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Approach for the structure analysis of complex molecular systems at computer simulation

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Abstract

The structure of complex inhomogeneous systems is a current problem in the physics of liquids, glasses, polymers, molecular biology, and material science. To understand the physical properties of such materials, one should study the structure in "micro" and "macro" levels, which demands a unified rigorous approach for structure investigations. We demonstrate that the Voronoi–Delaunay technique, which is well known in mathematics and in computer simulations, can be used for this purpose. The Voronoi–Delaunay tessellation contains complete information about the structure of a computer model. The method is applied for studying the intermediate range order to show that the behavior of the so-called prepeak in the structure factor is defined by a motif of spatial distribution of voids in the model. A large model of dense packing of spherical atoms in the process of crystallization from non-crystalline phase is analyzed. The extended linear defects of the diverse types are revealed. Investigation of the free volume distribution in the lipid bilayer in water is carried out. The results obtained can help for understanding a mechanism of diffusion of small molecules across lipid membranes.

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1. Introduction

Complex molecular and heterogeneous materials are objects for present day computer simulations. A typical molecular dynamic model of such systems contains tens of

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thousands of atoms. The models should be large enough because of large-scale structure peculiarities in such materials. Different scale levels characterize the structure in this case. To study the macroscopic properties, we should take into account both the local order (nearest surrounding of atoms) and the "extended" structure. A known example of different length scale manifestation is the so-called prepeak in the structure factor of some glasses and liquids obtained in diffraction experiments. This phenomenon was a challenge for theorists for years to explain the nature of this rather sharp peak for the completely non-crystalline materials; see for example [1] and references therein. The problem of the structure of heterogeneous materials treats a wide variety of physical and chemical properties [2]. The analysis of the structure of such systems needs a unified rigorous means of characterizing the structure in "micro" and "macro" levels. In this paper we show that the Voronoi–Delaunay technique, which is well known in mathematics and some fields of physics, can be a base for the approach [3,4].

2. The method

The Voronoi–Delaunay method is based on the general mathematical theorems about division of space between centers in an ensemble of discrete centers. The centers (atoms) can be distributed arbitrarily in space: orderly or disorderly, homogeneously or non-homogeneously [3,4]. Therefore, the method is claimed for studying the structure of liquids and glasses, where the approaches of crystallography do not work, and for any heterogeneous material with different structure scales.

The main geometrical constructions of the method are the Voronoi polyhedra and Delaunay simplices. They have been used in computer simulation for structure characterization of the local order of atoms for many years, see e.g. Refs. [4,5]. Usually they are calculated separately to get a histogram of a statistical distribution of topological or metrical characteristics of local order. However, to study the whole structure of a system, one should use the whole Voronoi–Delaunay tessellation, Fig. 1. In this case, one can analyze the spatial distribution of specific atomic configurations to study extended structure correlations. A helpful construction for this work is the Voronoi network: the network of edges and vertices of the Voronoi polyhedra. This network permeates through the systems, and can be a background for studying structural motifs in the model. Every vertex of the Voronoi network is simultaneously the circumcenter of a Delaunay simplex. The Voronoi network lies "in the depth" of empty space between atoms, and thereby can also be used to study the free volume distribution.

There are different algorithms for calculation of the Voronoi polyhedra, Delaunay simplices and the Voronoi network [3,4]. Input data for this calculation is a set of coordinates of atoms for a given atomic configuration. The Voronoi network is defined by a set of coordinates of the Voronoi vertices (array {D}), and a table of connectivity of the vertices (array {DD}).

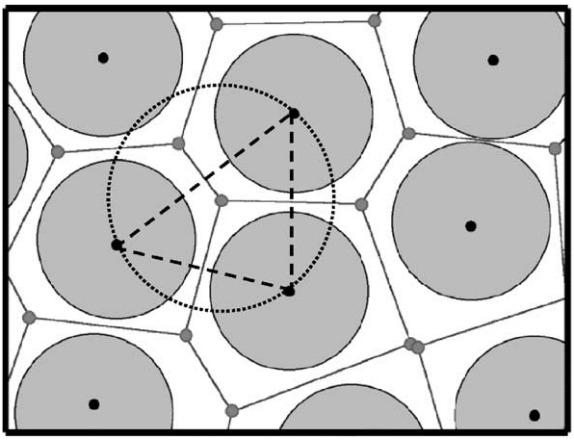

Fig. 1. Voronoi–Delaunay tessellation of a 2D atomic system: (a) *The Voronoi polyhedron* for a given atom is a volume of space, all points of which are closer to a given atom than to any other atom of the ensemble (polygons around disks). (b) *The Delaunay simplex* is a triangle (tetrahedron in 3D) defined by atoms, the circumsphere of which is empty, i.e., there are no other atomic centers inside the circumsphere (dashed lines). (c) *The Voronoi network* of a given atomic system is a network of edges and vertices of the Voronoi polyhedra (solid lines and points between atoms).

3. Investigation of the intermediate range order

Recently, a simple procedure to prepare models with a given intermediate order was proposed [6]. The idea is to remove some atoms from an original packing to get a new model with extra voids. Using different rules for removing atoms, one can get models with different spatial distribution of extra voids, and study their physical manifestation.

The densest non-crystalline packing of 27,000 Lennard-Jones atoms generated by the Monte Carlo method in a model box with periodic boundary conditions is used as an original configuration. The atoms which are the closest to the sites of a given "stencil" are removed. Any system of sites with a desired spatial distribution can be used as a stencil. Fig. 2 demonstrates a model obtained after removing 15% of atoms from the original packing. A stencil used here is a system of centers of the densest disordered packing of spheres with radius three times larger than radius of atoms in the original packing. So the new length scale has been added in the model. The structure factor of the model is like the one for the original model (Lennard-Jones glass): clear main peak and damping oscillations with increasing q. The only difference is a clear prepeak at the small value of q, Fig. 3 (on the top). The position of the prepeak (one-third of the position of the main peak) corresponds to the new length scale inserted in the model. It is an interesting and non-trivial result. Indeed the extra voids in the model are very diverse every one is a result of removing a different number of atoms (one or a few), and the remaining atoms are not moved from their original positions. So there are no obvious reasons to get a sharp peak in the structure factor. However, the calculation demonstrates earnestly that the generated long-distance correlations manifest a sharp peak, Fig. 3 (on the top).

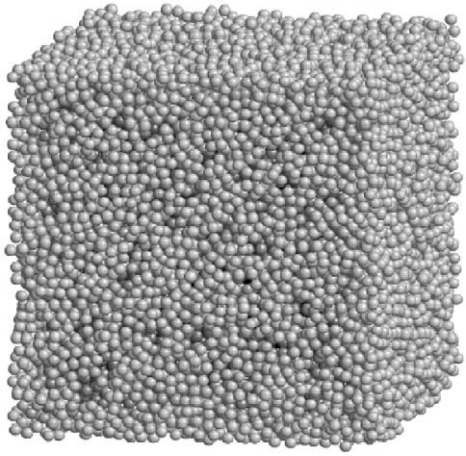

Fig. 2. Model with an intermediate order. Dense packing of spherical atoms with extra voids distributed according to a given motif, see text.

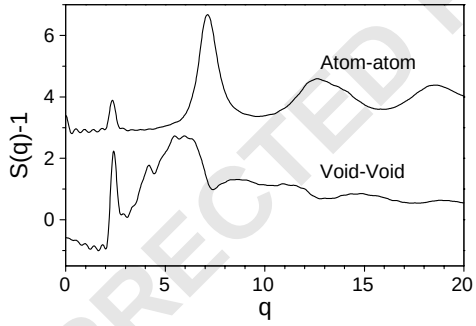

Fig. 3. Structure factors of the model shown in Fig. 2. Usual atom–atom structure factor (on the top), void–void structure factor (at the bottom), see text.

The structure factor calculated for the system {D} of the model is shown in Fig. 3 (at the bottom). (It is a Fourier transformation of the radial distribution function of the Voronoi vertices, see Fig. 1.) This function characterizes distribution on empty space in the model, because points of {D} lie in the depth between the atoms. A clear sharp peak in this void–void structure factor coinciding with the prepeak in the atom–atom structure factor indicates that the intermediate range order is conditioned by voids. Thus the Voronoi–Delaunay method helps us to ascertain a role of voids in the development of the intermediate range order.

4. Investigation of lineal defects in model of a dense crystal

The other example of application of the Voronoi–Delaunay method is analysis of the model of crystal with defects. The model understudied contains 16,382 atoms in the box with periodic boundary conditions. It was prepared by molecular dynamic relaxation with Lennard-Jones potential starting from the model of hard spheres packing generated in Ref. [7], where crystallization of a large disordered system of hard spheres was studied. The model obtained is a dense crystal with regions of f.c.c. and h.c.p. structure, Fig. 4. Now we demonstrate the Voronoi–Delaunay approach for analysis of the structure at the border of these regions, where a crystalline order is broken.

For investigation of extended structure peculiarities, one can study spatial distribution of Delaunay simplices of a specific shape. Studying defects in a crystal, it is natural to work with simplices, whose shape is atypical for a given crystalline structure. Location of such "imperfect" simplices reveals defects in the model. This approach was used in Ref. [8], where defects in a crystal after plastic deformation were studied in the computer simulation. A quantitative measure of shape can be easily defined to select the simplices, see e.g. Refs. [9,4].

Only a few percent of the Delaunay simplices in the model in Fig. 4 have shape, which can be marked as atypical for the given crystalline structures. We used 1.2% of the more imperfect simplices, and display their positions inside the model box, see Fig. 5. As explained in Fig. 1, the position of the Delaunay simplex is defined by the Voronoi vertex (unfortunately, these points are invisible in the scale of Fig. 5). Neighboring Voronoi vertices corresponding to the imperfect simplices are connected by line (i.e., the Voronoi edge between such vertices is drawn). So, aggregates of the Delaunay simplices of a given type are displayed as clusters on the Voronoi network. We see these clusters of Fig. 5. The approach to show structure motifs on the Voronoi network was used for analysis of the structure of liquids and glasses in Ref. [10].

The clusters of imperfect simplices are very expressive, Fig. 5. Except for some complex aggregates one can see distinct clusters like straight lines, stairs, and chains. Knowing atoms in the simplices, one can obtain an arrangement of atoms corresponding to given clusters, Fig. 6. Line-type defect is a pile of triangles of atoms. Stairs-type defect is a pile of rhombs. Atoms in these piles are located one after another, which is unusual for the densest crystals, where atoms of one plane are located in the cavity between atoms of another plane. These defects are very stable and remain during a long period of relaxation of the model. The chain-like cluster is a tube of fives of atoms. It is an amusing result: we see "a five folder order " construction in the crystal.

Note that we have obtained only linear extended defects. They are nuclei and intersections of dislocations presented in the model. The dislocations change alternation of the crystallographic planes of atoms, and define flat borders between regions of f.c.c. and h.c.p. structures, see Fig. 4. However, we do not see the flat defects in Fig. 5. It is because the Delaunay simplices in these dislocations have the typical shape for the f.c.c. and h.c.p. crystals and therefore have not been detected here.

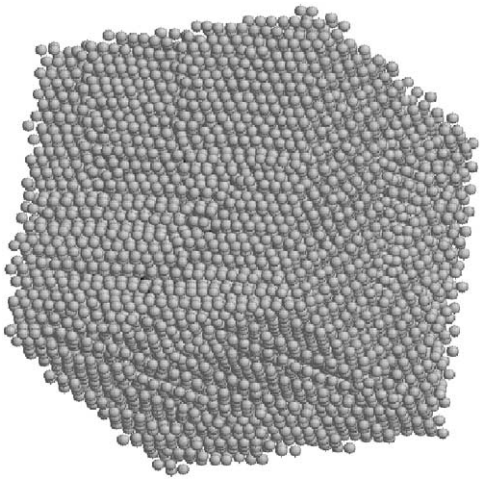

Fig. 4. Model of crystalline phase of 16,386 Lennard-Jones atoms. Breaking of interchanging crystalline planes is visible. The model contains regions of f.c.c. and h.c.p. structures.

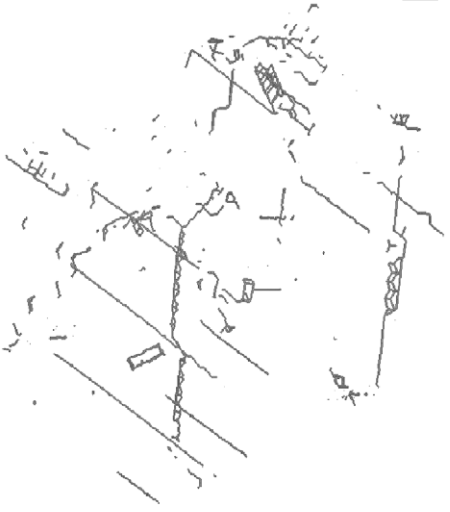

Fig. 5. Distribution of defects inside the model shown in Fig. 4. Clusters indicate the location of the Delaunay simplices, whose shape is atypical for given crystalline structures, see text.

Thus, linear defects in the molecular dynamic model of dense crystalline phase are revealed. For this purpose the spatial distribution of the Delaunay simplices, whose shape is atypical for the crystalline structure, was investigated.

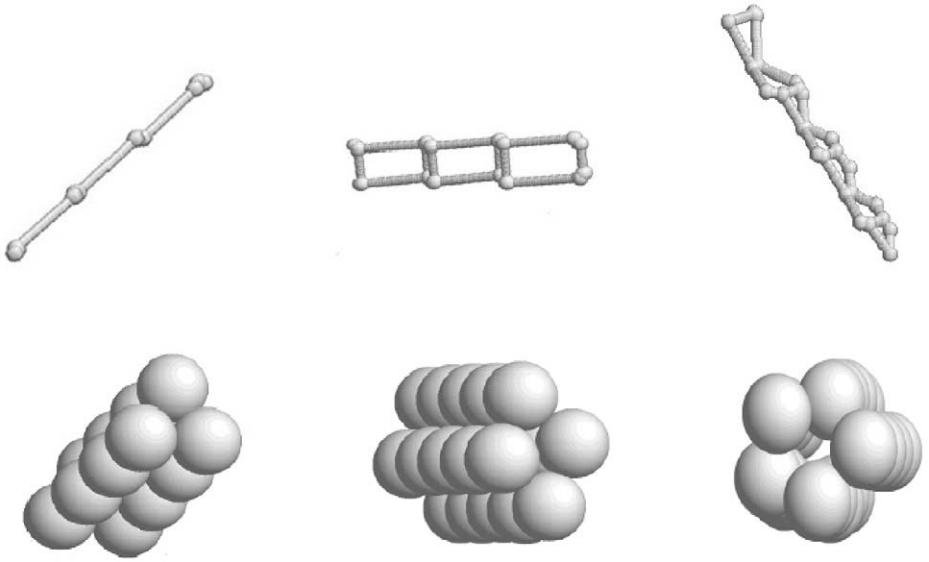

Fig. 6. Clusters on the Voronoi network for imperfect Delaunay simplices from Fig. 5 (on the top), and corresponding atomic configurations (at the bottom). Line-type (left), stairs-type (center), and chain-like defects (right).

5. Investigation of free volume distribution in a lipid bilayer

The molecular dynamic model of a lipid bilayer in water was generated by Schmelter and Geiger [11]. The model box with periodic boundary conditions contains 32,125 atomic units: 200 molecules of phospholipid DPPC (dipalmitoyl-*sn*-glycero-phosphatidylcholin) with 130 atomic units, and 6125 water molecules. The van der Waals radii of the atomic units were used in the analysis. From a mathematical point of view, this complex molecular system is also an ensemble of spheres. But it has some differences in comparison with the ensembles of uniform spheres discussed above. At first, the radii of the spheres are different: the solvent and lipid molecules consist of different atoms. It is an important point for our problem to study free volume between atoms. Second, some spheres of our ensemble are overlapping: the distance between centers of chemically bonded atoms is less than the sum of their van der Waals radii. The methods of taking all of these complexities into consideration are known and discussed in detail in Ref. [4].

Distribution of the largest empty spheres inscribed between atoms gives the simplest and obvious picture of the free volume inside the model. All empty spheres can be found at the calculation of the Voronoi network of the model. (Remember, every Voronoi vertex is a center of one of these inscribed spheres.) We carried out analysis of empty spheres with radius greater than 1.4 A. (It is a radius of water molecule, so we look at voids where a probe-like water molecule can be placed.) It was found that a number of such spheres are located in the mid of the bilayer: between hydrophobic

ends of the lipids. It is natural that the tails of the lipids do not pack densely. A number of large empty spheres are also in bulk water. It is known that water has a low dense structure with cavities of the size of the water molecule. A more unexpected result is the absence of large voids in the region of the hydrophilic ends of lipids (region of contact of bilayer with bulk water). This fact can be connected with strong interaction of atoms in this region, but it cannot exclude large voids a prior. However, the recent molecular dynamic calculation of Schmelter and Geiger demonstrates that water molecules penetrate into this region. Seemingly, these molecules fill in all large voids in this area [12]. All this information is helpful for understanding the mechanism of diffusion of small molecules across lipid membranes.

6. Conclusion

The Voronoi–Delaunay method is an extremely helpful tool for analysis of the structure of computer models of complex molecular systems. It enables one to study both local order of atoms and extended structure correlations of atoms, as well as voids between atoms.

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