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LETTER TO THE EDITOR

Structure of simple liquids as a percolation problem on the Voronoi network

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Abstract. Analysis of the mutual arrangements of Delaunay simplices is formulated as a site-correlated percolation problem on the Voronoi network. Typical cluster configurations of simplices of tetrahedral and octahedral form (the main structural elements of simple liquids) are found and percolation thresholds for them are obtained.

For liquid and amorphous substances the regularities of atom packing have not, so far, been formulated. Since there is no translational symmetry in such systems, when studying their structure one confines oneself to the investigation of a local order. Thus the pair distribution function, topological and metric characteristics of the Voronoi polyhedra are calculated (Finney 1970, Medvedev *et al* 1986) and the interatomic holes are catalogued (Frost 1982, Lançon *et al* 1984), i.e. the nearest coordination shell of an atom or the configurations of a small number of particles are investigated. Studying the laws of spatial patterns of definite structural units (distinguished atomic configurations) over the whole volume of a specimen seems to be the next step in understanding the structure. In this letter we propose a method for solving this problem and report our first results on its application to a dense Lennard-Jones liquid.

Assume the Voronoi tesselation to be carried out by constructing Voronoi polyhedra for all atoms of the computer model of a liquid according to known algorithms (see, e.g., Tanemura *et al* 1983, Medvedev 1986). The collection of its edges forms a space filling network (the Voronoi network). This network possesses remarkable geometric properties. For every disordered system exactly four edges meet at a vertex (site) of the network. Each site of the Voronoi network is equidistant from the centre of four atoms, the Voronoi polyhedra of which meet at this site, being the centre of their circumsphere. These four atoms represent the vertices of a figure (tetrahedron of a general form) which is called the Delaunay simplex (DS). Thus every site of the Voronoi network is in correspondence with a definite Delaunay simplex. Each bond of the network joining two sites shows two corresponding simplices to be contiguous, i.e. to have a face in common. Hence it follows that the Voronoi network yields a simpler way to describe the clusters of the chosen simplicial configurations than the direct examination of the coordinates of all atoms engaged in these aggregates.

Analysis of the computer models of the dense random monatomic systems has revealed an important law: most Delaunay simplices belong to figures which are close in shape to the perfect tetrahedron and a quarter of the perfect octahedron (quartoctahedron) (Medvedev and Naberukhin 1987a, b, c). These types of polyhedra are therefore

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the main structural elements in such systems. We aim to study their connectivity, i.e. their mutual arrangement throughout the space. One may introduce the quantitative characteristics of proximity of the Delaunay simplex to the perfect tetrahedron (call this parameter the tetrahedricity T) and to the perfect quartoctahedron (octahedricity O) (see below). This allows one to ascribe a definite number to every site of the Voronoi network and then to colour those sites which correspond to a chosen range of values of the characteristics T (or O). As a result, the problem of spatial arrangement of the Delaunay simplices of a definite form can be formulated as the problem of percolation of the characteristics of this form (T or O) through the coloured sites of the four-coordinated Voronoi network.

Here we illustrate this idea using the model of the Lennard-Jones liquid. The atom coordinates were generated by the Monte Carlo method for 108 particles in a cube with periodic boundary conditions at the reduced density $\rho^* = 0.9$ and temperature $T^* = 0.719$. The parameters of the LJ potential were in line with those of argon. To remove the superfluous chaos we did not analyse these instantaneous structures (I structures) but the 'frozen' ones (F structures) which resulted from each I structure by the additional Monte Carlo relaxation at $T = 0$ K (Naberukhin *et al* 1987, Medvedev and Naberukhin 1987c). When passing to the F structure, all the particles shift to the local potential minima, thus eliminating the chaos of thermic excitations but conserving the topological disorder in the liquid. For our F structures there were 655 sites of the Voronoi network inside the basic cube.

The form characteristics of the Delaunay simplices were defined according to Medvedev and Naberukhin (1987a, b, c):

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

for tetrahedricity and

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

for octahedricity. Here l_i is the edge length of a given DS, l_m is the length of the maximum edge and $\bar{l}$ is the average edge length. T and O vanish for the perfect tetrahedron and quartoctahedron, respectively (in the latter, one of the edges is $\sqrt{2}$ longer than the others). Therefore by a small value of the parameter T (or O) we may choose among all DS the simplices which are close in form to the perfect tetrahedron (or quartoctahedron).

Figure 1 depicts the result of T colouring of the Voronoi network for one of the realisations of our model of the liquid. The figure displays only 100 network sites conforming to the most tetrahedral Delaunay simplices (for which $T < 0.011$) and the bonds in between. About 20% of the selected sites are seen to be isolated. The rest build up the clusters in the form of chains or five-membered rings, both with shoots. Increasing the amount of coloured sites (we have proposed (Medvedev and Naberukhin 1987a) to assign those with $T < 0.016$ to the tetrahedral simplices) results in decreasing the number of single sites, lengthening and branching the chains and creating new five-membered rings. Analysis of other independent realisations of the liquid shows the described picture of clusters on the Voronoi network to be typical.

Figure 2 demonstrates the atomic configurations corresponding to the simplest fragments of the clusters revealed by T colouring of the Voronoi network. Note that configurations in the form of an icosahedron are not available among them. On the

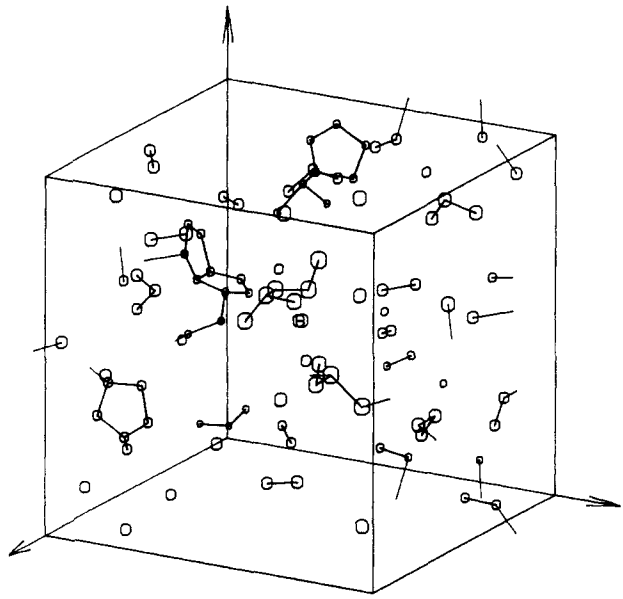

Figure 1. T colouring of the Voronoi network for a realisation of the Lennard-Jones liquid. 100 sites are depicted (among the total number of 655 of the network sites) corresponding to the most tetrahedral Delaunay simplices (circles). The bonds sticking out of the cube are directed to the images of atoms.

Voronoi network, such an aggregate would correspond to a cluster of five-membered rings in the form of a dodecahedron. Nothing similar is detected in any realisation.

O colouring of the Voronoi network of the same liquid realisation as in figure 1 is shown in figure 3. It also depicts 100 sites which correspond to the most octahedral Delaunay simplices (with $O < 0.01$) and the bonds in between. The picture obtained differs substantially from that for the T colouring of the same network (figure 1). About 35% of sites are isolated. 20% of sites are combined in pairs with very short bonds which correspond to semioctahedral atomic configurations (figure 4(b)). There are three tetramers in which four sites are joined by short bonds in four-membered rings; they obviously represent the octahedral atomic configurations. However surprisingly, the O colouring gives rise to a large number of long bonds. A long bond shows two quartoctahedra to be in contact by those faces which do not contain the longest edges of the simplices (see figures 4(c), (d)). Such clusters fail to be part of a single octahedral atomic configuration. With increasing number of O-coloured sites, the amount of long bonds increases, and they form chains involving the above-mentioned octahedral and semioctahedral aggregates.

The increase in concentration of the T- or O-coloured sites on the Voronoi network leads to colouring more and more distorted tetrahedral or quartoctahedral simplices. However, the typical picture of clusters described above rests unchanged at least up to the concentrations corresponding to a percolation threshold.

Table 1 presents values of the threshold concentrations p_c for our colouring obtained by averaging over five independent realisations of the Voronoi network. As a percolation threshold, such a concentration of coloured sites has been taken at which at least one cluster crosses the opposite faces of the basic cube. First, a very low threshold for percolation through the T-coloured sites should be noted, which is indicative of

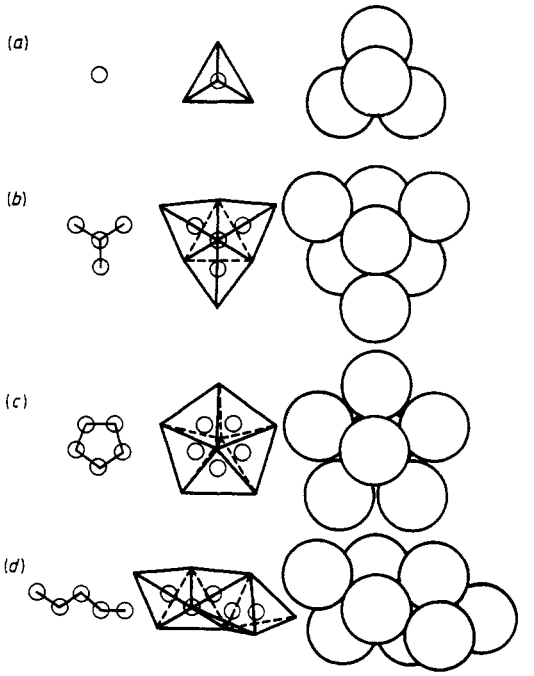

Figure 2. Correspondence between the clusters of the T-coloured sites on the Voronoi network and atomic configurations. On the left are sites of the Voronoi network and bonds joining the neighbouring sites. In the middle are the Delaunay simplices. On the right are atomic configurations. (*a*) A single tetrahedron; (*b*) a three-rayed star, a branching point of a cluster; (*c*) a five-membered ring, a decahedron; (*d*) a linear chain, the so-called Boerdijk spiral.

a strong correlation in the mutual arrangement of the tetrahedral configurations in the dense Lennard-Jones liquid. A non-random character of the T colouring has a profound physical origin. As Bernel (1964) has argued, a polytetrahedral arrangement of particles ensures the maximum possible local density of particle packing and hence the minimum local energy. Therefore the T colouring leads to a correlated percolation problem.

The percolation threshold for the octahedral simplices is considerably higher than for the tetrahedral ones but lower than the threshold for random colouring of the same networks. This results from the shape of the quartoctahedral clusters: they form long chains rather rarely and in this respect are distributed in space more randomly than tetrahedra.

Note that the threshold p_c for random colouring of the Voronoi network differs from p_c for the diamond lattice (our estimate of p_c for the latter (see table 1) is consistent with a value $p_c = 0.428 \pm 0.004$ of Sykes *et al* (1976)). This difference should be accounted for by the different ring statistics in these four-coordinated networks. In the diamond lattice, there are only six-membered rings while in the Voronoi networks the distribution from three-membered to eight-membered occurs, equivalent with the distribution of the edge numbers in the faces of the Voronoi polyhedra; see, e.g., Finney (1970) and Medvedev *et al* (1986).

In summary, the proposed methods for colouring the Voronoi network sites allows one to establish the characteristic spatial correlation of the main structural elements

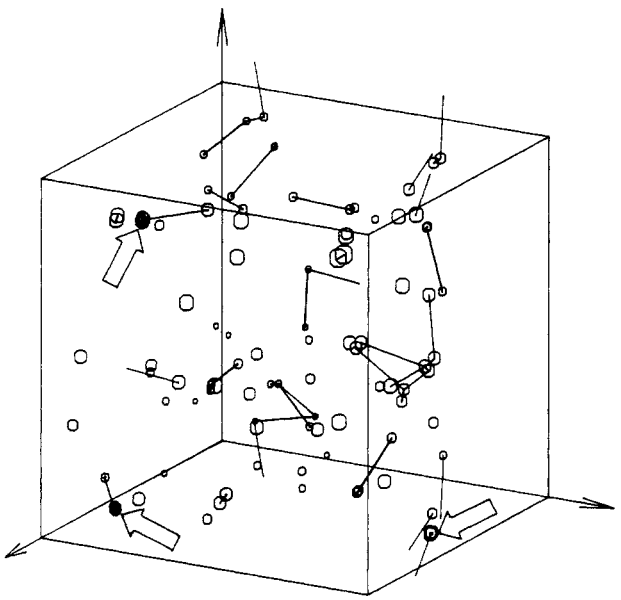

Figure 3. *O* colouring of the Voronoi network for the same realisation as in figure 1. 100 sites are depicted which correspond to the most octahedral Delaunay simplices. Arrows indicate octahedral atomic configurations.

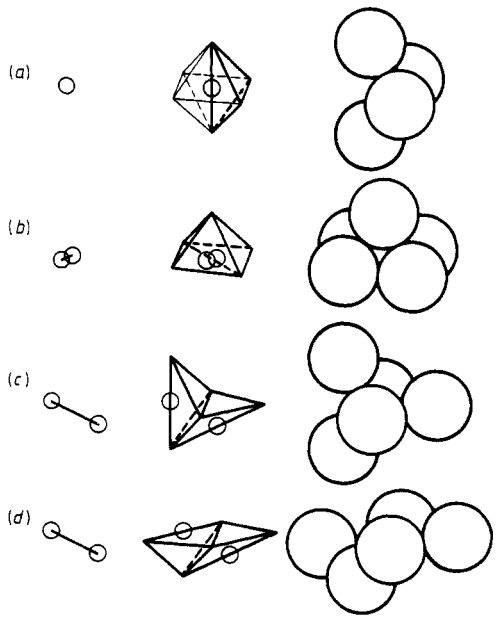

Figure 4. Correspondence between the clusters of the *O*-coloured sites and atomic configurations. (*a*) A single quartoctahedron; (*b*) a semioctahedron; (*c*) and (*d*) a 'non-octahedral' pair of quartoctahedra.

Table 1. Percolation thresholds for different site colouring of four-coordinated networks and critical values of T and O characteristics at the percolation threshold.

Colouring type		$p_c \pm \sigma$	
The Voronoi network	T	0.286 ± 0.020	$T_c = 0.0161$
	O	0.423 ± 0.032	$O_c = 0.0297$
	Random	0.476 ± 0.019	
The diamond lattice Random colouring		0.437 ± 0.018	

of simple liquids in terms of percolation theory. The tetrahedral simplicial atomic configurations tend to associate in the branched chains with built-in five-membered rings. The quartoctahedral arrangements unite sometimes in semioctahedral and octahedra, but mainly they line up in chains which are not the parts of octahedral configurations.

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