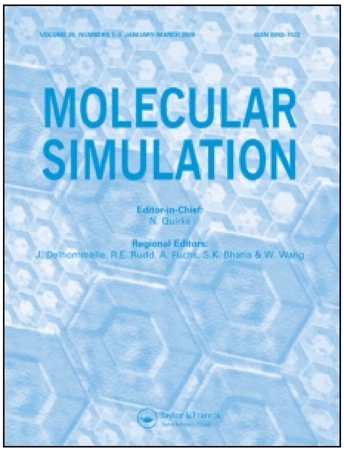


Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Can Various Classes of Atomic Configurations (Delaunay Simplices) be Distinguished in Random Dense Packings of Spherical Particles?

V. P. Voloshin[a]; Yu. I. Naberukhin[a]; N. N. Medvedev[a]
[a] Institute of Chemical Kinetics and Combustion, Novosibirsk, USSR

To cite this Article Voloshin, V. P. , Naberukhin, Yu. I. and Medvedev, N. N.(1989) 'Can Various Classes of Atomic Configurations (Delaunay Simplices) be Distinguished in Random Dense Packings of Spherical Particles?', Molecular Simulation, 4: 4, 209 — 227

To link to this Article: DOI: 10.1080/08927028908022364

URL: http://dx.doi.org/10.1080/08927028908022364

Molecular Simulation, 1989, Vol. 4, pp. 209–227
Reprints available directly from the publisher
Photocopying permitted by license only

CAN VARIOUS CLASSES OF ATOMIC CONFIGURATIONS (DELAUNAY SIMPLICES) BE DISTINGUISHED IN RANDOM DENSE PACKINGS OF SPHERICAL PARTICLES?

V.P. VOLOSHIN, YU. I. NABERUKHIN and N.N. MEDVEDEV

Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, USSR

(*Received February 1989, accepted April 1989*)

One-dimensional and two-dimensional distributions of the characteristics introduced previously for the forms of Delaunay simplices – tetrahedricity and octahedricity – have been investigated in computer models of a crystal, a liquid and an amorphous solid. It has been established that in the absence of thermal perturbations (in the proper structure of the liquid and in an amorphous substance) there exists a distinguishable class of simplices with five almost equal edges and the sixth being longer. This class of simplices named isopentacmons, in turn includes the types of good tetrahedra and good quartoctahedra (a quarter of octahedron). In disordered systems the fraction of tetrahedra relative to quartoctahedra exceeds substantially that in the FCC crystal.

KEY WORDS: Random dense packing, liquid structure, Delaunay simplices.

INTRODUCTION

Computer modelling provides coordinates of all the atoms of model systems at any time. This information is exhaustive but any structural conclusions can hardly be made in disordered systems by analyzing only the atom coordinates. In order to understand the structure of our models, the main structural elements should be chosen and the principles of their mutual arrangement should be determined. The present paper is devoted to further investigations of the Delaunay simplices as the main structural elements reported [1–7] to be a convenient tool for structural analysis.

The Delaunay simplices are tetrahedra with vertices at the centres of four "nearest" atoms, so called geometric neighbours (the atoms whose Voronoi polyhedra have a face in common). Since in disordered systems four polyhedra (the minimum possible number) meet at each vertex of a Voronoi polyhedron such a vertex is equidistant from four geometric neighbours and is the centre of the circumsphere. The centres of these four neighbours are just the vertices of the Delaunay simplex. In other words, each vertex of the Voronoi polyhedron is the centre of the circumsphere of some Delaunay simplex constructed on the atoms the Voronoi polyhedra of which, meet at this vertex.

Thus the Delaunay tesselation of space is the geometric dual of the Voronoi tesselation. Both are fully determined by the configuration of the system atoms and fill space without gaps and overlaps. The structural difference between these tesselations consists in that the Voronoi polyhedron describes the coordination of the nearest atomic environment whilst the Delaunay simplex describes the shape of the cavities between the atoms.

The Delaunay simplices may be constructed without appealing to the Voronoi polyhedra using the following Delaunay theorem on the empty sphere [8,9]: inside the sphere circumscribed around any Delaunay simplex (around the centres of four geometric neighbours) there are no centres of other atoms. This is a significant difference between the Delaunay simplex and an arbitrary simplex, i.e. tetrahedron constructed on any four atoms. The theorem suggests, in particular, that a flat configuration of four atoms fails to be the Delaunay simplex: the circumsphere around them has an infinite radius and always contains other atoms of the system (except for a degenerate case when the centres of four atoms lie on the same circle as in octahedral configuration).

The cavity language is widely used in crystallography. For example, the structure of the FCC crystal is convenient to describe as the packing of tetrahedral and octahedral configurations (cavities). Bernal has shown the models of random dense packed hard spheres to involve also a great number of tetrahedral configurations [10]. A physical reason for this is that the packing of four atoms arranged in form of a regular tetrahedron is the most dense and, consequently, the most favourable energetically. The space, however, cannot be filled by regular tetrahedra only. More loose configurations must be present inevitably.

A question arises as to whether other characteristic atomic configurations except tetrahedral ones, e.g. octahedral, can be distinguished in a liquid. Bernal considered that in a liquid there are only five types of cavity polyhedra including tetrahedron [10]. The edges of the polyhedra are the shortest distances between the atoms. The computer calculations [11–13] indicate, however, a much wider variety of the thus determined polyhedra. Therefore leaving these cavities of an intricate form for future analysis, we are going to treat here the elementary cavities, i.e. the simplicial atomic configurations. Hence, the main problem is whether some other separated types of the Delaunay simplices exist in liquids along with the tetrahedral one.

2. MODELS

The present paper is primarily concerned with the models obtained by the Monte Carlo method (Metropolis algorithm) in the NVT-ensemble with periodic boundary conditions for 108 atoms interacting with the Lennard-Jones potential

$$u(r) = \varepsilon\,[(r_m/r)^{12} - 2(r_m/r)^6].$$

All the results for the crystal have been averaged over five realizations at reduced density $\varrho^* = \varrho r_m^3/\sqrt{2} = 1$, and reduced temperature $T^* = kT/\varepsilon = 0.719$. The results for the liquid have been averaged over ten realizations at $\varrho^* = 0.9$ and $T^* = 0.719$. Each realization contained about 650 Delaunay simplices.

Besides the instantaneous structure (I structure) of the liquid resulting directly from computer experiment we have also studied so-called frozen structures (F structures). Each F structure corresponds to a definite I structure and is obtained from it by an additional Monte Carlo relaxation at 0K. When producing the F structure we aim to eliminate the thermal excitation in atomic configurations of the liquid, i.e. to remove an additional thermic chaos and to reveal the *proper structure* of liquid [14] (other terms - the inherent or hidden structures [15,16]) describing its true topological disorder [14]. For the F structure this aim is achieved by random shifts of each atom towards the local potential minimum.

It is natural to search for the quantitative laws for liquid structure in the proper structures (in particular in the F structure) rather than in the I structure. This is the case with crystallography where the structure laws are formulated for ideal crystals in which the atoms are situated in the local potential minima (i.e. for the proper structure) rather than for the configurations of atoms shifted randomly from their equilibrium positions by thermal perturbations (I structure).

Our procedure for obtaining the F structure ensures a constant acceptance rate, approximately 50%, in the Monte Carlo algorithm. In this case, on freezing, the length of the maximum step decreases rapidly so that in 500–600 moves (per one atom) it reduces to zero. Thus the freezing goes very fast and by 600 moves the walk in the system practically ceases.

We have also employed a well-relaxed molecular dynamics model with periodic boundary conditions for 686 atoms with the Ar^{-12} potential, kindly presented to us by Prof. D.K. Belaschenko (Moscow). The relaxation has been performed by the steepest-descent method along the potential energy gradient with increasing walk step from time to time [17]. This model mimics well the amorphous state, particularly, it reproduces a doublet structure of the second peak of the radial distribution function. The model contains 4116 Delaunay simplices.

As a length unit the position of the potential minimum, r_m, has been taken in models with the Lennard-Jones potential and the position of the first maximum of the pair correlation function — in the Belaschenko model.

3. ONE-DIMENSIONAL CHARACTERISTICS OF DELAUNAY SIMPLICES

In order to distinguish between various classes of simplices it is necessary to choose the characteristics most sensitive to the assumed differences in their form. Let us consider the differences in the form of the Delaunay simplices in the FCC crystal. This crystal contains two cavity types viz. tetrahedral and octahedral. In terms of the Delaunay simplices each tetrahedral cavity corresponds to one simplex in the form of a regular tetrahedron, and each octahedral cavity consists of four Delaunay simplices of a particular form with one edge (octahedron diagonal) being $\sqrt{2}$ times longer than the other five. Such a simplix (a quarter of the perfect octahedron) was named by us quartoctahedron [7].

One of the characteristics allowing us to distinguish between tetrahedra and quartoctahedra is the size of the cavity associated with a given simplex. As a rule, the size is characterized by the radius of the sphere inscribed between four atoms forming the Delaunay simplix. It is more convenient, however, to use the circumradius of the simplex. It is equal to the sum of the atomic and inscribed sphere radii but is independent of the atomic radius value that in the models of soft spheres fails to be determined accurately.

Figure 1 presents the histograms of the distribution of the Delaunay simplex circumradii in various models. This radius is equal to $\sqrt{3/8} \approx 0.612$ for a perfect tetrahedron and to $\sqrt{2}/2 \approx 0.707$ for a perfect quartoctahedron. Hence one may assume that the left lower maximum in the distribution for the FCC crystals corresponds to the distorted tetrahedral simplices and the right higher one – to the distorted quartoctahedra. The other distributions, besides that for the liquid I structure, also

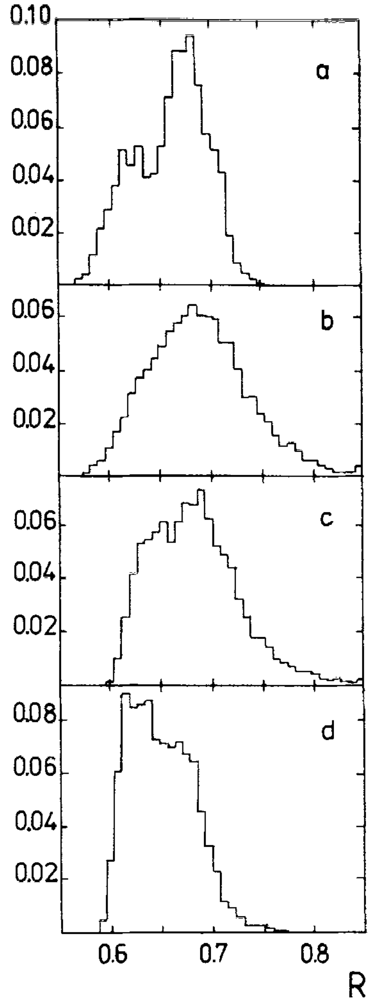


Figure 1. Distributions of the circumradii of the Delaunay simplices.
(a) I structure of FCC crystal; (b) I structure of liquid;
(c) F structure of liquid; (d) the amorphous solid.
The last cell of the histograms sums up here and later the populations of all cells outside the limits of the picture.

display two maxima although less pronounced. Note than in the F structure of the liquid the left maximum supposedly related to the tetrahedral cavities is lower as in the FCC crystal whereas in the Balaschenko model it is substantially higher.

This bimodality of distribution shapes seems to favour the possibility of separating two types of the Delaunay simplices. The question is whether the correlation between circumradius and simplex form is unambiguous. The simplex whose circumradius is approximately 0.6 cannot differ considerably from the regular tetrahedron since the length of simplex edges fails to be much less than unity due to the mutual repulsion of atoms. Thus the left distribution maximum may definitively be associated with the slightly distorted tetrahedra. Alternatively, for high R values, the correspondence in question is ambiguous. The circumradius of about 0.707 may belong not only to the perfect quartoctahedron but also, e.g., to the simplex in which one face has unit edges and three other edges are equal to 1.256. Thus the second distribution mode cannot be related to the Delaunay simplices of a definite form.

Figure 2 shows the volume distributions of the Delaunay simplices. The volumes of perfect tetrahedron and quartoctahedron are just the same. Therefore only one maximum is observed in the FCC crystal distribution as well as in all the others. Of more interest in this case is the presence in all the models of simplices of a very small volume, although in minor amounts.

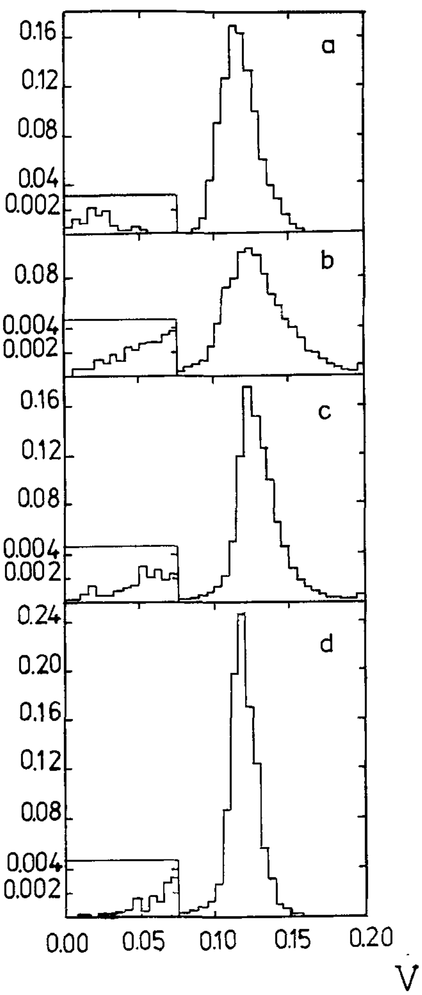


Figure 2. Volume distributions of the Delaunay simplices. In the insert the scale along the ordinate is changed by a factor of 10. Notation is the same as in Figure 1.

In the I structure of the crystal the Delaunay simplices of small volumes appear of necessity from the splitting of octahedral cavities due to thermic perturvations. Depending on the symmetry of distortions the octahedral cavity is divided into either four slightly distorted quartoctahedra or five simplices. In the last case the central simplex is a square with diagonals slightly withdrawn out of the plane; the other four are close in their form to quartoctahedra and are attached to its faces (see Appendix). We will name these square, almost flat Delaunay simplices the Kijé simplices (after the name of the well-known Russian literature hero who "had no figure" [18]). They actually have no volume and produce a minor effect on the form of the surrounding quartoctahedra. Without them, however, it is impossible to correctly divide space into the Delaunay simplices.

The circumradius of the Kijé simplex is close to those of the adjacent quartoctahedra. Consequently, these two types of simplices cannot be distinguished in Figure 1. In other models the Delaunay simplices of small volumes are believed to be similar in form to the Kijé simplices since with another form the simplices of small volumes would have very large circumradii which is impossible in dense systems in virtue of the Delaunay theorem.

In [4] we considered some other characteristics proposed by different authors for describing the form of the Delaunay simplices. The main defect of those and of the two above, is their ambiguous relation to the simplex form. In the same paper (see also [5]) two novel characteristics were suggested - tetrahedricity and octahedricity, allowing one to distinguish separately the tetrahedral and quartoctahedral simplices. The definition of octahedricity was then changed slightly [7] to distinguish better between these two simplex types.

The tetrahedricity of the Delaunay simplex is determined as follows:

$$T = \sum_{i>j} (l_i - l_j)^2/15\bar{l}^2 \tag{1}$$

and octahedricity as

$$O = \sum_{\substack{i>j \\ i,j\neq m}} (l_i - l_j)^2/10\bar{l}^2 + \sum_{i\neq m} (l_i - l_m/\sqrt{2})^2/5\bar{l}^2 \tag{2}$$

where l_i is the length of the i-th simplex edge, l_m is the length of the maximum edge and $\bar{l}$ is the average edge length of a given simplex. The value of T vanishes for the perfect tetrahedron and increases with its distortion. Similarly, the O value is zero for the perfect quartoctahedron and increases with its distortion.

Figures 3 and 4 depict the histograms for tetrahedricity and octahedricity of the Delaunay simplices in various models. A pronounced bimodality of the distributions in the I structure of the crystal testifies to the preservation of two simplex types. The first peaks in the T and O distributions relate, obviously, to the weakly distorted tetrahedra and quartoctahedra, respectively.

In the distributions for the liquid the bimodality vanishes. In the I structure a negligible quantity of very good tetrahedra and quartoctahedra is observed; in the F structure their quantity increases substantially. This difference in distributions for I and F structures demonstrated fairly well the meaning of the introduction of the liquid F structure. It is useless to search for certain metric regularities in the I structure. A thermal chaos disturbs any regular geometric figures and violates all the quantitative relations. On going from I to F structure we recover a true regularity in the liquid structure hidden by thermal fluctuations. Although the F structure contains

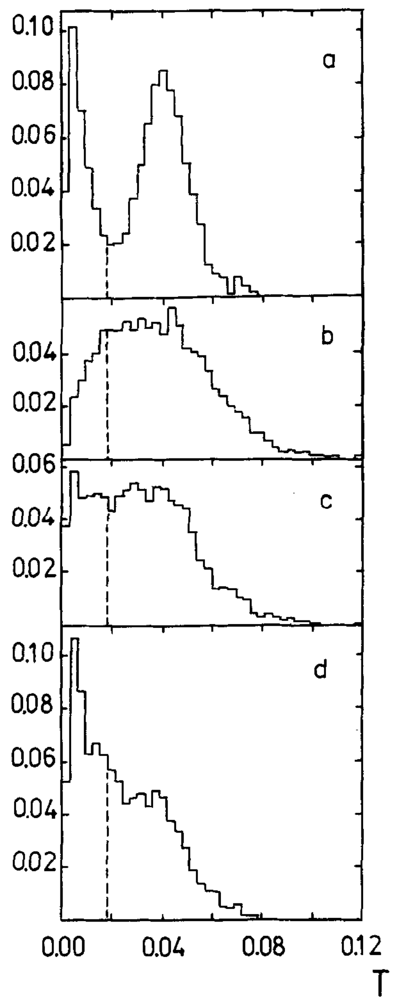


Figure 3. Tetrahedricity distributions of the Delaunay simplices. Dashed line - the boundary of good tetrahedra, $T_B = 0.018$. Notation is the same as in Figure 1.

a great number of good tetrahedra and quartoctahedra they do not manifest themselves in the isolated maxima; it is difficult therefore to separate them from simplices of a different form.

The distributions for the amorphous state (Figures 3d and 4d) resemble those for the F structure of liquid rather than those for the I structure. It is quite clear since the static relaxation in the Belaschenko model shifts the particles to the deep potential minima which excludes thermic perturbations. There are, however, some differences. In the distributions of the amorphous state no plateau is observed, and the region of good quartoctahedra and, particularly, tetrahedra has a height different from that for more distorted simplices. This implies that despite the absence of a distinct boundary it is reasonable to distinguish the region of good tetrahedra and quartoctahedra in all distributions.

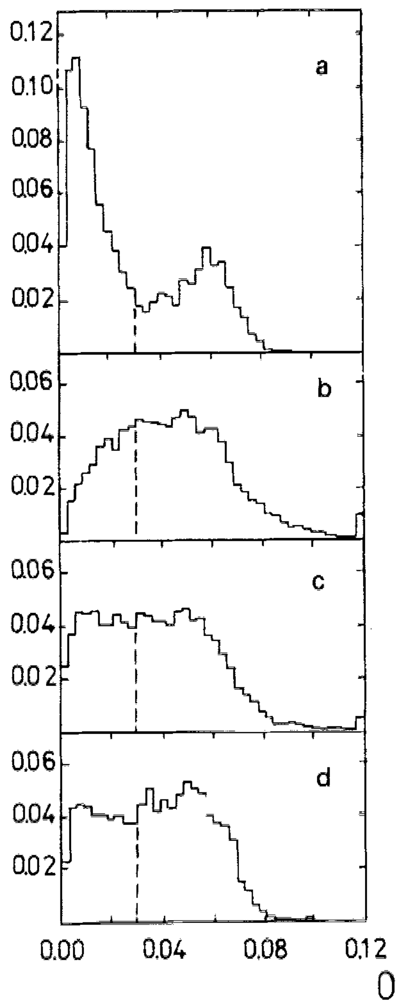


Figure 4. Octahedricity distributions of the Delaunay simplices. Dashed line - the boundary of good quartoctahedra, $O_B = 0.030$. Notation is the same as in Figure 1.

Table 1 The fraction of good tetrahedral (n_T) and good quartoctahedral (n_0) simplices in various models. The numbers without brackets were derived from one-dimensional *T*- and *O*-distributions; those in brackets - from the joint (*T*,*O*)-distribution.

Model		n_T	n_O	$n_T + n_O$	n_T/n_O
Crystal	I	0.30(0.31)	0.57(0.63)	0.87(0.94)	0.53(0.50)
FCC	F	0.33	0.67	1	0.5
Liquid	I	0.15(0.18)	0.20(0.29)	0.36(0.47)	0.75(0.62)
	F	0.24(0.29)	0.27(0.40)	0.51(0.70)	0.88(0.72)
Amorphous solid		0.37(0.44)	0.32(0.39)	0.69(0.82)	1.18(1.13)

The positions of the minima of the distributions for the I structure of the crystal may serve as the natural boundary between these regions. Thus we shall consider as good tetrahedra those Delaunay simplices for which $0 \leqslant T \leqslant 0.018$ and as good quartoctahedra the simplices with $0 \leqslant O \leqslant 0.03$. Integrating all the distributions within these limits we determine the fraction of good tetrahedra (n_T) and good quartoctahedra (n_o) among all the simplices in each system. These figures may be found in Table 1.

The Table shows that in the I structure of the crystal this procedure records 87% of all the simplices. The rest 13% are the simplices of intermediate forms and the Kijé simplices. In disordered systems the number of such simplices is higher of course. Nevertheless, in the F structure of liquid the good tetrahedra make up about 50% of all the simplices and in the amorphous substance - even about 70%. Hence these two classes of simplices may be considered, indeed, as the basic structural elements of disordered systems.

4. JOINT DISTRIBUTIONS OF TETRAHEDRICITY AND OCTAHEDRICITY OF THE DELAUNAY SIMPLICES

Such characteristics as tetrahedricity and octahedricity allow one to distinguish unambiguously only the Delaunay simplices of a preassigned form. The problem, however, is: how many types of the Delaunay simplex forms do exist in the liquid at all and what is the difference between them? It is, probably, impossible to construct such one-dimensional characteristics which could reflect the whole of the variety of the Delaunay simplex forms. Hence we are going to extend the usefulness of the available characteristics by studying their joint distributions.

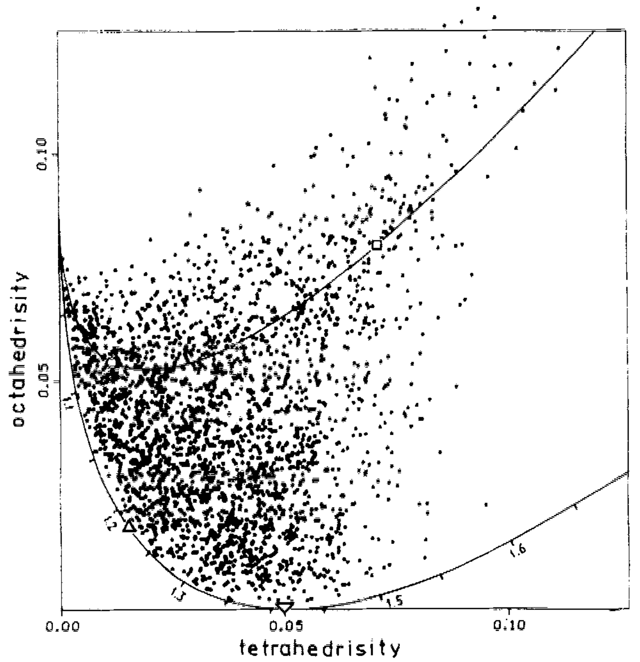
Figure 5 demonstrates the joint distributions of the T and O characteristics as spot diagrams for the I and F structures in the liquid. In the ideal FCC crystal this distribution should be depicted with two points: one with coordinates $T = 0$; $O = O_T = (\sqrt{2} - 1)^2/2 \approx 0.086$ for the perfect tetrahedra, the second — with coordinates $T = T_0 = 12(6\sqrt{2} + 7)^{-2} \approx 0.050$; $O = 0$ for the perfect quartoctahedra. When considering these two distributions it is seen that (i) they are bounded from below by some curve; and (ii) the transition from I to F structure leads to a noticeable concentration of the points along this curve. The meaning of the boundary curve is clear from formulas (1) and (2). At any fixed value of tetrahedricity there is the minimum value of octahedricity realized for the simplex with five equal edges (the first sum in (2) vanishes) and the sixth one being longer than the others.

In order to derive the equation for the boundary curve let us consider first a more general problem: the localization in the (T, O)-diagram of the simplices in which n edges ($1 \leqslant n \leqslant 5$) are of the length $l > 1$ and the rest 6-n edges are of unit length. Excluding l we obtain from (1) and (2) the equation which in the reduced coordinates, $X = T/T_O$, $Y = O/O_T$, is of the form:

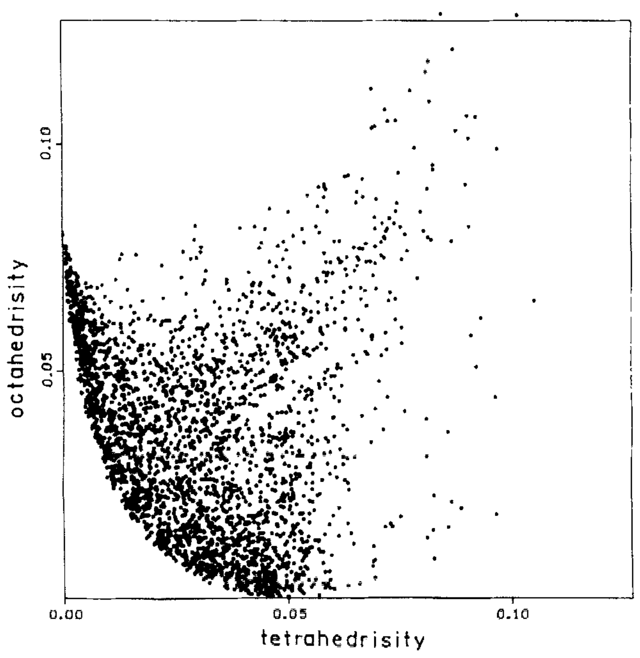
$$Y = 1 - 2\left(\frac{6-n}{5n}X\right)^{1/2} + \left[1 + \frac{6(n-1)}{n(6\sqrt{2}+7)^2}\right]X. \qquad (3)$$

The equation for the line, bounding from below the region of simplex residence in the (T,O)-diagram is a particular case of formula (3) for n = 1:

$$Y = 1 - 2\sqrt{X} + X. \qquad (4)$$



(a)



(b)

Figure 5. The joint distribution of tetrahedricity and octahedricity for the Delaunay simplices. Each point corresponds to one simplex with its own T and O. About 2600 simplices are shown. (a) I structure of liquid. An arrow at abscissa indicates the position of the perfect quartoctahedron. The lower curve is described by Equation (4); in this curve the simplex of the maximum volume is designated by a triangle; the numbers along the curve denote the values of the maximum edge length of the simplex. The upper curve is described by Equation (3) with n = 2; circle shows the position of the Delaunay simplex for the BCC crystal, square gives the position of the perfect Kijé simplex (flat square); (b) F structure of liquid.

This boundary line is shown in Figure 5a. It starts at point $T = 0$; $O/O_T = 1$ corresponding to the perfect tetrahedron ($l = 1$) and passes through point $T = 0.0156$; $O = 0.0167$ corresponding to the "orthogonal" simplex with $l = \sqrt{3/2}$ and two equilateral faces perpendicular to each other. This is the point of the maximum simplex volume on this line. Then the boundary line is tangent to the tetrahedricity axis at point $T/T_0 = 1$; $O = 0$ corresponding to the perfect quartoctahedron ($l = \sqrt{2}$) and ends at point $T = 0.1419$; $O = 0.0401$ describing a fully expended flat simplex with $l = \sqrt{3}$. Note that such simplices, according to the Delaunay theorem, cannot exist in real systems.

Another interesting particular case of formula (3) is the line with $n = 2$ which passes through a highly populated area of the (T,O)-diagram (Figure 5a). It also starts at the point of the perfect tetrahedron, passes through point $T = 0.0115$; $O = 0.0537$ corresponding to the Delaunay simplex of the ideal BCC crystal with $l = 2/\sqrt{3} \approx 1.1547$, then through the point with $T = 0.0706$; $O = 0.0795$ reflecting the Kijé simplex ($l = \sqrt{2}$) and ends at the point $T = 0.2692$; $O = 0.2646$ corresponding to another flat simplex with an infinite circumradius in which two long edges ($l = (2 + \sqrt{3})^{1/2} \approx 1.93$) meet at the same vertex.

The characteristic features of the (T,O)-diagram for different systems are revealed when presenting them in the form of isolines, especially in colour (Figure 6). The isolines are constructed from the smoothed histograms : each cell of the histogram (125 cells per each axis) is smoothed by the Gaussian distribution with a root-mean square deviation equal to two cell sizes.

For the instantaneous crystal structure (Figure 6a) we detect two large well separated regions elongated towards each other. One of them corresponds, obviously, to distorted tetrahedra, another — to distorted quartoctahedra. But even in the I structure of the crystal there are simplices of intermediate shapes forming the pedestal for these two mountain tops. In Figure 6a it is not observed since its height is less than one tenth of the maximum height of the mountain range. Besides, a low isolated hillock is detected at large values of T and O which corresponds to the Kijé simplices resulting naturally from the distortion of octahedral configurations (see Appendix).

The mountain relief of the instantaneous structure of the liquid (Figure 6b) is drastically different from that of the crystal. Here we observe a great variety of simplex forms. Most of them deviate strongly from the ideal tetrahedron and quartoctahedron forms. Another pecularity of this (T,O)-picture is that it represents a heavily broken terrain: deep twisty ravines furrow both the high and low areas of the relief. This intermittency demonstrates a substantially chaotic pattern inherent in the I structure of the liquid. Simple regularities are evidently difficult to find in such a picture.

The picture changes significantly when passing to the F structure of the liquid and further to the model of the amorphous state (Figures 6c and 6d). Here the intermittency disappears and the distribution shrinks to the boundary line described by Equation (4) forming along it a high and narrow mountain range, resembling the Cordilleras. It is the concentration of the Delaunay simplices along the boundary curve (seen well at the spot diagrams, too, Figure 5) with decreasing thermal chaos that is the basic regularity revealed by the (T,O)-diagrams.

Table 2 illustrates this regularity quantitatively. It contains the fractions of such Delaunay simplices whose root-mean square deviation of the lengths of five edges (except for the maximum one of the length l_m) is below 0.04. This means that the lengths of these edges are different from each other by no more than 10%. We see that

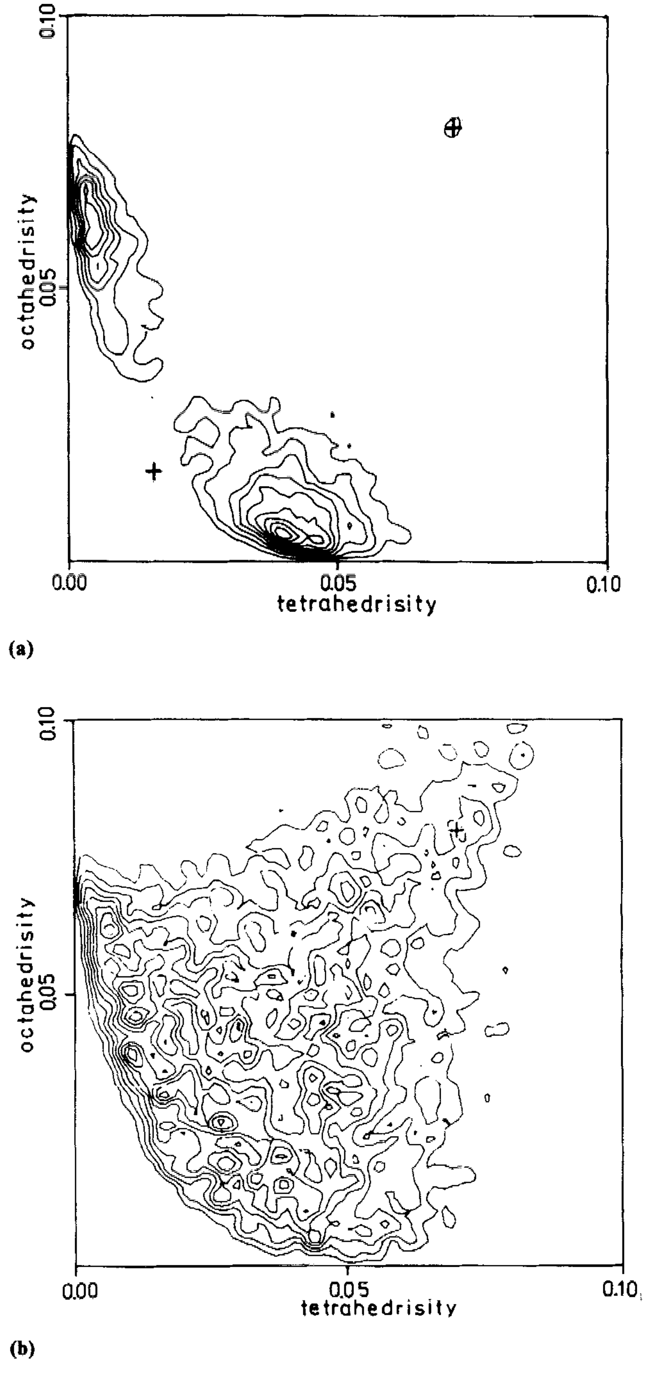
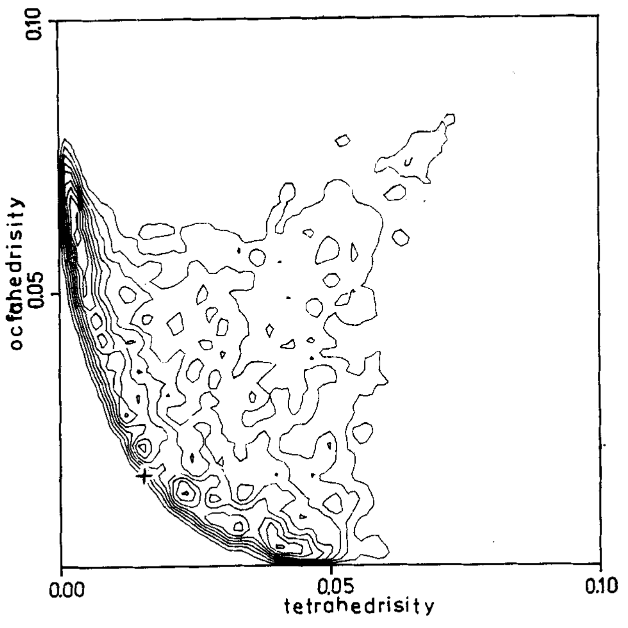
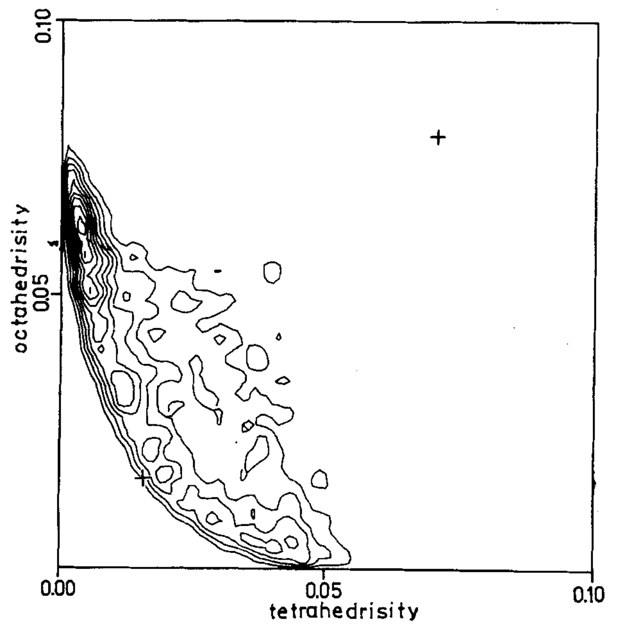


Figure 6. (See Colour Plate XII at the back of this volume.) The joint distribution of tetrahedricity and octahedricity for the Delaunay simplices in the form of isolines. (a) I structure of the FCC crystal; (b) I structure of liquid. Ten population levels are shown in all the figures.



(c)



(d)

Figure 6. (See Colour Plate XII at the back of this volume.) (c) F structure of liquid; (d) the amorphous solid. Ten population levels are shown in all the figures.

Table 2 The fraction of the Delaunay simplices situated near the boundary line described by Equation (4).

Model		*Fraction of simplices,%*
Crystal	I	40.3
FCC	F	100
Liquid	I	10.2
	F	32.2
Amorphous solid		43.2

the number of such simplices is high enough in all the models and increases substantially with eliminating the thermal excitations.

Thus the (T,O)-diagram allows one to distinguish a specific class of the Delaunay simplices in the proper structures of disordered systems. It is important that the principle of distinguishing is not associated with the comparison of the simplex shapes with the perfect crystalline forms of tetrahedra and quartoctahedra. A novel class of simplices is wider: these are the simplices whose five edges are of approximately equal lengths (say, they differ by no more than 10%) and the sixth edge is longer. The simplex of such a specific form may be called in Greek *isopentacmon* [19]. Its form may be characterized by a single parameter — the length of the maximum edge , l, which may vary continuously from 1 to $\sqrt{3}$.

5. HOW MANY CLASSES OF THE DELAUNAY SIMPLICES DO EXIST IN LIQUID

Now we are going to consider a question of whether it is possible to distinguish discrete types in the novel class of the simplices with five equal edges (isopentacmons). The most exhaustive information about this is provided by the (T,O)-diagram in which isopentacmons are situated along the boundary line and are depicted by the Cordilleras chain. An additional information may be extracted from the histograms for the distribution of the maximum edge length of isopentacmons varying monotonously along the boundary line (Figure 7). When examining these pictures for the F structure of the liquid we see that the distributions along the Cordilleras are inhomogeneous: the whole chain is crossed by more or less high mountain passes. The lowest one is at the level of 40–50% coloured in yellow in Figure 6. The position of this pass is conserved in the different realizations of the F structure, i.e. is statistically significant. The existence of such a low mountain pass gives us good grounds for dividing the class of isopentacmons into two sorts which may be identified entirely with the types of "good tetrahedra" and "good quartoctahedra" introduced above by analogy with the crystal.

Indeed our mountain pass in the F structure of the liquid is situated in the region of a deep valley separating the high peaks of good tetrahedra and good quartoctahedra in the I structure of the crystal. This is seen well while comparing Figures 6a and 6c and from Figure 7 in which our pass corresponds to l_{max} = 1.24–1.26. The above one-dimensional T- and O-distributions are the projections onto the axes of the joint (T,O)-distribution. Figure 6 shows quite distinctly that the presence of an extensive although low foot-hill smoothes substantially the distributions of one-dimensional projections due to the admixture of highly distorted simplices. Alterna-

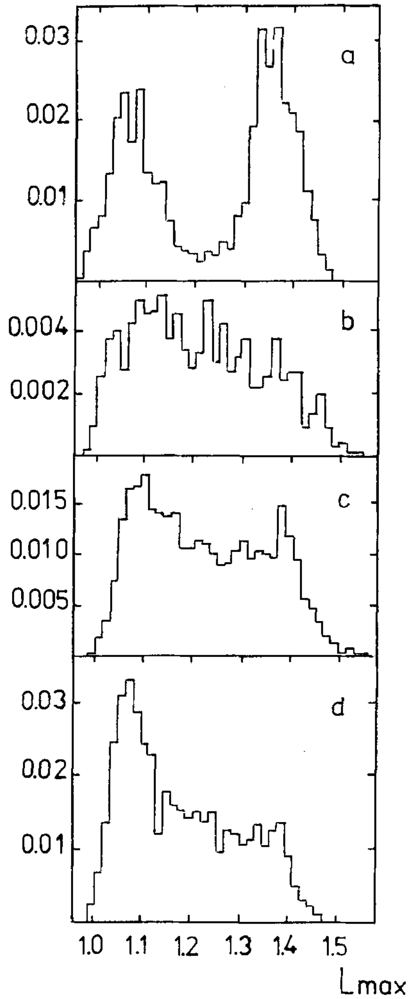


Figure 7. The distribution of the length of the maximum edge for the Delaunay simplices with five almost equal edges (isopentacmons), which differ in length by no more than 10%. Notation is the same as in Figure 1.

tively the distributions in Figure 7 are free from this defect. They exhibit a discrete structure being, however, less pronounced than in the two-dimensional distributions in Figure 6.

The position of the mountain pass under study is hardly occasional. Note that it is situated near the point of the simplex of the maximum volume (in the class of isopentacmons) exceeding the volume of perfect tetrahedron and quartoctahedron by 6%. This simplex with $l = \sqrt{3/2} = 1.225$ is given in Figure 6 by a lower cross. Even in the I structure of the liquid it corresponds to a deep lowland (Figure 6b). In the model of the amorphous state the picture of the mountain passes is somewhat different due to a sharp drop in the quartoctahedron peak (Figure 6d). A new pass appears in the mountain range of good tetrahedra seen well in Figure 7d, too. But a deep valley separating the regions of good tetrahedra and good quartoctahedra is also preserved here.

Thus despite a more intricate structure of the (T,O)-diagram relief we may distinguish , as the initial classification, two types of the Delaunay simplices — good tetrahedra and quartoctahedra. The one-dimensional T- and O-distributions have already been used in Section 3 for estimating a relative quantity of these simplices (n_T and n_O, respectively). Such an estimation may be performed also on the basis of the two-dimensional distributions. Assign, in all the models, the simplices whose representing points in the (T,O)-diagrams are in the region bounded by a 10% isoline in the I structure of the crystal to good tetrahedra and good quartoctahedra (Figure 6a). The resulting numbers are listed in Table 1 in brackets. It is seen that both methods of estimation yield fairly close numbers. An exception is the numbers for the F structure of the liquid. A two-dimensional diagram provides, probably, an overestimated number of quartoctahedra due to a greater number of these simplices in the I structure of the crystal and due to the fact that their area at the 10% level is too wide.

Distinguishing two sorts of the Delaunay simplices and knowing their numbers we may reveal the interesting relationships. Firstly, the transition from I structure to F structure of the liquid leads to a noticeable increase in the number of good tetrahedra and quartoctahedra. The increase in the number of regular forms is a trivial result of eliminating the thermic perturbations. Secondly, the number of these simplices in the model of the amorphous state appears to be higher than in the F structure of the liquid. This fact is not trivial as it indicates to a systematic difference in the structure of these models. Thirdly, we observe a dramatic increase in the number of good tetrahedra relative to the number of good quartoctahedra when passing from crystal to I structure, F structure of the liquid and further to the amorphous state (see the last column in Table 1). In the amorphous substance the number of tetrahedra becomes high than that of quartoctahedra whilst in the crystal it is less by half. This is indicative of surprising properties of the random close packings, the meaning of which is to be ascertained.

Worth attention is the marked population in the region of the Kijé simplices in all diagrams in Figure 6 (not seen in Figure 6d containing, however, here also a hillock the height of which is somewhat higher than 5%). Since the Kijé simplices result from octahedral configurations their presence testifies not only to the existence of quartoctahedra but also to their junction into octahedral cavities. When passing from the liquid F structure to the amorphous state the number of good quartoctahedra increases (Table 1) with decreasing number of the Kijé simplices (cf. Figures 6c and 6d). This implies that quartoctahedra in the amorphous state do not tend to join into the octahedra, i.e. the principles of its structure are quite different from those of the crystal. The non-octahedral mutual arrangement of quartoctahedra in the liquid F structure has already been the object of our attention [7].

So how can we answer the question: how many types of the Delaunay simplices do exist in the liquid? On the one hand we are dealing with continual distribution of simplex forms, and any method for determining the sorts will give intermediate forms. This constatation, however, does not reflect a specific situation represented in Figure 6 and simplifies it substantially. Approaching the (T,O)-distribution to the boundary curve, while eliminating thermal perturbations in the liquid and passing to the amorphous state, indicates convincingly the necessity for distinguishing the class of the boundary simplices with five almost equal edges (isopentacmons). The existence of a separate sort of "good tetrahedra" in the isopentacmon class is also beyond doubts as this type manifests itself in the high peak in the proper structures of disordered systems (Figures 6c and 6d). The question may perhaps arise of the quantitative criteria for determining this sort. The separation of some other types is more questionable. The above type of "good quartoctahedra" is a reasonable step towards further classification. It is justified by the existence of a low mountain pass in the main range of the Cordilleras and by the analogy with the crystal structure.

However, each of two Cordilleras ranges is crossed in turn by more or less high passes (Figures 6c and 6d) resulting in peculiar "quantization" of the boundary classes of the Delaunay simplices (isopentacmons). These lower tops may be compared with definite simplex sorts providing further studies will testify to their statistical significance. A structural meaning of this "quantization" is even more difficult to understand. The existence of the preferable lengths of the maximum edge indicates, probably, a discrete number of packing schemes of simplices. If this is the case the classification should be based not only on the form of separate Delaunay simplices but also on the character of their connectivity to the nearest neighbours.

6. CONCLUSION

We have shown that the Delaunay simplices of random dense packins of atomic particles may successfully be classified by their form. The proposed characteristics of the form — tetrahedricity (T) and octahedricity (O) — appeared to be a convenient means for this purpose, especially when using their joint distributions. The (T,O)-diagrams are of a rather peculiar form for each phase state (crystal, liquid, amorphous solid) and are sensitive to thermal excitations (differ strongly for I and F structures). The interpretation of all the details of these diagrams needs further studies.

The main conclusion from the consideration of the two-dimensional (T,O)-distributions is a specific role of the class of the Delaunay simplices with five approximately equal edges (isopentacmons) which appeared to prevail in the proper structures of disordered systems (F structure of the liquid and amorphous substance). Two simplex sorts — good tetrahedra and quartoctahedra — may be distinguished within the isopentacmon class with less assurance. The above classification of the Delaunay simplex forms allows one to reveal, inter alia, the principal differences in the structures of crystal and disordered dense systems. In the former the tetrahedral and quartoctahedral simplices are separated quite well, the latter contain a great number of intermediate forms. All the above sorts are distinguishable in disordered systems only after removing the thermal fluctuation (in the proper structures, e.g. liquid F structure). Another pecularity of disordered systems is that the fraction of the tetrahedral simplices relative to the quartoctahedral ones exceeds that in the crystal, especially in the amorphous state.

The basic line of further investigations concerning the geometric structure of liquids is, to our mind, the transition from studying the properties of the single Delaunay simplices to considering the regularities of the mutual arrangement (connectivity) of the simplices of a definite form. To this end we have proposed [7] to use the ideology of percolation theory. Only the studies of the Delaunay simplex connectivity appears to help in elucidating the meaning of such details in the (T,O)-diagram as the "quantization" of the maximum edge length.

APPENDIX. SPLITTING OF THE OCTAHEDRON INTO DELAUNAY SIMPLICES. APPEARANCE OF THE KIJÉ SIMPLEX.

Here we are going to demonstrate how the octahedral cavity breaks down into the Delaunay simplices when its form deviates from the ideal one. For illustration let us consider a special kind of distortion with vertices A and A′ shifted downwards by value h, and vertices B and B′ — upwards by the same value relative to their position in the perfect octahedron; the vertices C and C′ may be shifted only along the diagonal CC′ (see Figure 8). Altogether there are 15 combinations of six octahedral vertices taken four at a time. Which of these 15 tetrahedra do correspond to the Delaunay simplices? In order to answer this question we make use of the Delaunay theorem (see Section 1). A given tetrahedron is the Delaunay simplex if two remaining octahedron vertices are situated beyond the circumsphere of this tetrahedron. By calculating the coordinates of the centres of the circumspheres for 13 tetrahedra (flat figures CAC′A′ and CBC′B′ cannot be the Delaunay simplices, see Section 1) we may obtain values Δ equal to the difference between the square of the distance from a given centre to the remaining octahedron vertices and the squared circumradius. All these values include the expression $\varepsilon = 2a^2 + h^2 - l^2$ equal to zero for the perfect octahedron ($h = 0$).

Based on this the tetrahedra CABA′, C′BA′B′, CA′B′A, and C′B′AB are readily shown to be not the Delaunay simplices at any octahedron distortion since their circumspheres include of necessity one of the remaining vertices. Indeed, the differences specified are equal to $\Delta_1 = -2l\varepsilon/(l + h)$ and $\Delta_2 = 4h\varepsilon/(l + h)$ and have the opposite signs at any values of parameters a, l, h (with $h > 0$).

The remaining tetrahedra are divided into two groups whose behaviour depends in

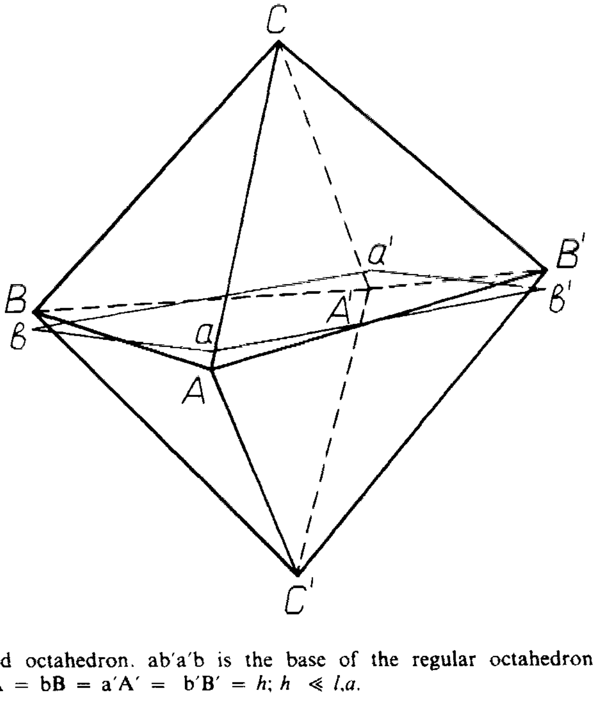


Figure 8. Distorted octahedron. ab′a′b is the base of the regular octahedron (square). ab′ = a; OC = OC′ = l; aA = bB = a′A′ = b′B′ = h; $h \ll l, a$.

different ways on the sign of value ε. The first group involves the tetrahedra CC′AB, CC′BA′, CC′A′B′, and CC′B′A. For them $\Delta = 2\varepsilon$. The second one involves the tetrahedra CBA′B′, C′A′B′A, CB′AB, and C′ABA′ for which $\Delta_1 = -2l\varepsilon/(l-h)$ and $\Delta_2 = -4h\varepsilon/(l-h)$, and the tetrahedron ABA′B′ for which $\Delta = -\varepsilon$. Thus, if $\varepsilon > 0$, i.e. when the octahedron is squeezed along the diagonal CC', the tetrahedra of the first group become the Delaunay simplices, and the octahedron at weak distortions is splitted into four Delaunay simplices close in form to the quartoctahedra. On the contrary, when $\varepsilon < 0$, i.e. the octahedron is extended along the diagonal CC′, the tetrahedra of the second group turn to be the Delaunay simplices. The octahedron splits, in this case, into four quartoctahedra and the practically flat tetrahedron ABA′B′ close in form to the square — the Kijé simplex.

Hence when squeezing the octahedron along the diagonal, the four quartoctahedral Delaunay simplices into which it splits have a common edge (CC′) coinciding with this diagonal. Under the extention of the octahedron, the long edges of quartoctahedra (BB′ and AA′) are in the plane perpendicular to the direction of extention; since now they fail to coincide, have different orientation and are common only for two quartoctahedra, a novel simplex — the Kijé simplex — appears between the pairs of the latter.

References

[1] J.L. Finney and J. Wallace, "Interstice correlation functions; a new, sensitive characterization of non-crystalline packed structures", *J. Non-Crystalline Solids*,**43**, 165 (1981).

[2] M. Kimura and F. Yonezava, "Nature of amorphous and liquid structures — computer simulations and statistical geometry", *J. Non-Crystalline Solids*,**61–62**, 535 (1984).

[3] Y. Hiwatari, T. Saito and A. Ueda, "Structural characterization of soft-core and hard-core glasses by Delaunay tesselation", *J.Chem.Phys.*, **81** 6044 (1984).

[4] N.N. Medvedev, V.P. Voloshin and Yu.I. Naberukhin, "Study of atomic configuration shapes in dense Lennard-Jones systems", *Zhurnal Strukturnoi Khimii (in Russian)*, **28**, No. 2, 62 (1987).

[5] N.N. Medvedev and Yu.I. Naberukhin, "Shape of the Delaunay simplices in dense random packings of hard and soft spheres", *J. Non-Crystalline Solids*, **94**, 402 (1987).

[6] N.N. Medvedev and Yu.I. Naberukhin, "Study of the structure of simple liquids and amorphous solids by the statistical geometry methods", *Zhurnal Strukturnoi Khimii (in Russian)*, **28**, No. 3, 117 (1987).

[7] N.N. Medvedev, V.P. Voloshin and Yu.I. Naberukhin, "Structure of simple liquids as a percolation problem on the Voronoi network", *J. Phys. A: Math. Gen.*, **21**, L247 (1988).

[8] B.N. Delaunay, "Sur la sphère vide", Bull. Acad. des Sci. USSR, *Classe Sci. Math. Nat.*, **6** 797 (1934); *Soviet Math.*, **2** 812 (1961).

[9] M. Tanemura, T. Ogawa and N. Ogita, "A new algorithm for three-dimensional Voronoi tesselation", *J. Comput. Phys.*, **51** 191 (1983).

[10] J.D. Bernal, "The structure of liquids", *Proc. Roy. Soc. London*, **A280** 299 (1964).

[11] H.J. Frost, "Cavities in dense random packings", *Acta metall.*, **30**, 889 (1982).

[12] M. Ahmadzadeh and B. Cantor, "Interstitial structure and diffusion in DRP metallic glasses", *J. Non-Crystalline Solids*, **43**, 189 (1981).

[13] F. Lançon, L. Billard and A. Chamberod, "Structural description of a metallic glass model", *J. Phys. F. Met. Phys.*, **14**, 579 (1984).

[14] Yu.I. Naberukhin, V.P. Voloshin and N.N. Medvedev, "Proper structures of condensed media. Computer modelling of Lennard-Jones systems", *Melts (in Russian)*, **1**, No.2, 71 (1987).

[15] F.H. Stillinger and T.A. Weber, "Hidden structure in liquids", *Phys. Rev.* **A25** 978 (1982).

[16] T.A. Weber and F.H. Stillinger, "The effect of density on the inherent structure in liquids", *J. Chem.Phys.*,**80**, 2742 (1984).

[17] D.K. Belaschenko, "Statistical analysis of inhomogeneity in single-component amorphous structures", *Melts (in Russian)*, **1**, No.3, 45 (1987).

[18] Kijé is a personage of the story by Tynyanov "Lieutenant Kijé" who appeared due to clerk's mistake and never existed in reality but was successful under Paul I. Once he was arrested. The guards were instructed that "the prisoner was secret and had no figure". Soon he was released and was appointed as a general.

[19] Isopentac