Japan J. Indust. Appl. Math., 22 (2005), 151–165 Area ⟨3⟩

The Coloring of the Voronoi Network: Investigation of Structural Heterogeneity in the Packings of Spheres

A. V. ANIKEENKO[1], M. L. GAVRILOVA[2] and N. N. MEDVEDEV[1]

[1] *Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia*
E-mail: nikmed@ns.kinetics.nsc.ru
[2] *Department of Computer Science, University of Calgary, Calgary, AB, Canada*
E-mail: marina@cpsc.ucalgary.ca

Received August 11, 2004
Revised December 16, 2004

The paper describes how the Voronoi-Delaunay approach can be used for investigation of the structural heterogeneity during the process of liquid crystallization. The basic geometric structure for the analysis is the Voronoi network (the Voronoi diagram in a 3-dimensional space). Every site of the Voronoi network is associated with a Delaunay simplex: four neighboring atoms representing the simplest element of the liquid structure. Having a quantitative measure for the shape of simplexes, we suggest to mark (color) Voronoi sites according to a given physical criterion. As a result, the structural investigation is reduced to a task of cluster analysis on a network. Evolution of aggregates of atoms comprised of tetrahedral configurations is studies on an example of Lennard-Jones liquid crystallization. The experiments show that pseudocrystalline aggregates of pentagonal bipyramids spring up along with the genuine crystalline nuclei. The pseudonuclei can stimulate crystallization at the first stage of the process, but slows it down in the final stage of fusion of crystal regions. The results obtained are important for in-depth understanding of the process of the homogeneous crystallization of simple liquids.

Key words: liquid crystallization, Voronoi diagram, FCC and HCP configurations, simplex form measures, fivefold symmetry

1. Introduction

Structure transformation in liquid, amorphous and crystalline phases is one of important problems in material sciences. Many questions explaining the process of homogeneous crystallization of liquids remained unanswered up until present. Mechanisms of crystalline nuclei initiation, their growth and fusion are not fully investigated. The process of relaxation and structural reorganization in the amorphous phase is a current subject for theoretical and experimental research. Today's interest in this issue is related to the problem of stability of nanomaterials, and their aging [11, 14].

One of the distinct features of the atomic substances in these conditions is their structural heterogeneity. This means that in the sample there can be areas of various structure, both disordered and crystallized. It is not an easy task to investigate these structural features. With the help of diffraction experiments it is

possible to extract only information averaged over a sample, without taking into account heterogeneity. Computer modeling provides coordinates of all atoms in a sample, however special approaches are needed to extract physically substantial information from them.

The traditional statistical analysis of the Voronoi polyhedra, based on studying the nearest environment of an atom [7, 10, 18], is not very helpful in analyzing the structural heterogeneities. Indeed, the distribution of volumes (for instance) of the Voronoi polyhedra might indicate the presence of porous areas in a system, but will not reveal their spatial arrangement. Ability to find and analyze regions of different structure within the model is very important for many physical applications, including studying the process of crystal nucleation. For the purpose of such analysis, it is possible to use the Voronoi polyhedra. In this case clusters of atoms having crystalline surroundings represent crystal nuclei. This approach, based on investigation of clusters of objects bearing intrinsic physical information, and their spatial distribution, is referred to a general problem of mark correlation [4]. The interplay of the objects properties (marks) with the spatial clustering is extensively used in many applications ranging from studying the structure of the galaxies to simulating the pores in sandstone [16].

In our case, in order to study structural heterogeneities in systems of spherical particles, it is convenient to use the classical Voronoi-Delaunay partitioning of a space. Then it is possible to proceed from considering atoms with their surroundings to analyzing Delaunay simplexes, which allows characterizing the structure in more details. In addition, it is advantageous to use the Voronoi network for studying spatial correlations. This approach is more productive than to reveal correlations between objects (atoms) in a continuous space [17].

In the following, we use quantitative measures of the Delaunay simplexes to identify the most typical configurations of densely packed spherical particles. After that we mark (color) Voronoi network sites (vertices) for the subsequent analysis of clusters from these vertices. We conducted studies of models with 7000 Lennard-Jones atoms obtained using Metropolis Monte-Carlo method in NPT ensemble in boxes with periodic boundary conditions. The sequence of configurations during crystallization process is considered. The structural heterogeneity which arises during the process is identified.

2. Preliminaries

The Voronoi diagram is a fundamental structure known for over a hundred years in mathematics. Presently, it is utilized extensively not only in the computational geometry area, but in a variety of applied sciences, such as molecular biology, mechanics, materials studies, physics, climate control, and geography, to name a few. It is generally defined as a partitioning of the space $\mathbf{S}$ into regions associated with the set of *generators*, each of the regions being the location of elements from $\mathbf{S}$ closer to the generator $\mathbf{P}$ than to any other generator from $\mathbf{S}$.

The above general definition can be specialized to the set of sites in the Eu-

clidean metric according to Okabe et al. [19]:

DEFINITION 1. *An* Euclidean Voronoi diagram *for a set of generators S in R^d is the set of generalized Voronoi regions*

$$EVor(P) = \left\{\mathbf{x} \in R^d \mid d(\mathbf{x}, P) \leq d(\mathbf{x}, Q),\ \forall Q \in S - \{P\}\right\},$$

where $d(\mathbf{x}, P)$ is the Euclidean distance between a point $\mathbf{x}$ and a generator $P \in S$.

The above concept can be used to describe numerous models corresponding to real-world phenomena, including dynamics of the fluids [20], structure of the proteins [6, 12], models of lipid bi-layers [1], growth of the corrals [8], study of pores in the granular-material systems [16], spatial analysis in GIS [5] and planning a collision-free path for a robot avoiding enemy attacks [13]. The diversity and extend of the Voronoi diagram applications, that range from investigation of the structure of the atom to the study of the global phenomena, is indeed astonishing. It can be contributed to the mathematical properties of this data structure: the commonly known are the *empty-sphere property*, the *nearest-neighbor property*, and the duality to another remarkable data structure known as the *Delaunay tessellation*. It can also be contributed to the notable relationship to other well known geometric concepts: the all-nearest-neighbors, the Steiner tree, the minimum spanning trees, and the minimum enclosing circle problems among others. Finally, it also can be contributed to the versatility of the structure, allowing representation not only for the mathematical concept, but also for geometrical, topological, algebraic and attribute-based information associated with the entities being analyzed.

The present research serves as one more example of the enormous potential of the Voronoi diagram methodology as well as illustrates benefits resulting from the applications of this methodology to model analysis. The resulting chapters are organized as follows. Chapter 3 describes the methodology for Voronoi network for studying atomic systems. Chapter 4 classifies the local configurations of atoms that are typical in dense packing of spheres and introduces measures for identification of such configurations. In Chapter 5 we describe an approach for revealing embryos of a crystalline phase. The results of the application of the methodology to the Lennard-Jones model of atoms during the process of crystallization are described in Chapter 6. Chapter 7 presents conclusions and some observations, as well as outlines future work.

3. The Methodology Based on the Voronoi Network

To represent the liquid structure and to further study its structural heterogeneity during the process of liquid crystallization, we define the *Voronoi network*. The Voronoi network is a network of edges and vertices of all Voronoi polyhedra in a given system built on atomic centers (see Fig. 1). Each vertex (site) of the Voronoi network in 3D is a common vertex of four Voronoi polyhedra, originated by four atoms (three atoms in 2D). These atoms define a Delaunay simplex. In other words, each site of the Voronoi network is associated with a Delaunay sim-

plex, and, hence, any characteristic of a simplex can be attributed to this site. Each edge (or bond) of the Voronoi network, connecting a pair of sites, is shared by face-neighboring simplexes, i.e. simplexes that have the three atoms in common. Thus, the Voronoi network naturally establishes the neighboring relationship among Delaunay simplexes.

It is not a hard task to compute the Voronoi network for a system of atoms (see Okabe [19] for additional details). The information essential for construction of Voronoi network can be represented by array {D}, containing coordinates of vertices, and the table of their neighborhood {DD}. So, the Voronoi network contains geometric information about spatial arrangement of the atomic centers. To complement it with physical information, we attribute each vertex of the Voronoi network by a numerical measure. This data is stored in an array {C}. Such value may be, for example, a volume of a simplex, a radius of a sphere enclosing simplex [17], or a measure of shape of the simplex (see below). Note, that edges of the network can be also attributed with physical information. This approach can be useful for studying empty inter-atomic space. This aspect of coloring of the Voronoi network is also discussed in other works (see [1, 16]).

4. Simplex Form Measures

Tetrahedron and *octahedron* are the two local configurations of atoms that are typical in dense packing of spheres. The identification of those configurations (and clusters formed from them) is at the core of our attention. Difficulties in such analysis arise from the fact that in computer models (and even in real physical samples) there are no perfect configurations. Even in a crystal, atoms are always displaced from the sites of a crystal lattice due to the temperature fluctuations. Thus, it is necessary to introduce a quantitative measure, which will allow to relate a simplex to a given ideal form.

4.1. Tetrahedron

Tetrahedral configuration (Fig. 2a) is the densest local packing of four spheres. In addition, this configuration is the most favorable for spherical-symmetric potentials of interatomic interaction. Thus the good tetrahedra (close to the perfect configuration) are present in all dense systems of spherical particles. For identification of such configurations, we proposed to use a measure **T**, called *tetrahedricity* [15].

DEFINITION 2. *Measure* **T** (tetrahedricity) *is defined as the variance of the lengths of edges of a given simplex and computed as*:

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

where e_i *and* e_j *as the lengths of the* i*-th and* j*-th edges, and* $\langle e \rangle$ *is the mean edge length for a given simplex.*

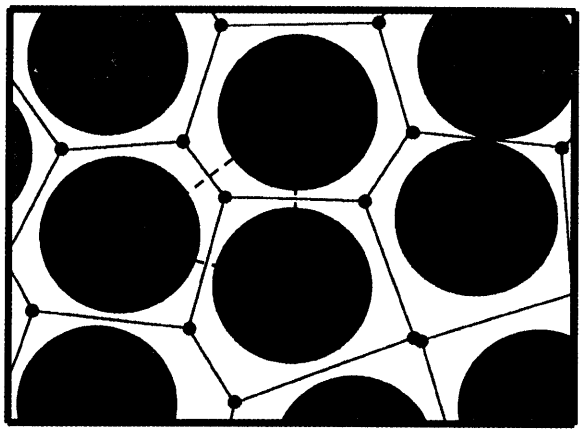

Fig. 1. The *Voronoi network* in 2D: a network of edges and vertices of the Voronoi polyhedra (solid lines). The *Delaunay simplex* is a triangle (tetrahedron in 3D) defined by atoms, which are incident to a given vertex of the Voronoi network (dashed lines).

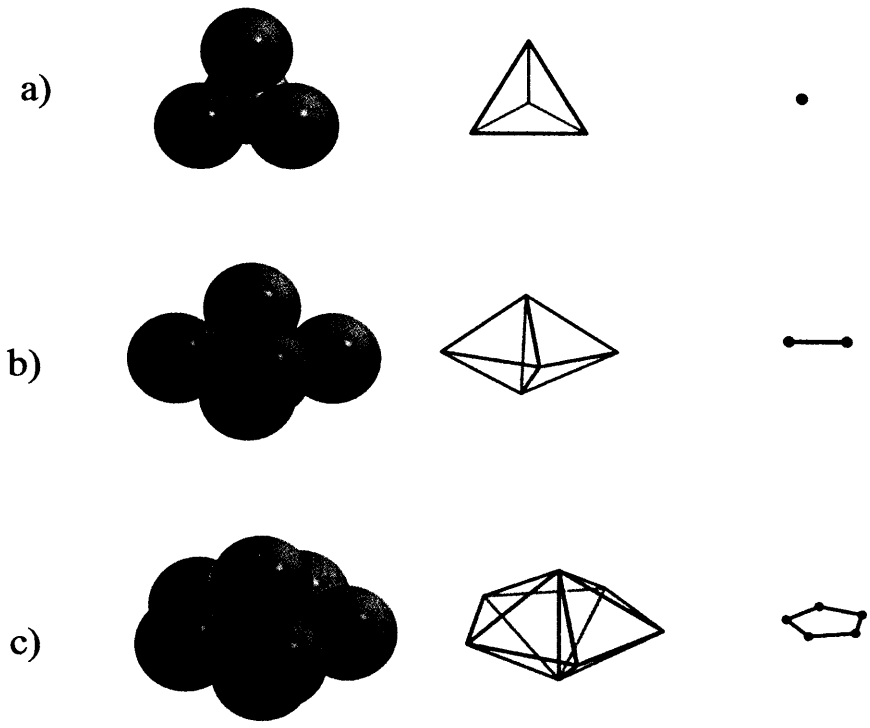

Fig. 2. Examples of clusters comprised of good adjacent tetrahedra. A single tetrahedron (a), a pair of adjacent tetrahedra forming a triagonal bipyramid (b), five tetrahedra forming a pentagonal bipyramid (c). At the right, representation of these clusters on the Voronoi network, see the text.

Note that in the above definition the coefficient 15 corresponds to the number of times the difference between edges lengths $(e_i - e_j)$ is computed and added together. The good tetrahedral configurations of atoms in a packing can be found as the Delaunay simplexes with value of **T** close to zero. Fig. 3b illustrates application of the proposed measure. We analyze a small model of crystal with 265 atoms, obtained by the Monte-Carlo method from the liquid phase. We show the arrangement of atoms inside the box with periodic boundary conditions (Fig. 3a) and the Voronoi network vertices with small values of **T** (Fig. 3b).

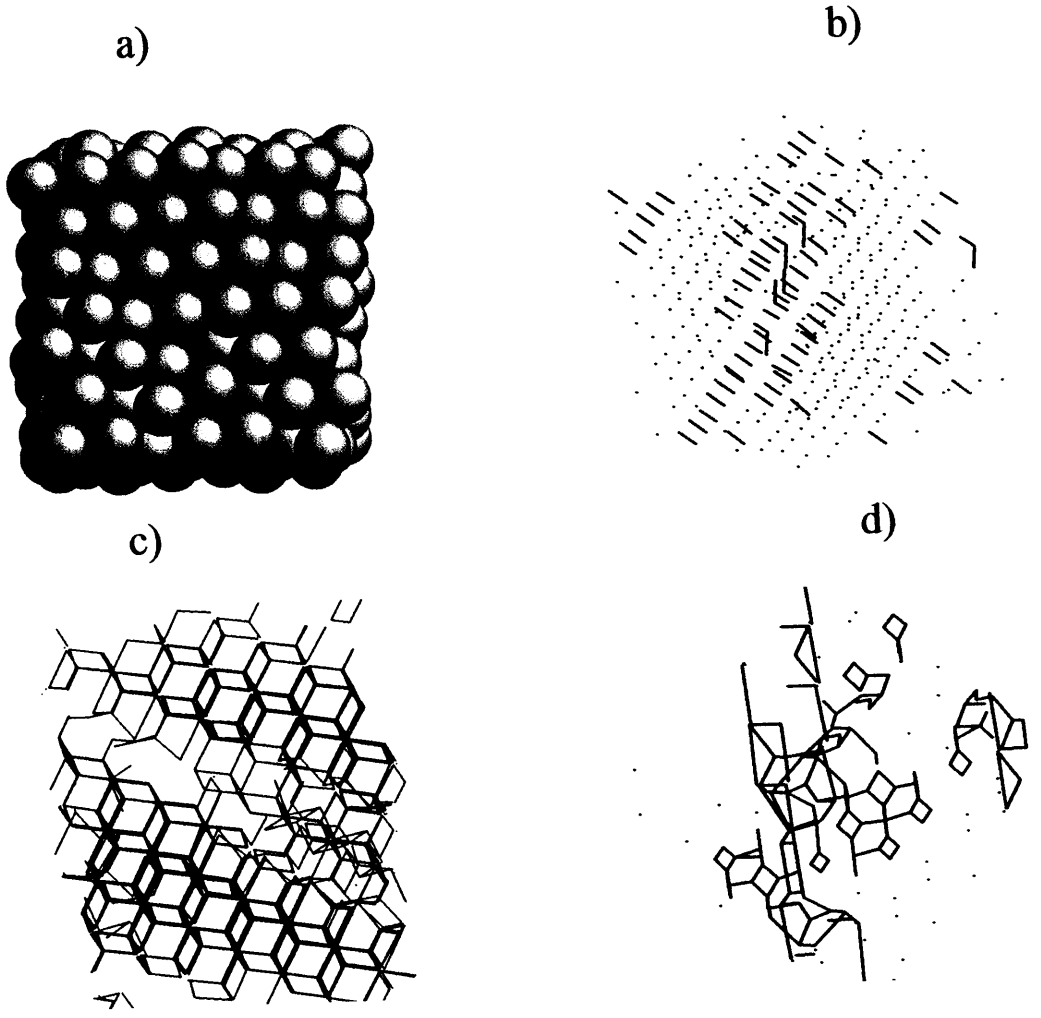

Fig. 3. Model of crystallized sample of Lennard-Jones atoms (a), and various coloring of its Voronoi network. T-coloring of the Voronoi network, sites correspond to good tetrahedral with $T < 0.01$ (b). S-coloring of the Voronoi network, sites corresponding to Delaunay simplexes typical for crystalline structures, $S < 0.008$ (c). S-coloring illustrates defects in the structure, $S > 0.012$ (d). Edges of the network connect nearest colored sites.

DEFINITION 3. *The procedure of selecting good tetrahedral configurations is called a* T-coloring of the Voronoi network [16, 17].

This crystal is not perfect, however rows of isolated sites in Fig. 3b show that it contains areas with the *Face Centered Cubic* (*FCC*) structure. Tetrahedral configurations in FCC do not share faces. Pairs of adjacent tetrahedron are identified by rows of short parallel segments (see Fig. 2b). Such configurations are typical for another dense structure: *a Hexagonal Close Packing* (*HCP*).

The presence of these two densest structures in one crystal sample is a known fact and is related with the stacking faults of crystalline planes in the model. At the same time there are other defects in our model (see below). More complex configurations of adjacent tetrahedra are typical for dense non-crystalline packings (see, for example, [17]). They form irregular branchy clusters and pentagonal bipyramids (Fig. 2c).

4.2. Quartoctahedron

The analysis of octahedral configurations is more complex since we need to consider six atoms. This configuration is not simplicial, moreover, it is degenerated, i.e. all six atoms belong to same circumsphere. However, as a result of even a slightest distortion, the configuration is divided into simplexes that can be analyzed in a usual manner. The resulting simplexes represent quarters of octahedron (see Fig. 4) and we refer to this configuration as *quartoctahedron*. A perfect quartoctahedron has one edge which is $\sqrt{2}$ times longer than the others. Value of measure **T** for such simplex is equal to 0.057, however, this measure cannot be used for identification of quartoctahedra due to the fact that many other simplexes may also correspond to this measure. For unique identification of quartoctahedra a new measure **Q** was proposed [15].

DEFINITION 4. *Measure* **Q** (quartoctaherdisity) *is defined as*

$$Q = \sum_{\substack{i<j \\ i,j\neq m}} (e_i - e_j)^2/10\,\langle e\rangle^2 + \sum_{i\neq m} (e_i - e_m/\sqrt{2}\,)^2/5\,\langle e\rangle^2.$$

This measure is very similar to measure **T**, only now the computation of variance of edge lengths is taken into account that one edge is $\sqrt{2}$ times longer than the others. Thus, the coefficients in the above formula correspond to computing the difference between shorter edges ten times and the difference between a short and the longest edge e_m five times. To compute **Q**, the longest edge e_m of a simplex needs to be found first, and then the calculation is carried out according to the above. It is obvious, that for almost perfect quartoctahedron, the value of measure **Q** approaches zero. The inverse is also true.

4.3. Simplex Kizhe

It is necessary to note that at the certain displacement of vertices the octahedron can be subdivided not on four, but on five simplexes [16, 21]. The four atoms located on a plane form the fifth simplex. Such subdivision occurs seldom and is caused by a configuration where two atoms on each ends of a diagonal of a square are elevated above a plane. Such simplex was found in [21] and was named

simplex Kizhe. To take into account occurrence of such simplexes, measure **K** was introduced. It is based on the same principle as measure **Q**, taking into account that in the simplex which resembles a flat square, two opposite edges have lengths $\sqrt{2}$ times longer than the other four edges.

DEFINITION 5. *Measure* **K** (Kizhe) *is defined as*

$$K = (e_m - e_n)^2/\langle e\rangle^2 + \sum_{\substack{i<j \\ i,j\neq m,n}} (e_i - e_j/\sqrt{2})^2/6\,\langle e\rangle^2 + \sum_{i\neq m,n} \left((e_i - e_m/\sqrt{2})^2 + (e_i - e_n/\sqrt{2})^2\right)/4\,\langle e\rangle^2$$

For a simplex that degenerated into a square, the value of measure **K** is equal to zero. At small distortions value **K** remains small. In order to compute the measure, edges e_m and e_n are selected as a pair of the longest opposite edges of a simplex.

When an octahedral configuration is divided on four quartoctahedra, it is represented on the Voronoi network by a small quadrangle (Fig. 4a). This quadrangle, as octahedral configuration approaches the perfect form, degenerates into a point. As experiments show, the probability of occurrence of Kizhe simplex in computer models of the densest crystals is less than a fraction of a percent. However when it arises, instead of a closed quadrangle two short segments result (pairs of quartohedra are separated by Kizhe simplex). If in this case we also color the network sites whose value **K** is small, the octahedral configuration will be represented by a cluster resembling a bow, also shown in Fig. 4a.

5. Determination of Simplexes Typical for FCC and HCP Lattices

We now describe a novel approach for revealing embryos of a crystalline phase. We need to solve the problem of simultaneous identification of all simplex forms typical for a crystal. To assist with this task, a special measure **S** is introduced.

DEFINITION 6. *Measure* **S** (suitability measure) *is defined as*

$$\mathbf{S} = \min(\mathbf{T}, \mathbf{Q}, \mathbf{K}),$$

where **T**, **Q** *and* **K** *are the tetrahedricity, the quartoctaherdisity and Kizhe measures.*

It is obvious that value of **S** is small if one of the specified measures is small. Thus Delaunay simplexes, typical for the most dense crystal structures, can be identified using this measure.

Fig. 3c illustrates S-coloring of the Voronoi network for our model. Coloring of the vertices with values $S < 0.008$ allows to identify 75% of "crystalline" simplexes. Fig. 3c shows connected compositions of rhombuses and trapezes. The former are typical for FCC structure, the later are common in HCP structure. It is worth noticing that these rhombuses and trapezes are in fact faces of Voronoi polyhedra of the corresponding structures. Fig. 5 shows local configurations of atoms, con-

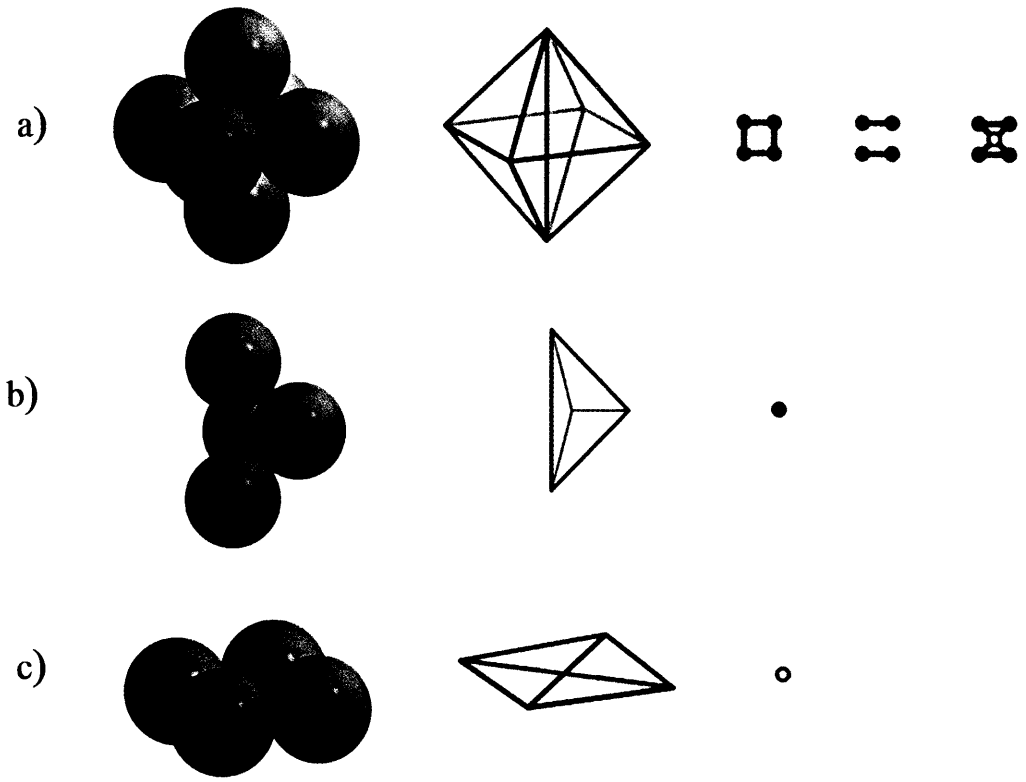

Fig. 4. Octahedral configuration (a) and comprising simplexes: quartoctahedron (b), and simplex Kizhe (degenerate square) (c). The corresponding clusters of Voronoi network are shown on the right.

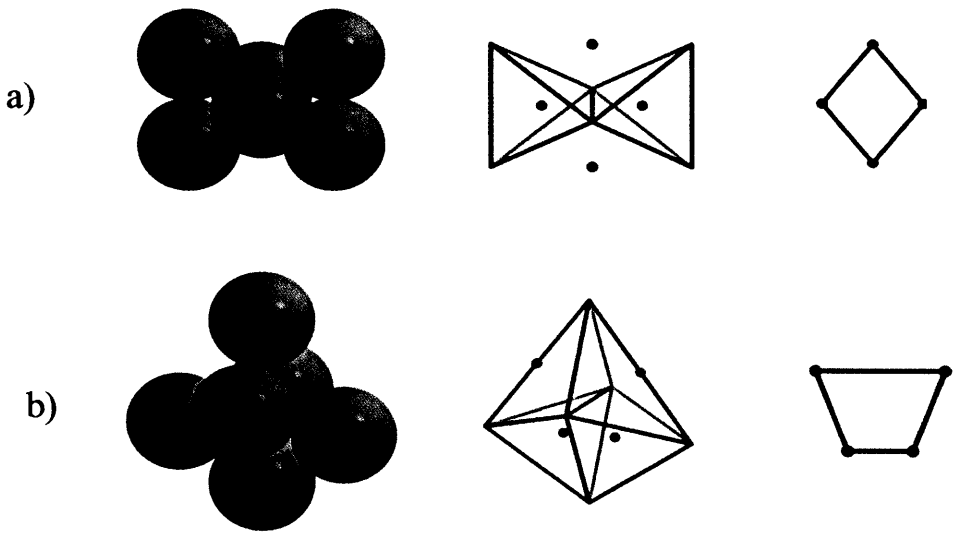

Fig. 5. Characteristic configurations from tetrahedra and quartoctahedra for FCC (a) and HCP (b) structures, and corresponding clusters of the Voronoi network (right).

sisting of tetrahedra and quartoctahedra in the crystals. Note that some of these quadrangles might have their vertices "cut off", i.e. they can in fact be pentagons or hexagons. The Voronoi network sites corresponding to octahedral configurations can be shown as small quadrangles or bows. Figure 4 does not clearly shows it, since octahedral configurations in the given model are close to perfect. Nevertheless, applying S-colouring, areas with crystalline structures become visible as clusters of rhombuses and trapezes.

Except for simplexes with close to perfect form, there can be other strongly deformed simplexes in the model. Such simplexes can be used for the analysis of defects in models of crystalline phase. Fig. 3d shows clusters of such "atypical" simplexes, having the largest value of measures **S** ($S > 0.012$). Note that "defective" simplexes can have regular form, which is rather different from regular crystalline simplexes. A regular behavior of some clusters in Fig. 3d confirms it.

6. Experimental Results

We now apply the above methodology to the Lennard-Jones model of atoms during the process of crystallization, obtained by Monte-Carlo method. The model contains 7000 atoms in a cube with periodic boundary conditions. First, we consider the behavior of the pair correlation functions $g(r)$ for three configurations of the model. This function shows the probability to find an atom at distance r from

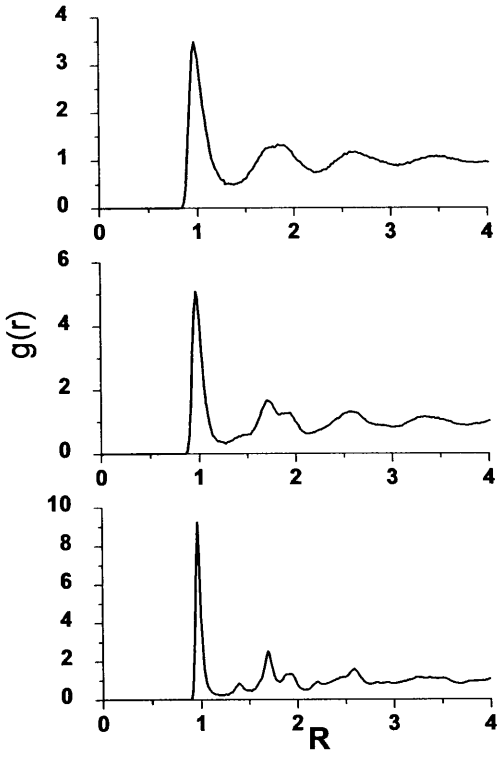

Fig. 6. Pair correlation functions $g(r)$ at different stages of crystallization: a) a non-crystalline (liquid) phase, b) an amorphous phase, an initial stage of crystallization, c) significant crystallization.

another atom of the model. To compute the pair correlation function, all mutual distances between pair of atoms are computed and plotted.

The results are shown in Fig. 6. First observation that can be made is that the structural transformation of the model corresponding to the process of crystallization take place. The first sample belongs to a non-crystalline (liquid) phase, $g(r)$ in this case has smooth fading oscillations. The second sample corresponds to an amorphous phase which is characterized by splitting of the second maximum of $g(r)$. However, appearance of a maximum (shoulder) on $g(r)$ at $r = 1.4$ identifies the beginning of crystallization: the occurrence of a significant number of octahedral configurations. The third configuration corresponds to a crystallized sample. The sharp peaks that appeared on $g(r)$ show orderliness of atoms outside the first coordination sphere. However the structure of this sample is still far from perfect.

Now, let us consider clusters on the Voronoi network, identified by T- and S-coloring (see Figure 7). For simplification of the resulting images, we used an idea from the percolation theory. Percolation theory deals with fluid flow (or any other similar process) in random media. We restricted the representation to only cycles of clusters for easy analysis. As can be seen from the figures, T-coloring identifies irregularly located five-membered rings in a liquid phase (Fig. 7a). These rings are typical for all dense non-crystalline systems of spherical atoms (such as simple liquids). S-coloring confirms the non-crystalline structure of the given sample, since the clusters of rhombuses or trapezes are not present in it. Dots on the right image in Fig. 7a correspond to octahedral configurations.

In the second sample (Fig. 7b), we can notice essential changes. First of all, S-coloring reveals clear clusters of rhombuses and trapezes, that uniquely identifies the presence of areas of crystalline structure. T-coloring identifies much more five-element rings, than in the previous case. This is related to increased density of the sample and lower temperature.

Now, let us note the pairs of parallel five-element rings (shown by arrows in Fig. 7). They represent pentagonal prism configuration of atoms also known as *twisted icosahedron* [18]. It is an association of two pentagonal bipyramids (see Fig. 8). The existence of pentagonal prisms seems quite natural since pentagonal bipyramids (Fig. 2c) are typical for all disordered packings of spherical particles. Note, that in a simple liquid they are also possible, but, apparently, are less probable then in amorphous phase (see an arrow on Fig. 7a). The distinctive feature of this structure is that there are square configurations of atoms (semi-octaherda) at its side, which can initiate occurrence of crystal nucleus.

Notice that such pair of five-membered rings is an embryo of a *Bagley structure*. In 1965 Bagley shown how to fill all the space by hard spheres which one axis of fivefold symmetry [3]. The central axis of this structure is the pile of pentagonal bipyramids, and in every of its five sectors is realized a crystalline structure close to FCC.

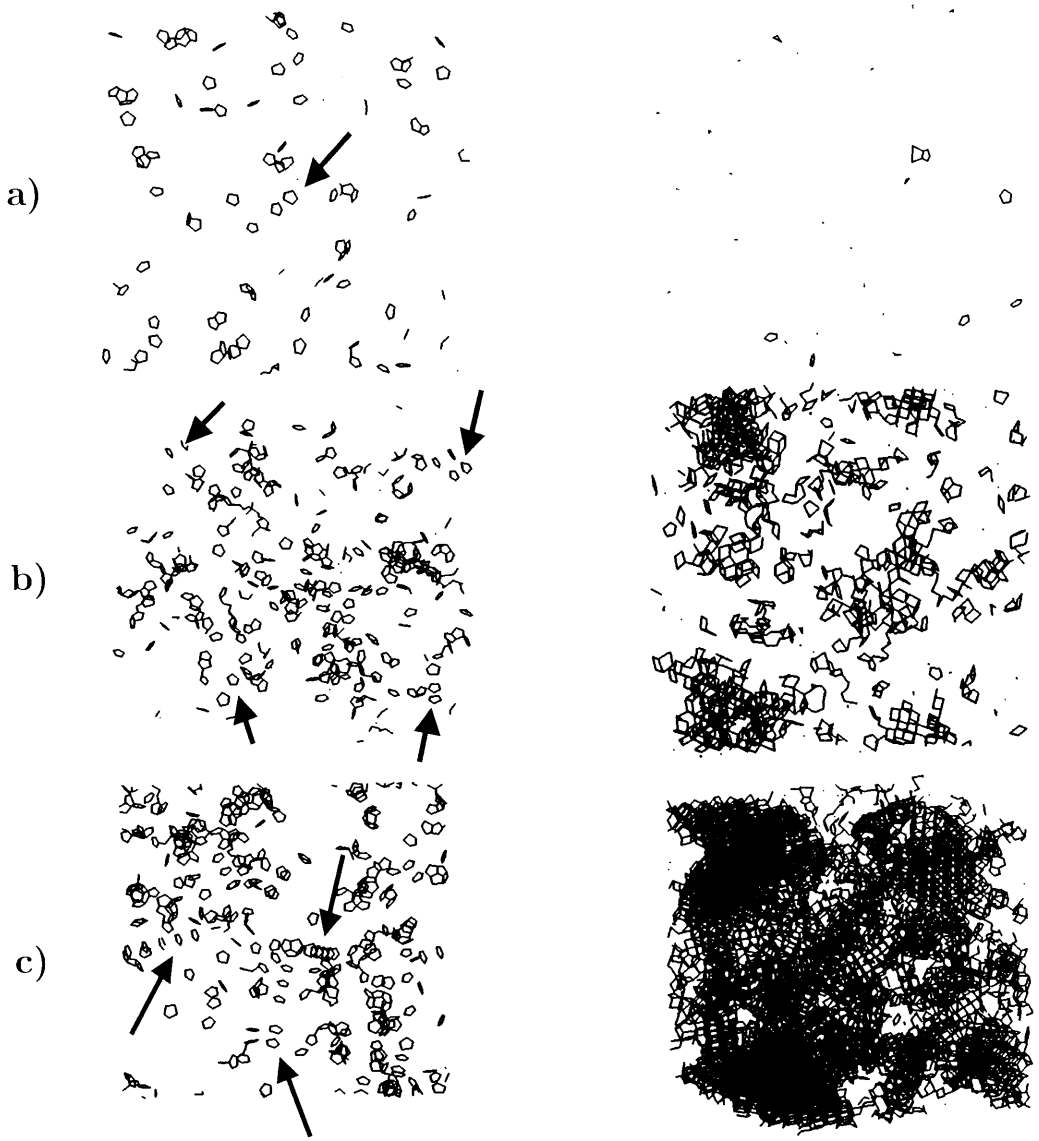

Fig. 7. T-coloring (on the left) and S-coloring (on the right) of the Voronoi network corresponding to Lennard-Jones model of atoms during crystallization process. Sites with values $T < 0.01$ and $S < 0.008$, are colored accordingly. Arrows show pseudocrystalline germs and a nucleus of the Bagley structure in a sample (c).

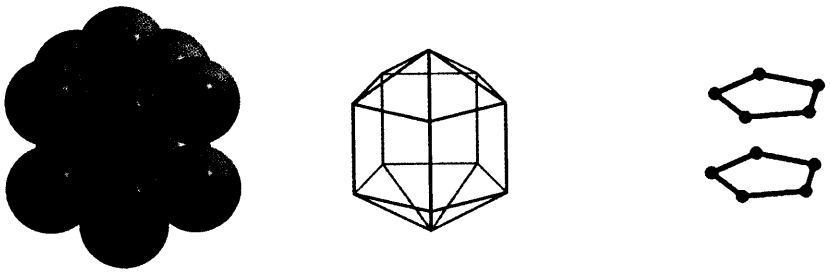

Fig. 8. Pentagonal prisms (twisted icosahedron), a configuration consisted of two pentagonal bipyramids. Square configurations of atoms at the side of this prism can initiate occurrence of crystal nucleus.

The central part of the Bagley structure can be identified by T-coloring of the Voronoi network as a stack of parallel five-membered rings. In Fig. 7c (left) they are marked by arrows. Thus, our computer experiments show that Bagley structures arise during the crystallization of simple liquids. However they can be found only when crystallization process has significantly progressed. S-coloring of the same sample reveals that specified piles are found at the existence of power areas of crystalline structure, Fig. 7c (right).

Structures with fivefold symmetry are known experimentally in physics of small particles and thin films [9]. Crystallographers explain this phenomenon as a multiple twinning. (Term "twinning" means an aggregation of crystalline units breaking the translational symmetry). The mechanism of appearance of such structures is not fully known. Studying this mechanism will help to understand the process of homogeneous nucleation. From Bagley's point of view, an origin of the fivefold symmetry structures is the growth of pentagonal bipyramids that initially present in liquids: configurations shown on Fig. 8 easily arise as liquid is cooling (see Fig. 7a, b), then they start "to acquire" atoms, generating around themselves sector with a crystalline structure. However, crystallographer suggests that the origin is at the crystal nuclei, which randomly merges under specified angles are achieved [9]. A more detailed analysis of molecular-dynamic models is necessary in order to fully understand these mechanisms.

7. Conclusion

Each site of the Voronoi network is associated with the Delaunay simplex, i.e. four atoms, representing the simplest element of the structure. We introduced quantitative measures **T**, **Q**, **K** and **S** for identification of a simplex form. They allow to uniquely recognize simplicial configurations typical for the densest crystalline structures. For studying spatial distribution of such configurations we proposed to colour vertices of the Voronoi network according to a specifically selected measure. The approach is successfully applied to investigation of structural characteristics of system of Lennard-Jones atoms during the crystallization process. The sequence of configurations during crystallization process was analyzed. The structural heterogeneity which arises during the process was also identified.

The proposed model allows to note an important phenomenon, an occurrence of structures with fivefold symmetry (twisted icosahedra), which can act as pseudo-nucleus promoting crystallization. These structures can be formed in a liquid through pentagonal bipyramid association. They contain square configurations of atoms, which are typical for crystalline structures, thus these pseudo-nuclei can serve as initiators of growth of actual crystal nuclei at an initial stage of crystallization. On the other hand, such pseudo-nuclei promote the growth of structures with fivefold symmetry (Bagley structures, pentagonal twinning). They, in turn, can prevent merging of crystalline regions into a uniform crystalline structure. This leads us to an important observation, that together with crystalline nuclei, it is necessary to take into account the abovementioned pseudo-nuclei which can play a

twofold role during crystallization. The question of an origin of the fivefold symmetry structures however needs further investigation and represents a challenging question that we hope to address in the near future.

Acknowledgements. The research is supported by the Grant CRDF No-008-X1, the OTKA Grant, the Canadian Foundation for Innovation Grant and the NSERC Grant.

References

[1] A.V. Anikeenko, M.G. Alinchenko, V.P. Voloshin, N.N. Medvedev, M.L. Gavrilova and P. Jedlovszky, Implementation of the Voronoi-Delaunay method for analysis of intermolecular voids. 4th Workshop Comp. Geometry and Applications, Lecture Notes in Computer Science, Springer-Verlag, LNCS 3045, Vol. III, May 2004, 217–226.

[2] B.G. Bagley, Journal of Crystal Growth, **6** (1970), 323–326.

[3] B.G. Bagley, Nature, **208** (1965), 674–675.

[4] C. Beisbart, M. Kerscher and K. Mecke, Mark correlations: Relating physical properties to spatial distribution. Morphology of Condensed Matter (eds. K. Meche and D. Stoyan), Springer, 2002.

[5] J. Chen, C.M. Li, Zhilin Li and Christopher Gold, A Voronoi-based 9-intersection model for spatial relations. International Journal of Geographical Information Science, **15**, No. 3 (2001), 201–220.

[6] F. Dupuis, J.F. Sadoc and J.P. Mornon, Protein secondary structure assignment through Voronoi tessellation. Proteins: Structure, Function, and Bioinformatics, Wiley Interscience, **55**, No. 3 (2004), 519–528.

[7] J. Finney, Random packings and the structure of simple liquids. Royal Society London, **319** (1970), 479–494, 495–507.

[8] M. Gavrilova and J. Pivovarov, 3D visualization of complex surfaces using dynamic Delaunay tessellation. Workshop on Modelling Morphogenesis and Pattern Formation in Biology, ICCS 2003, LNCS 2660, May 2003, 718–728.

[9] H. Hofmeister, Forty years study of fivefold twinned structures in small particles and thin films. Cryst. Res. Technology, **33** (1998), 3–25.

[10] C.S. Hsu and A.J. Rahman, Crystal nucleation and growth in liquid rubidium. Journal of Chemical Physics, **70** (1979), 5234–5240.

[11] K.F. Kelton, in Solid State Physics (eds. H. Ehrenreich and D. Turnbull), Academic, Boston, Vol. 45, 1991, 75.

[12] D.-S. Kim, Y. Cho, D. Kim and C.-H. Cho, Protein structure analysis using Euclidean Voronoi diagram of atoms. Proceedings of the 1st International Symposium on Voronoi Diagrams in Science and Engineering, Tokyo, Japan, September 2004.

[13] K. Kobayashi and K. Sugihara, Crystal Voronoi diagram and its applications to collision-free paths. 1st International Workshop on Computational Geometry and Applications, Computational Science ICCS 2001, Lecture Notes in Computer Science, 2073, 2001, 738–747.

[14] Eds. S. Komarneni, J.C. Parker, H. Hahn, MRS and P.A. Warrendale, Nanophase and Nanocomposite Materials. 2000.

[15] N.N. Medvedev and Yu.I. Naberukhin, Shape of the Delaunay simplexes in dense random packings of hard and soft spheres. Journal of Non-Chrystalline Solids, **94** (1987), 402–406.

[16] N.N. Medvedev, Voronoi-Delaunay Method for Non-Crystalline Structures. SB Russian Academy of Science, Novosibirsk, 2000 (in Russian).

[17] Y.I. Naberukhin, V.P. Voloshin and N.N. Medvedev, Geometrical analysis of the structure of simple liquids: percolation approach. Molecular Physics, **73**, No. 4 (1991), 917–936.

[18] B. O'Malley and I. Snook, Crystal nucleation in hard sphere system. Phys. Rev. Lett., **90**, No. 8 (2003).

[19] A. Okabe, B. Boots, K. Sugihara and S. Chin, Spatial Tessellations: Concepts and Applications of Voronoi Diagrams. Chichester, John Wiley, 2000.

[20] M. Serrano, G. de Fabritiis, P. Español, E.G. Flekkoy and P.V. Coveney, Mesoscopic dynamics of Voronoi fluid particles. J. Phys. A: Math. Gen., **35** (2002), 1605–1625.

[21] V.P. Voloshin, Y.I. Naberukhin and N.N. Medvedev, Can various classes of atomic configurations (Delaunay simplexes) be distinguished in random dense packing of spherical particles?. Molecular Simulation Journal, **4** (1989), 209–227.