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Distinguishing liquids from amorphous solids: Percolation analysis on the Voronoi network

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The mutual arrangement of the Delaunay simplices (configurations of four nearest atoms) has been studied for molecular dynamic (MD) models of liquid and quenched rubidium obtained by M. Tanaka [J. Phys. Soc. Jpn. **55**, 3108 (1986)]. The Delaunay simplices with large circumradii and low local density of atoms, the simplices with small circumradii representing dense atomic configurations, and the simplices close in shape to perfect tetrahedron representing "rigid" arrangements of atomic quadruplets were delineated. The Delaunay simplices form clusters; consideration of the latter constitutes a site percolation problem on the Voronoi network [N. N. Medvedev, V. P. Voloshin, and Yu. I. Naberukhin, J. Phys. A: Math. Gen. **21**, L247 (1986)]. Analysis of the MD results in these terms shows that low density atomic configurations in the liquid phase form a percolative cluster. Such a cluster does not occur in a solid phase. On the contrary, there is a percolative cluster in the solid sample, but formed by high density configurations which are nearly tetrahedral.

I. INTRODUCTION

The problem of structures of noncrystalline phases is far from being solved. For certain purposes, the existing methods of analysis of structures of various states of liquid and quenched (glassy, amorphous) phases do not provide sufficient detail. In fact, even in cases where the dynamics differs by many orders of magnitude, those conventional structural descriptions may reveal only minor differences. However, apart from the structural data obtained by diffraction experiments, reliable computer models also became available. Given a computer-generated set of coordinates for all model atoms, one may perform a detailed structure analysis, search for the rules of atom packing and study the structural peculiarities of various phase states.

Let us make a brief survey of the existing approaches. The most widely used is based on the use of the radial distribution function, also called pair correlation function $g(R)$, where R is the interparticle distance. This has been discussed in much detail for example by Rice and Gray¹ (for a shorter account see Chapter 5 of Ref. 2). Characteristics in terms of $g(R)$ has been provided not only for homogeneous phases, but also for inhomogeneous liquids³ and for liquid-vapor interfaces.⁴ However, $g(R)$ is a one-dimensional representation. Another approach, initiated by Bernal⁵ and followed

by others^{6,7} is based on searching for some basic atomic configurations typical for noncrystalline systems. There is also an approach of Steinhardt and his colleagues:⁸ the local atomic environment may be expanded in power series of spherical harmonics. Their invariants, which are independent of the coordinate system, were used to characterize model structures.⁹

Amorós, Solana, and Villar^{10,11} studied what they call excluded volume (we call it free volume v') of liquids and amorphous solids. They calculated volumes from several hardsphere models, compared them with experimental ones for amorphous solids, and also with results of computer simulations of fluids. They conclude that structures and properties of liquids and of amorphous solids are determined primarily by the repulsive forces.

A still different approach is based on partitioning space into the Voronoi diagram, that is a set of Voronoi polyhedra.¹² That approach has applications also outside of the field of materials science.¹³ For a physical system, the topological and metric characteristics of the Voronoi polyhedron of a given particle are defined by the arrangement of its nearest neighbors. Hence the structure of the system may be characterized by a distribution of Voronoi polyhedra. Models of liquids and crystals,^{14,15} the phenomena of homogeneous crystallization,^{16,17} and glass formation^{18,19,20} have been investigated. David and David²¹⁻²⁴ studied structures of aqueous solutions in terms of Voronoi polyhedra, while David²⁵ shows that the polyhedra constitute structure probes for biopolymeric systems.

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Further, structures of atomic systems can be described by Delaunay simplices.^{26,27} However, the simplices are duals of the Voronoi polyhedra. We can see that further progress in describing the structure of disordered systems is associated with a generalized Voronoi–Delaunay approach, using concomitant Voronoi–Delaunay tessellations rather than Voronoi polyhedra or Delaunay simplices separately. The generalized approach allows us to study not only the properties of separate tiles resulting from tessellations, but also to search for repetitive patterns. In Ref. 28 an arrangement of the Delaunay simplices close in form to a regular tetrahedron was studied. It was shown that in liquids defined by the Mie interaction potential the simplices are arranged as ramified branching chains interspersed with five-membered rings.

The next section of our paper is concerned with notions and properties of the Voronoi and Delaunay tessellations. Subsequently, the method is used to analyze models of liquid and quenched rubidium. The data obtained allow us to throw some light upon geometrical aspects of glass formation.

II. VORONOI–DELAUNAY METHOD

For any system of discrete centers, two space-filling tessellations of convex polyhedra may always be constructed. One of them is the Voronoi diagram. In mathematical systems, such as the perfect face-centered cubic lattice, degenerate neighbors¹³ of a given point are possible; the formalism takes care of such points also. Physical systems, to be specific noncrystalline ones, are practically always nondegenerate,^{29–31} only four Voronoi polyhedra meet at any vertex of the tessellation. Then there is a second tessellation: the four centers whose polyhedra meet at a particular vertex form a tetrahedron called the Delaunay simplex. The simplices are the building blocks of the Delaunay diagram or mosaic. Since the tessellations are dual, they may be constructed easily with the help of each other.

As suggested by Medvedev and Naberukhin³¹ below we are going to use both constructions. The Voronoi diagram provides a set of edges and vertices of Voronoi polyhedra. For our models of noncrystalline materials the diagram is four coordinated. Each site (each Voronoi vertex) includes exactly four bonds (Voronoi edges). The Delaunay tessellation divides the atomic system into quadruplets of nearest atoms (simplicial atomic configurations). They may be treated as elementary structural blocks involved in any atomic aggregate of the model. We note that every site of the Voronoi diagram corresponds to a definite Delaunay simplex, being its circumcenter; each edge of the Voronoi diagram which connects two neighboring sites indicates that the corresponding Delaunay simplices have a face in common. That is, the simplicial configurations corresponding to the neighboring sites of the Voronoi network have three atoms in common. Hence a mutual arrangement of simplicial atomic configurations is reflected in the Voronoi diagram of given atomic system.

Some simplicial atomic configurations have specific physical significance. Thus, simplices with large circumradii

correspond to low density configurations: within the circumsphere of any Delaunay simplex there are no other atoms (centers) of this system.³² Hence, if a circumradius exceeds an average value, the simplicial configuration circumscribes a larger volume than the average for a given system. On the contrary, simplicial atomic configurations with the minimum circumradius correspond to the most dense arrangements. We are also interested in studying simplices of particular forms. For example, there are a large number of “good,” that is nearly equilateral, tetrahedral configurations in models of amorphous phases of spherical atoms.^{26,27} Apparently such configurations play an important role in the structure.

We infer that, if we aim to study the spatial arrangement of specific simplicial atomic configurations for a given model of liquid or glass, we should construct the Voronoi diagram and color the sites which belong to the simplicial atomic configurations of the chosen type. Thus, understanding aggregates of atoms is reduced to the problem of studying the clusters of colored sites on the four-coordinated diagram. This approach seems to simplify substantially the understanding of the structural motives in noncrystalline phases.

III. MODELS

Three molecular-dynamic configurations of 864 atoms models of the liquid, supercooled and quenched states of rubidium, kindly supplied by Tanaka, have been investigated.

The model of liquid, denoted below (*l*), corresponds to the temperature $t_l = 315$ K, which is slightly higher than the melting point. The self-diffusivity determined from the mean-square displacement $D_l = 3.8 \times 10^{-5}$ cm² s⁻¹. The models of supercooled and quenched states have been created by cooling a liquid at the same density with a velocity of $\sim 10^{13}$ K s⁻¹. Details of the quenching procedure are given in Ref. 33. The model of a supercooled liquid, to be denoted (*s*), had the temperature $t_s = 203.2$ K and $D_s = 1.8 \times 10^{-5}$ cm² s⁻¹. The model of quenched state (*q*) was at $t_q = 4.5$ K. The self-diffusivity D_q is very small and was obtained with a large relative error. Tanaka³³ gave the upper limit as $D_q < 0.06 \times 10^{-5}$ cm² s⁻¹.

The (*l*) model is a typical liquid, exhibiting the usual radial distribution function $g(R)$. The (*q*) model corresponds to a solid (or a very viscous) phase: the second maximum of $g(R)$ is split into two sharp subpeaks³⁴ characteristic for amorphous phases. For the (*s*) model, the second maximum of $g(R)$ has a flat top. However, the self-diffusivity is only two times lower than that for a normal liquid (*l*). In the activation energy E language, we infer that E is quite small. Hence we can consider the (*s*) model as representative for a liquid. Moreover, $t_s \approx 2T_m/3$, where T_m is the melting temperature. This is higher than for the glass transition point estimated by Tanaka as $T_m/3$.

The Voronoi and Delaunay tessellations have been constructed for each configuration, allowing for the periodical boundary conditions. The number of sites in the Voronoi network inside the model box was equal to 5381, 5298, and 5187 for the (*l*), (*s*) and (*q*) models, respectively. The posi-

tion of the first peak of the radial distribution function $g(R)$ in the liquid was chosen as the unit of length.

Although only one instantaneous realization has been used for each thermodynamic state in our work, we believe in the physical significance of all results reported below. This because of the shapes of the $g(R)$ curves for each and because of numerical values listed above. Moreover, Tanaka models are fairly large and the main structural features are displayed already in one instantaneous realization.¹⁸ Further, we have made the usual Voronoi analysis of these models and found that our results for each given individual configuration are very close to the results obtained by Tanaka; he was using a set of configurations for each thermodynamic state.

IV. RESULTS

Figure 1 presents the histograms of the Delaunay simplex circumradii for the above models. For all the states, the distributions are wide enough to demonstrate a variety of the simplicial configurations. In order to study the space extension of the low density atomic configurations we R colored

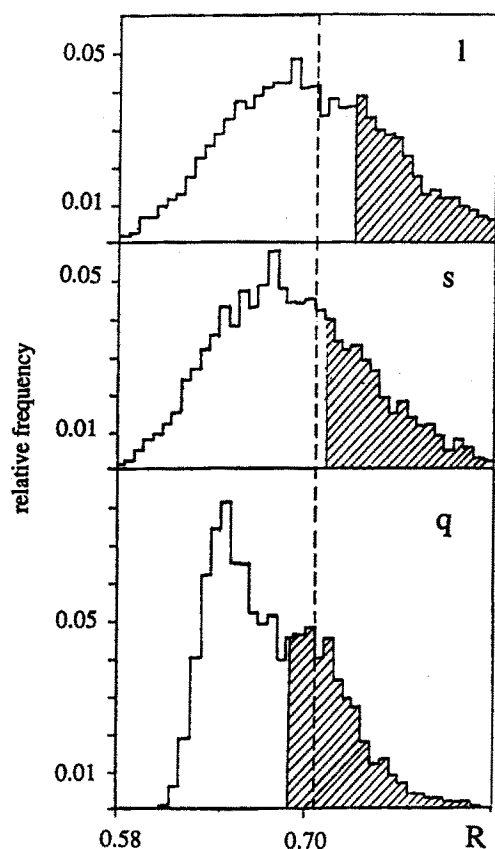


FIG. 1. The distribution of the circumradii of the Delaunay simplices for models of liquid (l), supercooled (s), and quenched (q) rubidium. The positions of the first peak of the radial distribution functions $g(R)$ are taken as length units. The hatched regions indicate the number of simplices considered (coloring the sites of the Voronoi network) at the appearance of a percolative cluster by R coloring. A dashed line shows the boundary for mobile simplicial configurations with $R > R_{\text{oct}}$; see the text.

TABLE I. Percolation thresholds for the R , r , and T coloring of the sites on the Voronoi network (see the text) for the models of liquid (l), supercooled liquid (s), and quenched state (q).

| | l | s | q |
|-------------|-------|-------|-------|
| $P_c^{(R)}$ | 0.308 | 0.318 | 0.374 |
| $P_c^{(r)}$ | 0.267 | 0.299 | 0.311 |
| $P_c^{(T)}$ | 0.300 | 0.292 | 0.324 |

the sites of the Voronoi network, corresponding to the simplices with large circumradii, beginning from the largest ones. When the fraction of colored sites is not large, small separate clusters are observed. At a definite threshold fraction $P_c^{(R)}$ a percolative cluster appears, i.e., the possibility of passing along the colored sites from one face of the model box to the opposite (Table I). This fraction determines the threshold value of radius R_c . In other words, we will obtain a percolative cluster on the Voronoi diagram when we color all sites corresponding to Delaunay simplices with circumradius greater than R_c (Table II).

Similarly, to study the dense regions we r colored the sites of the Voronoi network, corresponding to the simplices with small circumradii. The threshold fraction $P_c^{(r)}$ and value of threshold radius r_c for percolative cluster, are determined by coloring sites starting from the smallest radii (Tables I and II).

The hatched regions on Fig. 1 denote the simplices corresponding to R -colored sites on the Voronoi network at the moment of appearance of the percolative cluster. The dashed line shows the radius value $R_{\text{oct}} = 0.708$ equal to the circumradius of the regular octahedron with unit edges.

The value R_{oct} may serve as a qualitative boundary for a simplicial atomic configuration which we are going to call *fragile*; it is rigid, but the addition of even a small amount of free volume v^f can destabilize and destroy it. To understand it, let us look at Fig. 2, where a two-dimensional illustration is shown. The simplicial configuration of disks 1, 2, and 3 in the form of an equilateral triangle is a rigid one [Fig. 2(a)]. These disks cannot be moved if they are inside of dense environment of disks. If our disks do not form the equilateral triangle but the circumradius of a given simplicial configuration is less than or equal to $2^{1/2}$ (tetrahedrality) [see Fig. 2(b)], the neighboring disk 4 may prevent movements of disks 1 or 3. We shall then have a packing of four contiguous disks. It can also play the role of fragile local configurations

TABLE II. The threshold values for the circumradii of the Delaunay simplices and tetrahedrality for (l), (s), and (q) models.

| | l | s | q |
|-------|-------|-------|-------|
| R_c | 0.729 | 0.714 | 0.691 |
| r_c | 0.665 | 0.664 | 0.655 |
| T_c | 0.031 | 0.023 | 0.010 |

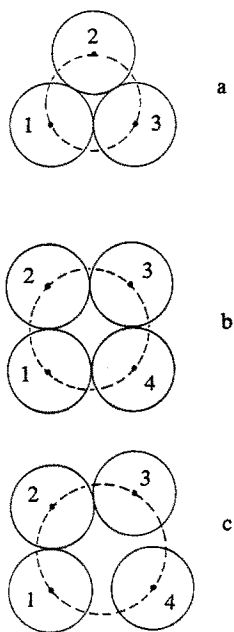


FIG. 2. Two-dimensional illustration of fragile and mobile simplicial configurations. (a) Equilateral triangle configuration of contiguous disks 1, 2, and 3. (b) If the circumradius of the Delaunay simplex is less than $2^{1/2}$, the neighboring disk 4 can be in contact with disks 1 and 3 to prevent a movement of these disks and creates a fragile configuration of four contiguous disks. (c) If the circumradius is greater than $2^{1/2}$, neighbor 4 cannot be in simultaneous contact with disks 1 and 3. Disks 1 and 3 can be moved instantly.

inside of dense neighborhood. However, if the circumradius is greater than $2^{1/2}$, any neighboring disk cannot be in contact with disks 1 and 3 at a given instant (there is a free volume in the interior of the Delaunay simplex circumsphere). We see that the simplicial configurations with large circumradii make atomic displacements possible [Fig. 2(c)]. In the three-dimensional space a regular octahedron should furnish the interior just as the square did in the two-dimensional space. Thus, a circumradius larger than R_{oct} provides mobility of spheres of a given simplicial configuration.

Admittedly, the rubidium atoms are not hard spheres. However, for a qualitative discussion R_{oct} is a quite reasonable limiting value between rigid fragile and mobile simplicial configurations. Values of R_c for models (l) and (s) exceed that of R_{oct} . Hence, in the liquid phase models, there is an aggregate spanning the entire specimen, consisting of mobile simplicial configurations. On the contrary, for the quenched state R_c is less than R_{oct} . This means that the percolative R -colored cluster contains a fraction of immobile simplicial configurations, and a mobile spanning aggregate is absent.

For r coloring, r_c is seen to be greater in the liquids than in the quenched state. Thus, the percolative cluster with a high density in the liquid contains a fraction of *less dense* simplicial configurations than in the quenched state. On the other hand, we can see in Fig. 1 that the distributions for the liquids are more extended towards the regions of small radii than for the (q) model. Therefore, there are more dense simplicial configurations in liquids than in the quenched state. Such "superdense" configurations are related to the temperature fluctuations (atoms being forced into each other). They have a short lifetime and do not relate directly to the glass formation. Therefore, the r coloring does not provide information useful for our structural investigations.

Of interest is the study of simplicial configurations with shapes close to the regular tetrahedron. They have high local

density, geometric rigidity, and the minimum local energy for atoms with a sphere-symmetrical interaction potential. We note that a large fraction of simplicial atomic configurations with small values of the circumradii have approximately tetrahedral form (the perfect tetrahedron has the minimum circumradius). In other words, r coloring and T coloring (see below) provide mostly the same Delaunay simplices. However, T coloring eliminates the simplicial configurations with large differences in the interatomic distances.

To determine good tetrahedral simplicial configurations, a measure T (tetrahedrity) has been introduced:^{27,31}

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

where l_i is the length of the i th simplex edge; $\langle l \rangle$ is the average edge length value for the simplex. With $T = 0$ the simplex is a regular tetrahedron. Low T values correspond to small distortions from the regular shape; also vice versa, the simplices close in form to the regular tetrahedra have low values of T .

Shown in Fig. 3 are the histograms of the tetrahedrity for our models. In liquids these exhibit monomodal distributions; in the quenched state there is drastic maximum at small T . This testifies to the presence of good (nearly perfect) tetrahedra. Probably, this fact is common for all dense noncrystalline systems: packings of hard and soft spheres²⁷ or frozen Mie liquids.³⁵

The hatched regions of histograms in Fig. 3 represent Delaunay simplices that had to be colored to create a percolating cluster. The threshold fractions of $P_c^{(T)}$ and the values of T_c are listed in Tables I and II. A dashed line in Fig. 3 corresponds to the value $T_b = 0.016$, restricting the class of "good" tetrahedral simplices. The T_b value is taken from³⁶ in which shapes of Delaunay simplices for Monte Carlo models of the fcc crystal at the melting point were studied. The tetrahedral atomic configurations of the crystal give a maximum on the T distribution at low T . The octahedral atomic configurations of the crystal give the next maximum at larger T . The T_b value is a visual boundary between the two classes of Delaunay simplices in the FCC model. In liquids T_c is substantially higher than T_b . Hence the percolative T -colored clusters in this case consist *not only* of good tetrahedral simplicial configurations. For the (q) model the boundary of the hatched region lies to the left. We infer that in the quenched states the percolative T -colored cluster involves only good Delaunay simplices. As for liquids, no percolative clusters of good tetrahedral configurations are found.

V. CONCLUSIONS

An application of the Voronoi–Delaunay technique verifies a principal difference in the structure of liquid and quenched phases. In the liquid there is a cluster with a low local density, spanning the whole of the specimen (in this respect it can be considered macroscopic). The atomic arrangement is such that in each simplicial configuration belonging to that cluster, atomic mobility is possible. It seems only natural that any specimen containing such a cluster is

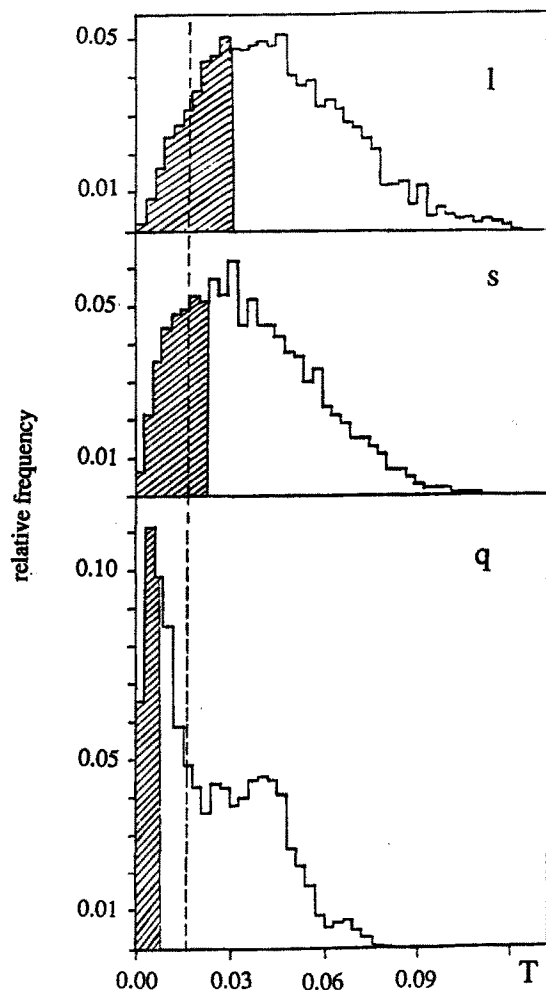


FIG. 3. The distribution of the Delaunay simplices of tetrahedrality T . The hatched regions correspond to the number of simplices when T coloring the sites of the Voronoi network at the appearance of the percolative cluster. A dashed line shows the boundary for "good" tetrahedra. $T_b = 0.016$ (Ref. 36).

fluid. The cluster has the capability of *macroscopic* structural reorganizations such as shear flow inherent to fluid systems.

In the quenched phase the liquid-like cluster is absent. Instead, there is a different percolative cluster consisting of atomic configurations close in form to the regular tetrahedron. This second type of a cluster may play the role of a backbone, imparting the mechanical rigidity to the specimen. Indeed, the regular atomic tetrahedral configuration in the system is more stable than any other (distorted) configurations. The cluster, involving several contiguous tetrahedral configurations (decahedrons or icosahedrons) should be more stable than a single tetrahedron: the atoms involved are less labile due to the geometrical "rigidity" of the cluster and lower local energy than other atomic configurations of this system. Conceivably, when the solid-like clusters are isolated, they may have no effect on the mobility of other atoms. However, if the aggregate becomes macroscopic (percolative), it will certainly hinder free diffusion of the

"liquid-like" atoms. A rigid "backbone" cannot explain low diffusivity, while it produces macroscopic "rigidity." To illustrate this point, consider an agarose gel. Mobility of water molecules in it is very high. At the same time, the agarose backbone causes macroscopic rigidity. Moreover, the aggregate may serve as an instantaneous "framework" for a given atomic system. The moment of appearance of this cluster seems to be the starting point of the transfer of the system to the solid state.

It seems that solid-like percolative clusters exist in all of glass phase models of spherical atoms and dense spheres. They always involve a high fraction of almost regular tetrahedral simplicial configurations²⁷ and a high fraction of pentagonal faces on the Voronoi polyhedra and the splitting of the second peak of the radial distribution function $g(R)$. They occur mainly due to the appearance of a large fraction of clusters of regular tetrahedral configurations with contiguous faces.³⁷

The two types of percolative clusters that we have found exhibit properties such as should be expected. One appears in the liquid, connects regions with low local density and high mobility. The other appears in the quenched system, connects tetrahedral regions with high segmental density, low overall energy, fairly rigid and with mobility virtually absent. Some years ago one of us³⁸ developed a statistical-mechanical model of free volume, assuming the existence of two types of holes: smaller, attached to atoms or molecules (interstitial) and larger or independent ones. The model includes, as special cases, earlier extreme models: that of Flory³⁹ who assumed that the entire free volume is attached to molecules or polymer segments, and that of Simha and Somcynsky⁴⁰ who assumed that only independent holes exist. The resulting distribution³⁸ was defined in terms of v_c , a critical or cut-off volume below which a hole is attached and above which it is independent. An *a priori* procedure for evaluation of v_c was not provided. Since then an accurate method of computation of molecular volumes was provided by Connolly.⁴¹ Now a procedure of computation of v_c can conceivably be developed on the basis of parameters pertaining to the two types of clusters which we have found to exist.

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¹ S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Wiley-Interscience, New York, 1965).

² W. Brostow, *Science of Materials* (Wiley, New York, 1979); W. Brostow, *Einstieg in die moderne Werkstoffwissenschaft* (Carl Hanser, München-Wien, 1985).

³ J. Harris and S. A. Rice, *J. Chem. Phys.* **86**, 5731 (1987).

⁴ S. A. Rice, *Proc. Natl. Acad. Sci. USA* **84**, 4709 (1987).

⁵ J. D. Bernal, *Proc. R. Soc. London Ser. A* **280**, 299 (1964).

⁶ H. L. Frost, *Acta Metall.* **30**, 889 (1982).

- ⁷F. Lançon, L. Billard, and A. Chamberod, *J. Phys. F*, **14**, 579 (1984).
- ⁸P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. B* **28**, 784 (1983).
- ⁹A. Baranyai, A. Geiger, Ph. R. Gartell-Mill, K. Heinzinger, R. McGreevy, G. Palinkas, and I. Ruff, *Faraday Trans.* **23**, 1335 (1987).
- ¹⁰J. Amorós, J. R. Solana, and E. Villar, *Mater. Chem. Phys.* **16**, 53 (1987).
- ¹¹J. Amorós, J. R. Solana, and E. Villar, *Mater. Chem. Phys.* **16**, 467 (1987).
- ¹²G. Voronoi, *Z. Reine Angew. Math.* **134**, 199 (1908).
- ¹³W. Brostow, J.-P. Dussault, and B. L. Fox, *J. Comp. Phys.* **29**, 81 (1978).
- ¹⁴J. L. Finney, *Proc. R. Soc. London Ser. A* **319**, 479, 495 (1970).
- ¹⁵N. N. Medvedev, V. P. Voloshin, and Yu. I. Naberukhin, *Mater. Chem. Phys.* **14**, 533 (1986).
- ¹⁶C. S. Hsu and A. Rahman, *J. Chem. Phys.* **70**, 5234; **71**, 4974 (1979).
- ¹⁷J. N. Cape, J. L. Finney, and L. V. Woodcock, *J. Chem. Phys.* **75**, 2366 (1981).
- ¹⁸M. Tanaka, *J. Phys. Soc. Jpn.* **55**, 3108 (1986).
- ¹⁹S. Nose and F. Yonezawa, *J. Chem. Phys.* **84**, 1803 (1986).
- ²⁰M. S. Watanabe and K. Tsumuraya, *J. Chem. Phys.* **87**, 4891 (1987).
- ²¹E. E. David and C. W. David, *J. Chem. Phys.* **76**, 4611 (1982).
- ²²E. E. David and C. W. David, *J. Chem. Phys.* **77**, 3288 (1982).
- ²³E. E. David and C. W. David, *J. Chem. Phys.* **77**, 6251 (1982).
- ²⁴E. E. David and C. W. David, *J. Chem. Phys.* **78**, 1459 (1983).
- ²⁵C. W. David, *Biopolymers* **27**, 339 (1988).
- ²⁶Y. Hiwatari, T. Saito, and A. Ueda, *J. Chem. Phys.* **81**, 6044 (1984).
- ²⁷N. N. Medvedev and Yu. I. Naberukhin, *J. Non-Cryst. Solids*, **94**, 402 (1987); *Doklady Akad. Nauk SSSR* **288**, 1104 (1986).
- ²⁸N. N. Medvedev, V. P. Voloshin, and Yu. I. Naberukhin, *J. Phys. A* **21**, L247 (1986).
- ²⁹N. N. Medvedev, *J. Comp. Phys.* **67**, 223 (1986).
- ³⁰V. Krishnamurthy, W. Brostow, and J. S. Sochanski, *Mater. Chem. Phys.* **20**, 451 (1988).
- ³¹N. N. Medvedev and Yu. I. Naberukhin, *Zh. Strukt. Khim.* **28**, No. 3, 117 (1987).
- ³²B. N. Delaunay, *Peterburgskaya shkola teorii chisel* (Akad. Nauk SSSR, Moscow, 1947), pp. 291–305; C. A. Rogers, *Packing and covering* (Cambridge University, Cambridge, 1964).
- ³³M. Tanaka, *J. Phys. Soc. Jpn.* **51**, 3802 (1982).
- ³⁴M. Tanaka, *J. Phys. Soc. Jpn.* **52**, 1270 (1983).
- ³⁵V. P. Voloshin, Yu. I. Naberukhin, and N. N. Medvedev, *Mol. Simul.* **4**, 209 (1989).
- ³⁶N. N. Medvedev, V. P. Voloshin, and Yu. I. Naberukhin, *Zh. Strukt. Khim.* **28**, No. 2, 62 (1987).
- ³⁷N. N. Medvedev, V. P. Voloshin, and Yu. I. Naberukhin, *Zh. Strukt. Khim.* **27**, No. 4, 91 (1986).
- ³⁸W. Brostow, *Polymer* **21**, 1410 (1980).
- ³⁹P. J. Flory, *J. Am. Chem. Soc.* **87**, 1833 (1965); P. J. Flory, *Discuss. Faraday Soc.* **49**, 7 (1970).
- ⁴⁰R. Simha and T. Somcynsky, *Macromolecules* **2**, 342 (1969).
- ⁴¹M. L. Connolly, *J. Am. Chem. Soc.* **107**, 1118 (1985).