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Empty interatomic space in computer models of simple liquids and amorphous solids

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Abstract. It is suggested to define the cavities that make up the empty interatomic space of any atomic model as associated overlapping interstitial spheres. The latter are determined unambiguously by the atomic arrangement with the help of the Voronoi–Delaunay methods for the division of space into polyhedra. Thus any complex cavity may be represented as a cluster of contiguous Delaunay simplices. These clusters are revealed by percolation analysis with the application of a special 'δ colouring' of the Voronoi network bonds. This paper presents a classification of all complex cavities discovered in computer models of crystals, liquids and amorphous solids. The number of cavity types is rather large and does not reduce to, say, the five canonical holes of Bernal. The latter occupy less than half of the volume. The greater part of the cavities represent branched chains with built-in rings of simplicial holes, octahedra and so on. Large clusters of more than 10 simplices are characteristic of liquids but they do not occur in amorphous solids.

1. Introduction

The structure of disordered systems (liquids, amorphous solids) can be characterized not only by atomic arrangement, but also by the form of the empty interatomic space. This possibility has long been used in crystallography to describe crystal structure; it was first applied to simple liquids by Bernal (1964, 1965). As is known, the close-packed crystals contain only two types of interatomic hole: tetrahedral and octahedral ones. Bernal believed that the idealized model of a dense liquid can be represented as an assembly of only five types of 'canonical' hole. Later, however, Bernal's ideas were thoroughly analysed on computer models of simple liquids and amorphous solids, and a great variety of 'non-canonical' hole configurations were revealed (Whittaker 1978, Ahmadzadeh and Cantor 1981, Frost 1982, Lançon *et al* 1984). Thus one was forced to abandon the optimistic expectation of being able to describe liquid structure by a small number of structural elements.

It is characteristic of the above works that they used different definitions of the hole configurations, all of which are, strictly speaking, arbitrary. This defect may hardly be remedied since it is impossible to indicate the exact quantitative criterion in a disordered system that could separate one type of configuration from others. However, one can always speak about more useful, simpler or more natural criteria. In this paper we continue the analysis of empty interatomic space using the Voronoi–Delaunay theory of the division of space into polyhedra. This method enables us to work with geometrical objects that are in one-to-one correspondence with the atomic arrangement in the model. Its adequacy for the problem discussed is based on the fact that one of the fundamental objects of the theory—the Delaunay simplex—corresponds to an elementary hole that is an interstitial sphere inscribed between the four nearest atoms. This enables us to give a natural definition of the complex

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hole as associated overlapping elementary interstitial spheres. For this it is necessary to know the atomic radius, the value of which has no exact definition in systems with a soft potential. We suggest compensating for this defect by percolation analysis of the Voronoi network, which offers the possibility to follow the overlap of the interstitial spheres in detail.

This paper is organized as follows: In section 2 we briefly discuss all the main concepts of the Voronoi–Delaunay and percolation methods specific to the problem studied, and formulate our approach to the analysis of empty space. In section 3, computer models are described in which we investigate the empty space. Percolation analysis of the overlap of the interstitial spheres in our models is given in section 4. In section 5 a classification of aggregates of overlapping interstitial spheres (i.e. complex holes) by size and topology is reported. Finally, in section 6 we compare our classification of holes with that in the basic work of Bernal.

2. Description of empty space

2.1. Review of the previous papers

It is evident that the empty space of a model is a simply connected region where wider areas are separated by narrow passages. Hence, empty interatomic space may be divided into separate cavities, each of which can be described by the configuration of the surrounding atoms. Bernal (1964, 1965) was the first to propose this method to describe the structure of simple liquids. He suggested to determine cavity configurations using a simplicial graph in which the centres of atoms—'the geometrical neighbours'—are connected. Eliminating the longest bonds in the simplicial graph, one can obtain a 'reduced' graph whose parts surrounding some empty space have the form of convex polyhedra.

Bernal assumed that the variety of all these polyhedra can be reduced to five basic 'canonical' types (figure 1). Two of these, namely, tetrahedron (*a*) and tetragonal dodecahedron (*e*), are deltahedra, i.e. they contain only triangular faces. The empty interatomic space within any deltahedron must be considered as a separate cavity because triangular faces correspond to the densest packing of three atoms and therefore represent the narrowest passages or 'necks' separating different cavities. Further we will always mean by *cavity* only the *cavity configuration in the deltahedron form*. Here, a tetrahedron and tetragonal dodecahedron represent separate cavities. In contrast, the remaining three canonical polyhedra that also contain square faces, i.e. half-octahedron (*b*), trigonal prism (*c*) and Archimedian antiprism (*d*), are elements of larger deltahedra and do not define separate cavities. Thus, two half-octahedra involved in one octahedron determine not two separate cavities but a common one.

Bernal's ideas on empty interatomic cavities were used by Whittaker (1978), Ahmadzadeh and Cantor (1981) and Frost (1982) to study computer models of simple liquids. A great variety of deltahedra were recognized in different models of dense disordered packings, which does not allow one to reduce the classification of cavities to a fairly small number of types. The authors did not succeed in representing this variety of deltahedra as a set of a small number of structural elements containing not only triangular but also square faces, not necessarily planar. The variety of these structural elements appears to be too large for a convenient classification.

The discussed direction of studies seems to be completed by Lançon *et al* (1984). They showed that all the methods of constructing cavities (deltahedra) proposed earlier were nothing but different rules for joining elementary cavity polyhedra, i.e. Delaunay simplices (though the authors do not use this term). This indication makes it useful to study in

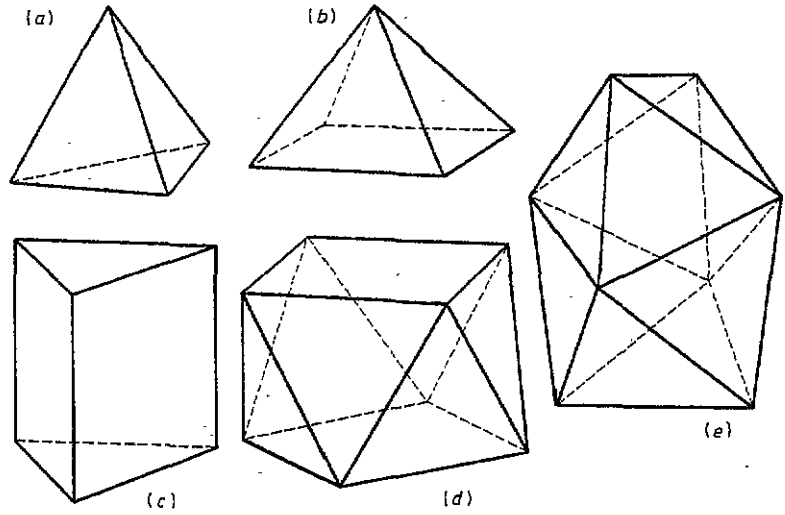

Figure 1. Bernal's canonical holes: (*a*) tetrahedron, (*b*) half-octahedron, (*c*) trigonal prism, (*d*) Archimedian antiprism, (*e*) tetragonal dodecahedron.

more detail the relation between the problem of empty cavities and the Voronoi–Delaunay methods for dividing space into polyhedra. These methods have been used for studying different aspects of the structure of computer models (Hiwatari *et al* 1984, Kimura and Yonezawa 1984, Medvedev and Naberukhin 1987a, b, Voloshin *et al* 1989, Naberukhin *et al* 1991). They offer further ways for investigating the problem of empty space.

2.2. Voronoi–Delaunay language of dividing space into polyhedra

This section contains only the main definitions and facts, and the reader who needs mathematical details and proofs is referred to the specialist literature: Delaunay (1934, 1947), Rogers (1964), Tanemura *et al* (1983), Medvedev and Naberukhin (1987a). The Voronoi polyhedron (VP) of a given atom is the region of space containing all points closer to the centre of this atom than to the centres of any others. The atoms whose Voronoi polyhedra have a common face are named geometrical neighbours. The set of vertices and edges of the Voronoi polyhedra of all model atoms makes up a network called the Voronoi network.

The division of space into Voronoi polyhedra is closely connected with the alternative division into Delaunay simplices. The Delaunay simplex is a tetrahedron of an arbitrary form with vertices at the centres of four atoms each being the geometrical neighbour for the other three. A set of vertices and edges of all Delaunay simplices of the model makes up the above-mentioned simplicial graph or the Delaunay network.

The relation between these two space divisions is characterized as follows (see figure 2). Each site of the Voronoi network, being a common VP vertex for four atoms (geometrical neighbours of each other), corresponds to the Delaunay simplex formed by these four atoms. The bond between two sites of the Voronoi network shows that the related simplices have one face in common. Hence, each site of the three-dimensional Voronoi network is connected with four other sites, i.e. the Voronoi network is four coordinated (or three coordinated in the two-dimensional illustration in figure 2). In perfect crystals, degenerate vertices are possible at which more than four VPs meet; in the disordered systems discussed here such situations are actually non-realizable.

A site of the Voronoi network is also the centre of the sphere circumscribed around the corresponding Delaunay simplex because this site, being the vertex common for four VPs, is equidistant from the centres of all the four atoms. It can readily be demonstrated that this sphere cannot involve the centres of other system atoms—Delaunay theorem on the empty sphere (cf. Delaunay 1934, Tanemura *et al* 1983). The centre of the circumsphere (diameter D_o) coincides with the centre of the interstitial sphere of a given Delaunay simplex (diameter D_i) that touches all four simplex atoms but does not cross and does not contain any atom of the system. The diameters of both spheres are related by the expression:

$$D_i = D_o - d \tag{1}$$

where d is the atomic diameter. The interstitial sphere is the sphere of maximum possible diameter that can be inserted between the atoms of the given simplex. Thus, the Delaunay simplex represents an elementary cavity configuration of atoms.

More complicated cavity configurations can be considered as a combination of several contiguous Delaunay simplices. Indeed, as has been mentioned, the cavity is represented by a polyhedron with triangular faces (deltahedron) constructed on a simplicial graph. Such a polyhedron can be always made up of Delaunay simplices.

Thus, the perfect octahedral cavity configuration of atoms must consist of four simplices, each of which has five edges of equal length and a sixth one that is $\sqrt{2}$ times longer and is common for all of them and passes inside the cavity. A simplex of such form was called a quartoctahedron (Medvedev *et al* 1988, Voloshin *et al* 1989). Each of them shares two faces with the other two quartoctahedra of the same cavity, whereas the two remaining faces contact with two Delaunay simplices of other cavities.

Hence, in composite cavities we must distinguish the internal faces that unite the Delaunay simplices into one cavity and the external faces that form the boundary between the cavities. The corresponding bonds of the Voronoi network will also be named *internal* and *external*.

In order to construct complex cavities of the Delaunay simplices one must elaborate a criterion by which one could indicate the simplices that must be joined into a complex cavity and those that must be retained as single elementary cavities. We suggest here to *join into a complex cavity such Delaunay simplices whose interstitial spheres overlap*. This criterion is rather clear (see figure 2) and especially useful since it enables us to formulate an empty-space problem in terms of percolation theory. Note that a similar criterion was used by Finney and Wallace (1981) to recognize cavities in dense sphere packings.

2.3. *Percolation approach*

The degree of overlap of the interstitial spheres may be characterized by the parameter

$$\delta_{ij} = R_i + R_j - R_{ij} \tag{2}$$

where R_i and R_j are the radii of the interstitial spheres of neighbouring Delaunay simplices, and R_{ij} is the distance between the centres of these spheres. For isolated spheres, the value of this parameter is equal to the shortest distance between their surfaces with a negative sign; and for overlapping spheres, it is equal to the length of the common part of the line segment connecting the centres of the interstitial spheres.

The δ_{ij} parameter characterizes the bond of the Voronoi network that connects the neighbouring sites i and j (the centres of the corresponding Delaunay simplices). Hence, a number δ_{ij} can be assigned to each bond of the Voronoi network. Then, in order to

find well overlapped interstitial spheres it is sufficient to select (*colour*) the bonds whose δ parameter exceeds a certain chosen boundary value δ_0. Complex cavities, i.e. aggregates of overlapping interstitial spheres, will correspond to clusters of contiguous coloured bonds on the Voronoi network. Such an approach makes it possible to apply the ideology of percolation theory, according to which our problem is characterized as the bond problem on a three-dimensional four-coordinated network.

In the percolation approach, the boundary value δ_0 is gradually altered to change a fraction of coloured bonds p (on one and the same network) as well as the number of clusters of coloured bonds and their topology. For some critical value δ_c the fraction of coloured bonds becomes so large that an 'infinite' cluster appears, i.e. a cluster spanning the whole model from one side to another. The value of this concentration, p_c (percolation threshold), is an important characteristic of both the network and the method of colouring its bonds. In the present paper we do not intend to perform a full percolation analysis of the Voronoi network for the 'δ colouring', but restrict ourselves to studying clusters for one, 'natural' choice of the boundary value—namely, $\delta_0 = 0$, which corresponds to the contact of two neighbouring interstitial spheres. We determine the percolation thresholds for δ colouring, too.

The method for uniting Delaunay simplices proposed by Lançon *et al* (1984) can also be formulated as a bond percolation problem on a Voronoi network. To this end, each bond of the Voronoi network should be characterized by the length of the maximum edge of the common face of the two Delaunay simplices whose centres are connected by this bond; then the bonds for which this characteristic exceeds r_m should be coloured. The Delaunay simplices involved in the same deltahedron according to this procedure will be connected on the Voronoi network by coloured bonds into one cluster.

In the present paper we follow a similar logic but use another bond characteristic on the Voronoi network to unite the Delaunay simplices, namely the parameter of interstitial sphere overlap, δ_{ij}. Only those Delaunay simplices for which the bonds between them satisfy the condition $\delta_{ij} > \delta_0$ are united into one cavity. This method seems more adequate for the problem of interatomic cavity construction. The edges of the Delaunay simplices are not represented on the Voronoi network and our method of constructing deltahedra does not require the removal of any edges. Some of these are located on the deltahedron surface (forming triangular faces), and the remainder are situated inside. Evidently, the long edges that are rejected according to the Lançon *et al* procedure are, as a rule, internal in our deltahedra as well. However, some external edges of one of the deltahedra can be longer than the internal ones in other deltahedra. Therefore, the edge length is not a good criterion for uniting Delaunay simplices.

3. Models

In the present paper we have mainly studied the liquid and crystal models calculated using the Monte Carlo simulation (Metropolis algorithm). Each model consisted of 108 atoms with the Lennard-Jones potential:

$$u = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{3}$$

in the NVT ensemble with periodic boundary conditions. The results for a liquid have been averaged over 10 independent models at reduced density $\rho^* = \rho\sigma^3 = 0.9$ and temperature $T^* = kT/\epsilon = 0.719$. In addition to these models, which determine the instantaneous

structure of the liquid (I structure), we have studied models of the frozen structure of the liquid (F structure). These are intended to reduce the influence of random thermal motion to structural laws and were obtained from the corresponding I structures by freezing out the basic thermal fluctuations, i.e. by shifting particles towards the minima of their local potentials (Naberukhin *et al* 1987). We performed the freezing by applying the Monte Carlo procedure to instantaneous structures at $T^* = 0$ K and the previous value $\rho^* = 0.9$. The acceptance rate was kept in the range from 35 to 65% by varying automatically the length of the maximum step upon relaxation. In 500–700 moves per atom this parameter decreased 10^5–10^6 times and the relaxation ceased. The freezing caused a 20% decrease of the full potential energy of the system, whereas the variations in atomic coordinates were (0.1–0.2) σ and no more than 0.5σ.

To study the crystal structure, the I structures of the FCC crystal were generated by the Monte Carlo method at $\rho^* = 1$ and $T^* = 0.719$. The results were averaged over five independent models. The model of 686 atoms with potential $u = ar^{-12}$, kindly supplied by Professor D K Belashenko (Moscow), was used as a model of the amorphous state. This model was calculated by molecular dynamics and then carefully relaxed by the steepest-descent method. The pair correlation function, $g(r)$, of this model demonstrates all the characteristic peculiarities of the amorphous state, particularly the doublet splitting of the second maximum (Belashenko 1987).

As a length unit we used the atomic diameter, which in Monte Carlo models was equal to the position of the minimum of the pair potential, and in the model of the amorphous state to the position of the first maximum of the pair correlation function. The periodicity of boundary conditions was taken into account when constructing the Delaunay simplices and Voronoi network. As a result, simplices situated near some boundaries involved both the atoms near the given boundary and the images of the atoms located at the opposite boundary. Similarly, clusters crossing the cell boundary involved simultaneously both the sites and the images of the sites of the Voronoi network.

The concentration of coloured bonds at which an 'infinite' cluster appears for the first time was taken as the percolation threshold p_c. Taking account of the periodicity of boundary conditions, the cluster was considered 'infinite' if it involved the sites of the basic cell together with the images of these sites beyond its boundaries.

4. Percolation analysis of the Voronoi networks

Figure 3 depicts the distributions of the overlap parameter δ for different models. In the FCC crystal the distribution is bimodal, which corresponds to two bond types: internal bonds in octahedral cavities (the right-hand maximum) and external bonds between tetrahedral and octahedral cavities (the left-hand peak). In other models it is impossible to correctly distinguish the two types of cavity. The disposition of the maxima in these distributions at negative δ values near the location of the left-hand maximum in the crystal allows one to assume that these models also contain a great number of triangular faces formed by three densely packed atoms. The corresponding bonds of the Voronoi network are sure to be external. However, there is no natural boundary between external and internal bonds in disordered systems. We will use the boundary value $\delta_0 = 0$, which corresponds to the minimum in the distribution for the crystal and has a clear geometrical meaning (see section 2.2).

In all our models the colouring of only internal bonds (with $\delta \geqslant 0$) gives no infinite cluster. To obtain such a cluster, it is necessary to colour some external bonds with the

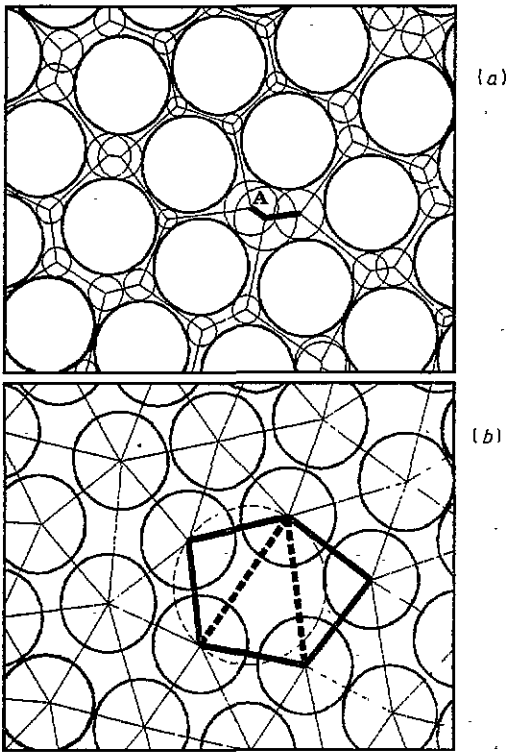

Figure 2. Two-dimensional illustration of the space division into Voronoi polyhedra (*a*) and Delaunay simplices (*b*). In (*b*) the circumsphere around one of the simplices is shown by a thin broken circle whose centre is defined by the Voronoi network site A. Each circumsphere corresponds to an interstitial sphere according to formula (1) and all such spheres are presented in (*a*). Overlapping interstitial spheres make up, by our definition, complex cavities. For example, the large hole in the centre of the figure is made up of three overlapping spheres (*a*), and its cavity configuration (*b*) is composed of three contiguous Delaunay simplices (internal edges are given by broken lines). This cavity configuration is represented on the Voronoi network (*a*) as a cluster of 'coloured' (thick) bonds, which connect the centres of the three simplices composing the cavity.

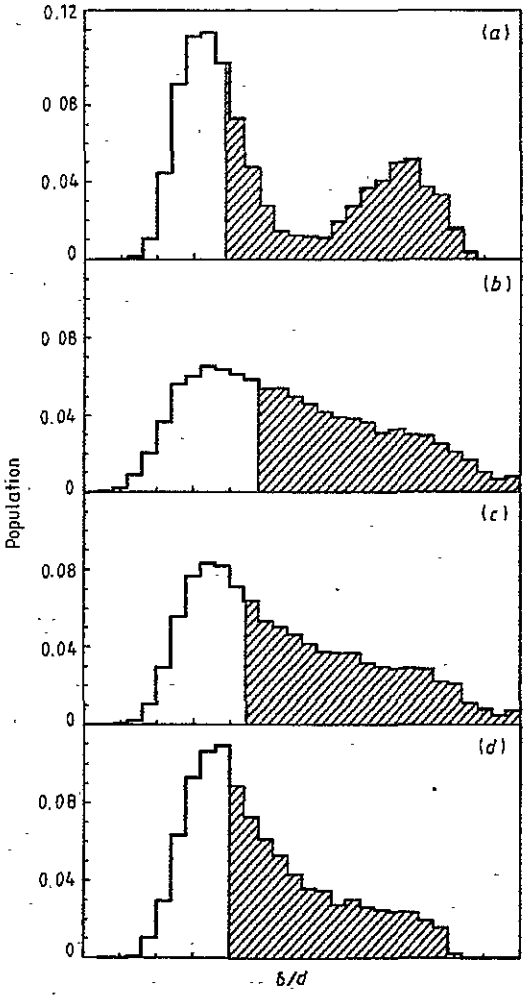

Figure 3. Distributions of the bonds of the Voronoi network according to the degree of overlap of the corresponding interstitial cavities (δ distribution) in different models: (*a*) FCC crystal, (*b*) I structure of liquid, (*c*) F structure of liquid, (*d*) amorphous solid. Shaded is the region corresponding to the network bonds that are coloured at the percolation threshold. The position of its boundary refers to the value δ_c presented in table 1.

highest value of parameter δ as well. Table 1 lists the values of the percolation thresholds p_c

in the δ colouring together with the corresponding critical values of the colouring parameter δ_c. It is seen that the crystal has the smallest value of δ_c and the I structure of the liquid has the largest. The threshold concentration p_c is the lowest in the crystal, and the highest in the amorphous substance, although the difference is quite small. In the random colouring of bonds on the same Voronoi networks, the threshold concentrations are similar for different models, $\delta_c = 0.406 \pm 0.029$, and practically coincide with the threshold for the random colouring of bonds on the diamond network, $p_c = 0.388$ (Stauffer 1985). Both of these numbers are substantially less than the threshold values for the δ colouring.

Table 1. Characteristics of the δ colouring: p_c, percolation threshold; δ_c, critical value of the overlap parameter; p_0, concentration of coloured bonds at $\delta_0 = 0$.

	p_c	δ_c	p_0
FCC crystal	0.543 ± 0.015	-0.211	0.339
Liquid I structure	0.565 ± 0.021	-0.120	0.408
F structure	0.577 ± 0.023	-0.154	0.374
Amorphous solid	0.587	-0.199	0.270

Thus, the cavities formed by the colouring of only internal bonds ($\delta \geqslant 0$) fail to percolate: they are small, substantially smaller than in a percolating cluster. The bond clusters corresponding to such cavities are spatially more compact than the clusters of randomly coloured bonds on the same network; this increases the coloured bonds' concentration necessary for the appearance of percolation.

We will further consider cluster properties of the bond coloured Voronoi network at $\delta_0 = 0$. Each of the clusters corresponds to an isolated cavity (as $\delta_0 > \delta_c$). All the bonds of the cluster are internal bonds of this cavity and correspond to faces joining the simplices that constitute the given cavity configuration (see figure 2). The boundary value $\delta_0 = 0$ determines a particular concentration value of the coloured bonds p_0 in each model (table 1). For the I structure of the crystal, the coloured bond concentration is nearly equal to 1/3, i.e. to a fraction of such bonds in the perfect FCC crystal. It is substantially higher in the I structure of the liquid. The value of p_0 decreases when passing to the F structure but has the smallest value in the amorphous structure, 1.2 times lower than that in the crystal. This correlates with a great number of tetrahedral configurations in the amorphous solids (Kimura and Yonezawa 1984, Medvedev and Naberukhin 1987a, Voloshin *et al* 1989).

The number of coloured bonds connecting any site with other sites can vary from zero to four. At random colouring the fraction of sites f_n having n coloured bonds is described by the binomial distribution

$$f_n = \binom{4}{n} (1 - p_0)^n p_0^{4-n}. \tag{4}$$

Figure 4 compares the δ and the random colourings. All the models demonstrate similar deviations from the random distributions, though to a different degree. We see in our models a greater number of sites with zero, two and four bonds (except sites with four bonds in the crystal) and fewer sites with an odd number of bonds. Hence, clusters of one Delaunay simplex (tetrahedral configurations) and clusters in the form of rings and chains are more frequent than at random colouring.

Thus data in table 1 and figure 4 demonstrate a significant correlation in dispositions of the elementary cavity configurations. They reflect definite regularities in the systems named disordered.

5. Cavity classification

This section is devoted to the topological and metric properties of clusters from contiguous internal bonds of the Voronoi network for which parameter δ is not less than zero, i.e. we will consider the shape of associated cavities formed by overlapping interstitial spheres.

5.1. The number of sites in a cluster

The simplest cluster characteristic is the number of network sites belonging to this cluster. For convenience of cavity classification, we will call an isolated site corresponding to a separate non-associated simplicial cavity a cluster, too, though it has only one site. Figure 5 depicts the distributions of cavity clusters in different models according to the number of sites. The perfect FCC crystal contains cavities of only two types, namely perfect tetrahedral and perfect octahedral, the number of tetrahedral cavities being twice as large. For a weak distortion of the perfect crystal structure, tetrahedral cavities will correspond to clusters of one site, and the octahedral ones to those of four or five sites depending on the character of the distortion (Voloshin *et al* 1989). A similar pattern is observed in our model of a thermally excited FCC crystal (figure 5(*a*)). Clusters with a different number of sites, mainly with two sites, make up only about 2% of the total number of clusters on the network.

The distributions for models of disordered packings, i.e. I structures and F structures of the liquid (figures 5(*b*) and (*c*)) and the amorphous state (figure 5(*d*)), are practically the same. Each of them, like the FCC crystal, contains a great number of clusters involving only one site. The I and F structures contain a smaller number of such clusters than the crystal while the amorphous state displays a larger number. However, the distributions of other clusters differ considerably from the crystalline ones. The main difference is that there are much less clusters with four sites and much more clusters with two sites; besides, clusters of seven and more sites appear. Thus we have enormous clusters with more than 14 sites in the I and F structures of the liquid. A cluster of complex form containing 58 sites was discovered in one of the I structures.

As seen from figure 5 there are no clusters with more than 15 sites in either crystal or amorphous state, and there are few of them in the I and F structures of the liquid. It might seem that they could be easily neglected when describing the liquid structure. However, the distribution of the cavity polyhedra volume fraction corresponding to clusters with different numbers of sites demonstrates that large clusters with 15 or more sites make up almost 15% of the model volume for the liquid F structure (figure 6(*a*)); in the I structure this fraction amounts to 20%.

It is interesting to compare this distribution obtained by colouring the Voronoi networks with the boundary value $\delta_0 = 0$ with that for the same Voronoi networks but coloured with $\delta_0 = 0.1$ (figure 6(*b*)). For this distribution, the volume fraction of the large clusters reduces to 2%. Decay of the large clusters causes the increase of the volume fraction of the smallest cavities, particularly those with one site. The new colouring decoloured the weakest bonds, i.e. those in which the interstitial spheres of the Delaunay simplices overlapped by no more than 0.1. Hence one may conclude that the large cavities consist mainly of relatively weakly bound, i.e. weakly overlapping, small cavities.

It is now to be determined which of the small cavities are most frequent and therefore most interesting for cavity classification.

5.2. Connectivity index

The number of sites in a cluster is its full characteristic only when the cluster consists of one or two sites. More complex clusters can display a different topology for the same number

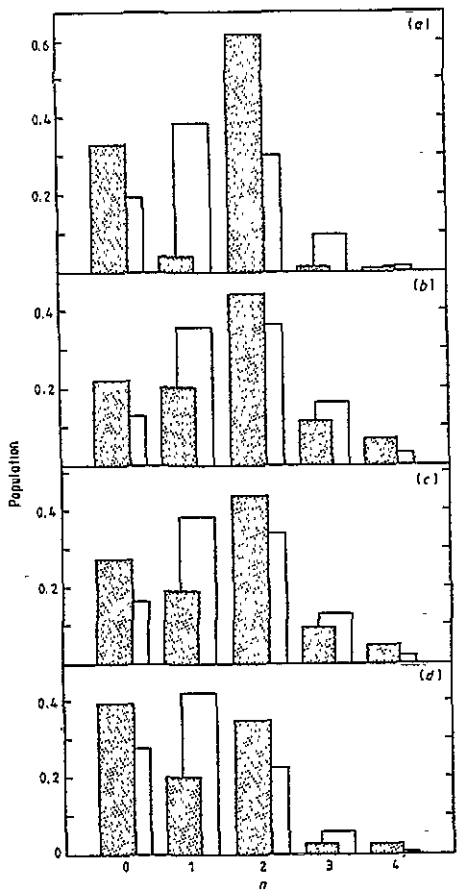

Figure 4. Distributions of the Voronoi network sites according to the number of coloured bonds in which they engage, n, for different models. Shaded columns correspond to the δ colouring with the boundary parameter $\delta_0 = 0$, and unshaded ones to the random colouring of the same Voronoi network at the same concentration p_0 calculated by formula (4) (see table 1). Model notations coincide with figure 3.

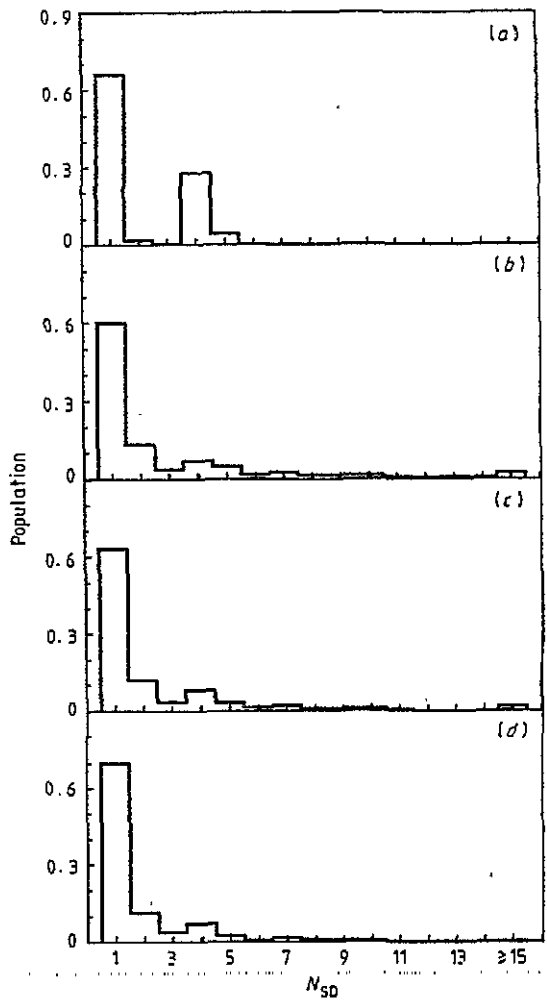

Figure 5. Distributions of clusters (associated cavities) according to the number of Delaunay simplices, N_{SD}, of which they consist. δ colouring at $\delta_0 = 0$. Notations are the same as in figure 3.

of sites. It is necessary to introduce some new characteristics to distinguish not only the size but also the topology of clusters. We use here a *connectivity index* composed of four numbers $n_1\,n_2\,n_3\,n_4$, where n_i is the number of cluster sites having i bonds, which connect them with the other sites of the given cluster. For a tetrahedral cavity, the connectivity index is 0000; for clusters consisting of two sites it is 2000; an octahedral cavity made up of four quartoctahedral Delaunay simplices has the index 0400; the index of clusters with three sites can be 2100 or 3000 depending on their topology; etc.

Table 2 gives the connectivity indices for almost all small clusters observed in all the

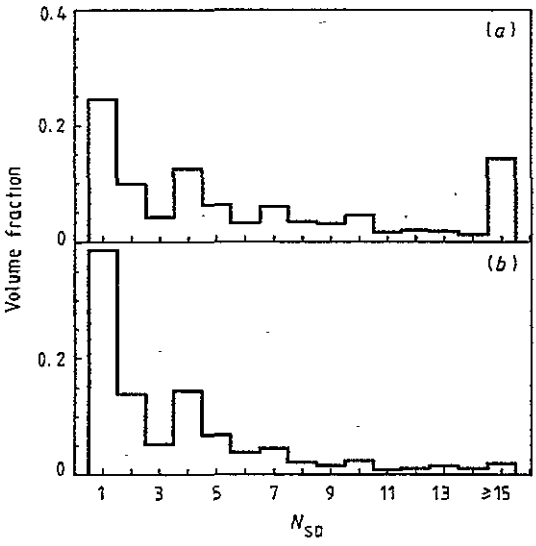

Figure 6. Volume percentages of clusters with a given number of Delaunay simplices, N_{SD}, for the F structure of a liquid at two different values of the colouring parameter: (*a*) $\delta_0 = 0$, (*b*) $\delta_0 = 0.1$.

four models with the boundary value $\delta_0 = 0$, and indicates the number of such clusters in each of them. At the bottom of the table there is the index for the largest cluster of 58 sites in the liquid I structure. Figure 7 depicts the graphs of the most important clusters.

When the cluster is small, the connectivity index determines the cluster topology unambiguously; but for larger clusters, there is no such correspondence. Therefore, to determine the cavity shape, we will use, in addition to the connectivity index, some metric characteristics of the Delaunay simplices that constitute the cavity, such as the radius of the interstitial sphere and the tetrahedricity and octahedricity of the simplex, introduced in the articles of Medvedev and Naberukhin (1987a, b), Medvedev *et al* (1988) and Voloshin *et al* (1989). Tetrahedricity T and octahedricity O of a simplex are quantitative measures of the deviation of simplex shape from the shapes of a perfect tetrahedron and quartoctahedron (a quarter of a perfect octahedron). As in the above articles we assign to *good* (slightly distorted) tetrahedra all the simplices with $T < 0.018$ and to *good* quartoctahedra the simplices with $O < 0.030$. For brevity, we will not document metric characteristics of all the simplices discussed and will restrict ourselves to two examples (tables 3 and 4).

5.3. Cluster statistics

Consider the clusters that according to table 2 are the most frequent in our models. In all the models the clusters with index 0 0 0 0 prevail, which consist of one site and undoubtedly represent isolated tetrahedral cavities. This is confirmed by the data on simplex size and shape in table 3. (Only in the liquid I structure are the simplices not good tetrahedra on average.)

The cavities of the next class, which are widely represented in liquids and amorphous solids and are rarely observed in FCC crystals, consist of two Delaunay simplices and have the connectivity index 2 0 0 0. Metric characteristics show that most of these simplices have no relation to either good tetrahedra or good quartoctahedra.

Clusters consisting of three sites can have the indices 0 3 0 0 and 2 1 0 0 (see figure 7). Note that such clusters are practically absent in crystals, whereas in liquid and amorphous states the clusters with index 2 1 0 0 prevail. The simplices involved in cavities with this index as well as the simplices of cavities with index 2 0 0 0 have no definite shape.

Table 2. Numbers of cavities of n interstitial spheres with a given index in different models.

n	Index	FCC crystal	Liquid		Amorphous solid
			I structure	F structure	
1	0000	1055	1384	1700	1610
2	2000	21	309	327	266
3	0300	—	11	6	3
	2100	5	72	87	89
4	0400	432	129	186	163
	1210	—	3	2	1
	2200	9	19	21	12
	3010	—	4	4	6
5	0401	34	22	21	15
	0500	—	18	10	8
	1310	38	49	47	20
	2300	—	16	8	12
	3110	—	4	3	—
6	0420	—	2	—	—
	0501	—	5	6	3
	1311	—	5	4	3
	1410	—	8	13	2
	2220	2	3	5	—
	2301	3	1	—	—
	2400	—	2	3	1
	3210	—	8	3	2
	4020	—	2	—	—
	4101	—	1	—	—
7	0502	—	7	5	—
	0520	—	5	8	2
	0601	—	19	21	10
	1330	—	—	1	—
	1411	—	3	2	—
	1510	—	15	16	18
	2221	—	—	1	—
	2320	—	7	2	2
	2500	—	—	1	2
	3130	—	1	—	—
58	7241512	—	1	—	—
	Total	1600	2323	2765	2291

Clusters consisting of four sites can have six different indices. However, only four of these were realized in all our models (see figure 7). Most frequent are the clusters with index 0400. They are mostly observed in FCC crystals. This is not surprising because both the topology of this cluster and the characteristics of the shape and size of its simplices show that this cluster corresponds to a weakly perturbed octahedral cavity. Other clusters of four sites mostly involve clusters with index 2200. The topological and metric characteristics of their simplices are similar to those of 'linear' clusters with the indices 2000 and 2100.

For clusters consisting of five sites, the number of possible indices reaches several

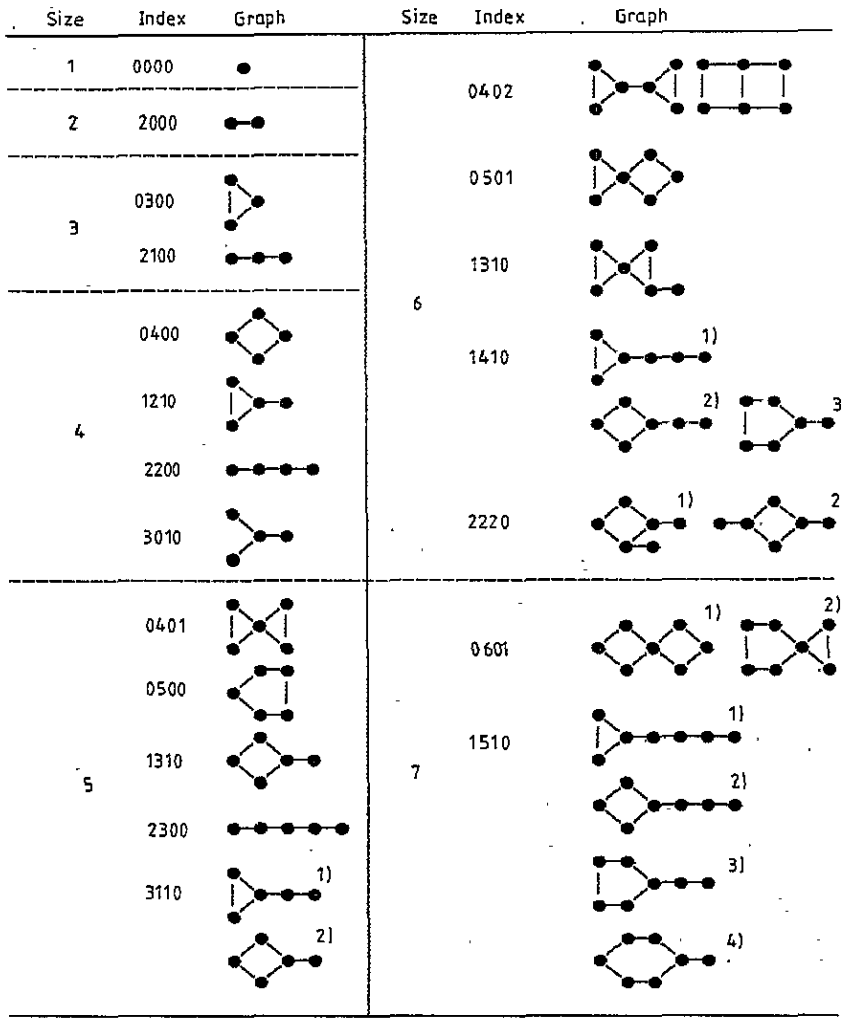

Figure 7. Graphs of the most frequent clusters.

Table 3. Characteristics of clusters with index 0000.

	FCC crystal	Liquid		Amorphous solid
		I structure	F structure	
Radius of interstitial sphere	0.119	0.129	0.133 ± 0.016	0.119
Volume	0.117	0.117	0.123 ± 0.006	0.116
Tetrahedricity	0.008	0.015	0.009 ± 0.007	0.009
Octahedricity	0.055	0.047	0.047 ± 0.016	0.049

dozens, the number of topological types being even larger. In our models only five of the above indices have been recorded. The most numerous are clusters with index 1 3 1 0. This index corresponds to clusters of two topological types (see figure 7). The first type can be

Table 4. Characteristics of clusters with index 0401.

	FCC crystal		F structure of liquid	
	Sites with two bonds	Sites with four bonds	Sites with two bonds	Sites with four bonds
Radius of interstitial sphere	0.193	0.194	0.198 ± 0.014	0.202 ± 0.012
Volume	0.113	0.023	0.114 ± 0.012	0.049 ± 0.019
Tetrahedricity	0.048	0.072	0.047 ± 0.003	0.067 ± 0.004
Octahedricity	0.011	0.080	0.017 ± 0.013	0.074 ± 0.006

considered as a combination of two clusters with the indices 0300 and 2000. However, such clusters seem to be rare, as there are only a few clusters with index 0300. The second type can be considered as an addition of a distorted tetrahedron to a distorted octahedron 0400.

Almost the same number of clusters have index 0401. Figure 7 depicts the topology of the cluster with this index, and table 4 gives the characteristics of the simplices for the FCC crystal and the liquid F structure. It is seen that in both crystal and liquid the sites with two bonds in this cluster are good quartoctahedra, and the site with four bonds corresponds to the simplex with the same radius of the interstitial sphere, with high values of tetrahedricity and octahedricity, and a very small volume. Earlier (Voloshin *et al* 1989) we showed that such simplices (named Kijé simplices) can arise from the division of distorted octahedral cavities into Delaunay simplices. The Kijé simplex is an almost planar square, its edges being formed by the edges and diagonals of the square. Thus, clusters with the connectivity index 0401 should be referred to as octahedral cavities with the same degree of distortion as in clusters with index 0400.

Among other clusters with five sites those with the indices 0500 and 2300 are the most interesting, as they are absent in FCC crystals. The former represent five-membered rings consisting of contiguous Delaunay simplices and correspond to pentagonal faces of the Voronoi polyhedra, a great number of which were found to be a specific feature of a liquid structure (Bernal 1964, Medvedev and Naberukhin 1987a, Voloshin *et al* 1989). Clusters with index 2300 belong to the above-mentioned class of 'linear' clusters or chains.

The number of clusters with six sites is much fewer. Especially interesting are clusters with index 1410. There are three variants of topology for these (figure 7). However, the simplex characteristics, as in the case with index 1310, show that most of these clusters correspond to distorted octahedral cavities with an added chain 2000; hence, their topology corresponds to the second variant in figure 7.

Among the clusters with seven sites, special attention is drawn to the indices 0601 and 1510. The latter seems to correspond to the combination of distorted octahedral cavities and much longer 'linear' clusters (the second variant of topology in figure 7). Cluster 0601 is interesting because, just like a cluster with index 0401, it involves a simplex with four bonds. In the second variant of topology presented in figure 7, the central simplex with four bonds must be similar to the Kijé simplex in cluster 0401. However, this possibility must be rejected because the volume of this central simplex is practically the same as the volumes of other cavity simplices. Clusters with index 0601 seem to belong to the first variant (two four-membered rings with a common site). This topological type is nothing but the fifth canonical Bernal polyhedron, the tetragonal dodecahedron.

6. Bernal holes

As has been mentioned, only two of the canonical Bernal holes can be considered as isolated, separate cavities. These are the tetrahedron and tetragonal dodecahedron (see figure 1). All the rest have square faces that must match each other when filling the space. According to Bernal statistics, most of these holes belong to semioctahedra. Therefore, it might be concluded that the square faces of other holes will be capped by these ones. Thus, one should consider not the canonical but five modified holes with triangular faces only (also introduced by Bernal), namely tetrahedron, octahedron, trigonal prism with three half-octahedral caps, Archimedian antiprism with two half-octahedral caps, and tetragonal dodecahedron. The connectivity indices of all these cavity types are presented in table 5, the two last being deduced when the possibility of the presence of Kijé simplices on the square faces is ignored.

Table 5. Volume percentage of polyhedra.

Cavity type	Index	Bernal	Finney 1.2	Finney 1.3	Lançon	This work
Tetrahedron	0000	48.40	19.01	40.24	71.04	24.71
Octahedron	0400 0401	13.2	6.66	15.77	20.69	15.81
Tetragonal dodecahedron	0601	14.80	5.15	9.14	3.77	2.27
Trigonal prism with caps	0621	20.52	0.49	3.75	1.05	0.96
Archimedian antiprism with caps	0641	3.16	1.21	3.03	0.05	—
Other types		—	67.48	28.07	3.40	56.25

Table 5 shows percentages of various modified cavities in the models of hard spheres by Bernal and Finney and in the models with soft interatomic potentials: results of Lançon *et al* (1984) and our data for the F structure of a liquid. Data for the modified cavities in the Bernal model were derived from statistics of canonical holes (Bernal 1964). For the Finney models we quote the results of an analysis by Frost (1982) at two values of the maximum edge length of the cavity polyhedra. All the authors agree on the predominance of tetrahedral holes. In all models except Bernal's, octahedra occupy the second place. Non-rigorous visual methods of determining the holes in the Bernal model have evidently led to the overestimation of the number of tetragonal dodecahedra and especially trigonal prisms. Other methods of hole analysis give the same result: the number of the three largest Bernal holes is substantially less than that of tetrahedra and octahedra. Among them the tetragonal dodecahedron is more frequent, as we have already mentioned above when discussing our models.

According to our data all the Bernal's holes occupy less than 50% of the liquid volume. The remaining volume belongs to holes represented by linear clusters of Delaunay simplices and also to cavities of a more complicated configuration. These linear clusters cannot be revealed by other methods of determining the holes, since the removal of the long edge performed by all of these methods leads to the joining of all the simplices sharing this edge and to the appearance of a ring on the Voronoi network, which corresponds to these simplices. Nevertheless, non-canonical holes are present in great number in Finney models. Lançon's data, which, in contrast, give a small number of such cavities, stand separately.

This seems to result from a very soft repulsive part of the potential in their model and from the thorough relaxation carried out to obtain an amorphous state. These factors also lead (as we will show elsewhere) to the increase in the number of tetrahedra.

7. Conclusion

Following Lançon *et al* we consider that interatomic cavities must be constructed from Delaunay simplices, since the latter are elementary cavity configurations. However, the simplices must be joined by their faces and not by their edges because it is the face that determines the size of the passage (the 'neck') between simplicial cavities. In such a way we can easily formulate the problem of cavity classification in terms of percolation theory by means of colouring the bonds of the Voronoi network, e.g. according to the degree of overlap of the interstitial spheres (δ colouring of bonds). This is one of the realizations of a general idea—the structure of liquids as a percolation problem on the Voronoi network (Medvedev *et al* 1988, Naberukhin *et al* 1991)—specified for studying empty interatomic space.

Analysis of clusters of Delaunay simplices representing interatomic voids shows that a simple classification of cavities in dense disordered substances is impossible. The reason is that a substantial part of the volume is occupied by cavities of complicated configurations consisting of a great number of simplices ($n \geqslant 10$ in liquids). These large cavities are wormlike rather than spheroidal (what was implied by Bernal in his pioneering works). The chains of cavities are branched; they unite some rings of the simplices and other associated cavities. All this results in an enormous variety of cavity forms.

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