disputable simplices in the disordered phase.

Noncrystalline types. The offered methodology for defining the structural type of a simplex can be also spread onto noncrystalline structures. The aggregates consisting of good tetrahedra adjacent by faces are known to be typical of a dense amorphous phase of spherical atoms. This arrangement of the tetrahedral is not peculiar to crystals as it is incompatible with translation symmetry. For their detection, it is possible to allocate the Delaunay simplices of good tetrahedral shape having at least a pair of good tetrahedra in their neighborhood:

$$T: T T^{**}. \tag{7}$$

Another pair of neighbor simplices (asterisks) can have, in general, any shape at that. All polytetrahedral clusters that are characteristic for the amorphous phase and, in particular, the five-member rings of tetrahedra (pentagonal bipyramids) will be inevitably detected by means of such structural type of the Delaunay simplices. Further we will call this type of simplices as *polytetrahedral*.

An interesting subclass of the polytetrahedral type is represented by the simplices which have in their neighborhood, apart from two tetrahedra, at least one good quartoctahedron:

$$T: T T Q^*. \tag{8}$$

This structure arises in the center of pentagonal prisms which, as the recent studies have shown, are present in noticeable quantities in dense systems of spherical atoms if there are the areas of the crystalline phase in them (see recent papers [6, 9, 14]).

THE MODEL

We have simulated a gradual cooling of a liquid in order to study potential nuclei of the crystal phase emerging at homogeneous nucleation. The model consisted of 10,000 Lennard–Jones atoms in a cubic model box with periodic boundary conditions. The Monte-Carlo method in *NPT* ensemble was used, i.e. when modeling the equilibrium state, constant temperature and pressure (which in this case was assumed to be zero) were maintained. A random packing of spheres relaxed at the temperature 0.8 (in units of ε/kT) has been taken as the initial configuration. The reduced density of the initial configuration equaled $\rho^* = 0.73$ (in units of σ^{-3}).

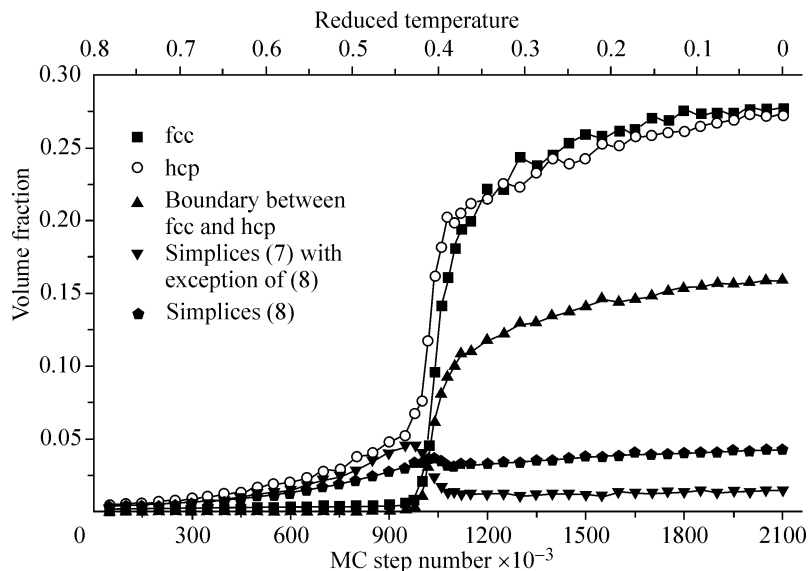


Fig. 1. Volume fraction occupied by the simplices of different structural types depending on crystallization depth. The bottom abscissa: the number of Monte-Carlo steps, the top one is the corresponding to the temperature of the model.

Modeling the cooling, we gradually lowered temperature of the model by a value of $\delta = 1.875 \cdot 10^{-4}$ after every 500 steps of the Monte-Carlo procedure. At a given temperature, the model has been relaxing during 500 Monte-Carlo steps for the system energy and density to equilibrate. After that, the temperature of the sample was lowered again by δ value, and the system was relaxing again till the following temperature decrease. This process was continued up to the achievement of zero temperature. Thus, the model has consistently passed through the states corresponding to a liquid, a supercooled liquid, and to a solid phase in the cooling process. The effective density increased at that to the value $\rho^* = 1.042$. The total number of the Monte-Carlo steps comprised 2, 134 000 that required about one and a half month of calculation on a PC Pentium 4, 1700 MHz.

RESULTS AND DISCUSSION

Fig. 1 illustrates the volume fraction of different structural components in our model depending on the number of the Monte-Carlo simulation steps. To calculate the volume occupied by the structure of a given type we sum up the volumes of all simplices of this type. Note that this approach to estimate a fraction of a required phase using the Delaunay simplices is the original one. Traditionally, “the carrier unit” of the structure is believed to be the atom having an appropriate nearest environment. The aggregates consisting of such atoms represent the area of the corresponding phase. This approach is quite acceptable for large aggregates when the boundary atoms can be neglected. The problem arises, if we deal with small units which consist of only few atoms. In this case, the atom together with its surroundings proves to be a rough structural unit (see the Introduction). Here it is better to use the Delaunay simplices. A simplex represents a minimal structural unit of the three-dimensional space — just a quadruple of atoms. Moreover, the Delaunay simplices fill the space, i.e. they represent “the building blocks,” which the whole system is made of. Therefore if to determine for each simplex its belonging to one or another structural type, then the analysis of spatial distribution of the given phase becomes a clear and well defined problem.

Three top curves in Fig. 1 describe the behavior of the crystalline phase. Note that the simplices corresponding to hcp dominate at the initial stage over the simplices of fcc type. When the sample is absolutely frozen, each of these structures occupies approximately 27% of the whole volume. If to consider additionally the disputable simplices representing the boundaries between the fcc and hcp areas (see above), the total crystalline phase is seen to present 70% of the sample.

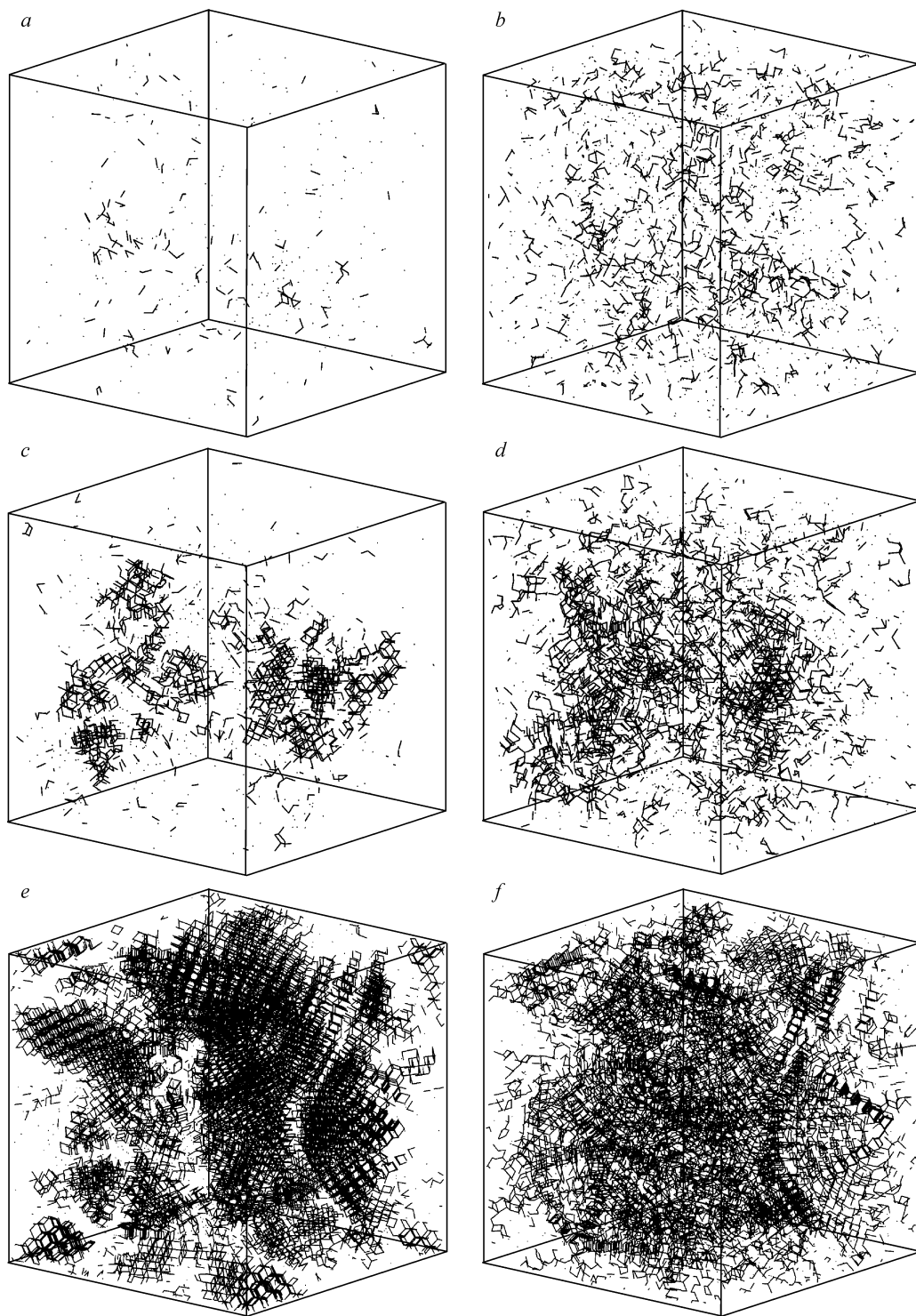


Fig. 2. Distribution of simplices of the fcc type (at the left) and of the hcp type (at the right) inside the model at different stages of crystallization. Before the beginning of crystallization (*a, b*), at the initial stage of crystallization (*c, d*), at the final stage of crystallization (*e, f*), see the text.

Two lowest curves in Fig. 1 refer to the polytetrahedral structural type (7). The lowermost curve shows a model volume fraction occupied by these simplices without allowing for the simplices peculiar to pentagonal prisms (8) which the second curve corresponds to. The maximum amount of polytetrahedral simplices is observed at the moment when sample

crystallization begins (at the temperature about 0.4). It is seen that that simplices (8) represent an essential fraction of all polytetrahedral simplices. This fact supports the assumption stated in [13] that nuclei of pentagonal prisms (pentagonal bipyramids and twisted icosahedra), present in a liquid, can promote the emergence of crystal nuclei. When the model is totally frozen, the volume fraction of simplices (8) makes approximately 4%. They are incorporated in fivefold twins of the fcc structure (Bagley structures [14, 18]). However, they can exist in other aggregates too, not forming the structures with the symmetry axis of the fifth order (see below).

Approximately 23% of the volume of our model does not belong to the specified structural types. These simplices relate either to a disordered phase which remained in the given model, or as the additional analysis indicates, many of them have quite a regular shape which is different from shapes (1)-(3).

Figs. 2 and 3 display the spatial distribution of the simplices of our selected structural types at different stages of crystallization process. Each simplex is marked by a point that is the node of the Voronoi network, to which this simplex corresponds. Lines designate the network bonds and link two neighbor nodes if their simplices are of the same type [3, 4].

The nodes and bonds of the Voronoi network related to the simplices of the fcc type are “colored” at the left of Fig. 2, at the right of it there are those of the hcp type. Figs. 2*a* and *b* demonstrate a configuration at the 980,000-th step of modeling (the temperature is 0.43) that corresponds to the state just before the beginning of crystallization. A few small clusters of the fcc structure and rather many larger aggregates corresponding to hcp are seen. The following pair of figures (2*c* and *d*) represents a configuration of the model at the initial stage of crystallization (temperature 0.41). The embryo of the fcc structure are noticed to have turned into quite distinct nuclei. The quantity of the hcp phase has also increased, but the corresponding simplices do not tend to form the localized hcp nuclei, but are still distributed over the whole model volume (see Fig. 2*d*). At last, the bottom figures represent the configuration in which the process of crystallization has been practically completed (temperature 0.01). Compact areas of the fcc structure are well distinguished, however, the resulting crystal phase does not form a uniform crystal (see Fig. 2*e*). There are both the isolated nuclei and twins, i.e. the areas where the crystal planes change their direction. All this is directly connected with the presence in the model of pentagonal prisms and Mackay structures appearing on the base of icosahedral packing of atoms. We remind that the existence of aggregates with the axes of five-order symmetry inside the crystal phase is connected with the ability of the fcc structure to fivefold twinning [19]. Turns of the fcc structure are caused by the stacking fault of crystal planes that leads to the emergence of hcp regions. In Fig. 2*f*, the rows of the hcp simplices repeating the boundaries of fcc areas in Fig. 2*e* can be seen. However, a plenty of hcp simplices is still diffusively distributed inside the sample.

Fig. 3 depicts the same configurations of model as Fig. 2, however, this time the nodes and bonds of the Voronoi network relating to the simplices of polytetrahedral type are singled out. The simplices peculiar to pentagonal prisms (8) are shown at the right, while at the left there are all the other simplices, selected according to (7), but without simplices (8).

Figs. 3*a* and *b* confirm the known fact that the presence of aggregates of good tetrahedra adjacent by faces is a characteristic structural feature of a dense noncrystalline phase. They represent linear and branching clusters among which there occur the five-member rings (pentagonal bipyramids). Quite a new information is given by Fig. 3*b* that the simplices of polytetrahedral type can have yet in the liquid phase a quatoctahedron among their neighbors.

At the initial stage of crystallization (Fig. 3*c*), many simplices of the polytetrahedral type forming irregular clusters are still remained. However, the stacks of five-member rings appear that signifies the presence of pentagonal prisms in the model (Fig. 3*d*).

After crystallization, the number of polytetrahedral simplices diminishes. Nevertheless, in Fig. 3*e* a few dodecahedra are seen which indicate the icosahedral atom environment. These icosahedra appear to be the centers of the Mackay structures [19,20], in whose sectors the structure of the fcc type is realized, on the border of two sectors the hcp structure presents, and stacks of decahedra “grow” from some icosahedron vertices, which are visible as piles of five-member rings in Figs. 3*d* and *f*.

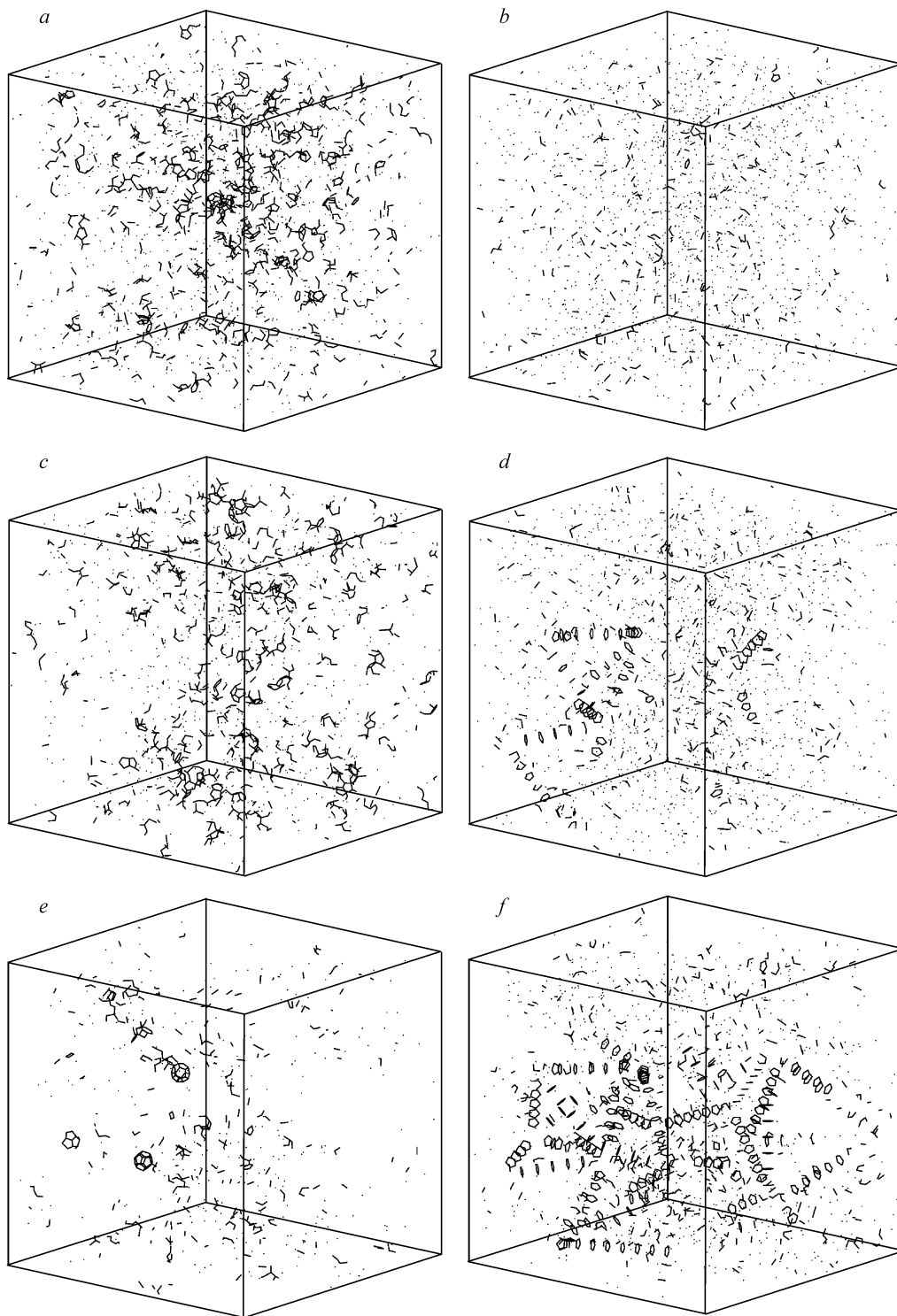


Fig. 3. Distribution of simplices of the polytetrahedral type inside the model at different stages of crystallization for the configurations displayed in Fig. 2. On the right there are shown the simplices which have in their neighborhood apart from two tetrahedra at least one quatoctahedron, type 8. On the left there are shown all the other simplices of polytetrahedral type, i. e. that have in their neighborhood two tetrahedra at least, but without quatoctahedra, see the text.

CONCLUSIONS

The model has been constructed, and the areas of various structures are studied that arise during slow crystallization of a Lennard–Jones liquid. The Delaunay simplices are used for the structure analysis. The efficiency of this approach is provided by that the simplex represents a minimal structural unit of the three-dimensional space, namely, the quadruple of atoms, thus serving as a building block which all system is made of. Therefore, discriminating the simplices of a given crystalline structural type, it is possible to investigate the presence and the spatial distribution of aggregates of the required structure. Such an approach can be used also in a general case to investigate any structurally inhomogeneous systems.

To determine the structural type of a Delaunay simplex we use simultaneously both the shape of the given simplex and of the neighboring ones. Simplices relating to the fcc, hcp structures and also to the polytetrahedral aggregates typical of dense noncrystalline packings of spheres are studied in this work. It is indicated that in a liquid state before crystallization the simplices corresponding to the hcp structure are met more often than the simplices of the fcc structure. The preference of hcp is kept at the first stage of crystallization too. The hcp simplices are distributed at that rather uniformly over the sample, whereas the fcc structure is observed as localized nuclei. Upon further crystallization of the sample, the portion of the fcc phase grows. In this particular case of a relatively slow cooling, a unified crystal does not arise. Instead there results a complex “polycrystalline” structure with multiple twinning of crystal areas, the presence of pentagonal prisms and elements of icosahedral structure.

This work was supported by RFBR grant No. 05-03-32647, YS INTAS grant No. 04-83-3865, and CRDF grant N-008-X1.

REFERENCES

1. G. F. Voronoi, *J. Reine Angew. Math.*, **134**, 198-287 (1908); *ibid.*, **136**, 67-181 (1909).
2. B. N. Delaunay, *Proc. Math. Congress in Toronto Aug. 11-16*, 695-700 (1924-1928).
3. N. N. Medvedev, *Voronoi–Delaunay Method for Noncrystalline Structures* [in Russian], Russian Academy of Science, Novosibirsk (2000).
4. Y. I. Naberukhin, V. P. Voloshin, and N. N. Medvedev, *Mol. Phys.*, **73**, No. 4, 917-936 (1991).
5. J. Finney, *Royal Society London*, **319**, 479-494; 495-507 (1970).
6. B. O’Malley and I. Snook, *Phys. Rev. Lett.*, **90**, No. 8, 085702 (2003).
7. P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. B.*, **28**, 784-805 (1983).
8. V. A. Luchnikov, A. Gevois, P. Richard, et al., *J. Mol. Liq.*, **96/97**, 185-194 (2002).
9. J. Bernal, *Proc. R. Soc. London.*, **A280**, 299-322 (1964).
10. F. Spaepen, *Nature.*, **408**, 781/782 (2000).
11. W. Brostow, M. Chybicki, P. Laskowski, and J. Rybicki, *Phys. Rev. B.*, **57**, No. 21, 13448-13452 (1998).
12. V. P. Voloshin, Y. I. Naberukhin, and N. N. Medvedev, *Mol. Simul. J.*, **4**, 209-227 (1989).
13. A. V. Anikeenko, M. L. Gavrilova, and N. N. Medvedev, *Jpn. J. Industr. Appl. Math.*, **22**, 151-165 (2005).
14. N. N. Medvedev, A. Bezrukov, and D. Shtoyan, *Zh. Strukt. Khim.*, **45**, 24-31 (2004).
15. A. Okabe, B. Boots, K. Sugihara, and S. Chin, *Spatial Tessellations: Concepts and applications of Voronoi diagrams*, John Wiley, Chichester (2000).
16. N. N. Medvedev and Yu. I. Naberukhin, *J. Non-Cryst. Solids.*, **94**, 402-406 (1987).
17. A. V. Anikeenko, M. L. Gavrilova, and N. N. Medvedev, *Lecture Notes Comp. Sci.*, **3480**, 816-826 (2005).
18. B. G. Bagley, *Nature.*, **208**, 674/675 (1965).
19. H. Hofmeister, *Cryst. Res. Technol.*, **33**, 3-25 (1998).
20. B. W. Van der Waal, *Phys. Rev. Lett.*, **76**, No. 7, 1083-1086 (1996).