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Order and Topology in Systems with Many Particles

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Abstract

The concept of dynamic Delauney systems and dynamic Voronoi–Dirichlet polyhedra is introduced. By means of this concept, the connection between the topology of systems with many particles with the presence or absence of short-range or long-range order is investigated. A number of topological criteria for the presence or absence of short-range order in model systems of ‘gas’ or ‘liquid’ type are proposed and tested. The features of the topology of crystal lattices of chemical substances and model multiregular systems of points, caused by the presence of long-range order in the arrangement of particles, are investigated.

1. Introduction

In our previous paper (Blatov, Shevchenko & Serezhkin, 1995), we presented the principles of the method of topological analysis of the crystal space M^3 by means of Voronoi–Dirichlet polyhedra (VDP) and considered the applications of this method to the investigation of some local and global topological properties of M^3 . The method, mentioned by Blatov, Shevchenko & Serezhkin (1995), is applied not only to three-dimensional systems of particles but also to aperiodic systems with or without short-range order to which the Delauney system of a common type corresponds. At the same time, if real aperiodic systems with many particles (*i.e.* gases, liquids or plasma) existing in thermodynamic equilibrium are considered, then limits connected with the necessary consideration of the tendency to a maximum of the configuration component of the entropy of the system (S_{conf}) are imposed on the mutual arrangement of particles. It is also necessary to take into account the influence of the dynamics of the system on its geometric/topological properties. So, in this case, we again deal with a subclass of Delauney systems, which is, however, wider than the class of multiregular systems in M^3 and includes it as a special case. Consideration of system dynamics, which is not usually taken into account when M^3 is investigated, also requires extension of the concept of a Delauney system and a VDP of points in this system.

2. Dynamic Delauney systems and dynamic VDPs

We define a dynamic Delauney system as a set of points $\{p_i\}$ in R^n where some evolution law (*i.e.* a number of rules according to which coordinates of each point p_i are changed with time) is given. In contrast to dynamic Delauney systems, we shall call Delauney systems in the definition of Galiulin (1984) static. It is clear that many properties of a dynamic Delauney system have a probabilistic nature. For example, in dynamic systems, probability distributions, whose image is determined by the evolution law, correspond to discreteness (r) and covering (R) parameters of static systems and values of r_{min} (the left limit of distribution of the discreteness parameter), R_{max} (the right limit of distribution of the covering parameter) and corresponding average values $\langle r \rangle$, $\langle R \rangle$ are significant characteristics of the system.

The connection between static and dynamic Delauney systems can be established with the help of the concept, well known in statistical mechanics, of an ensemble of systems. In this case, a dynamic Delauney system may be considered as an ensemble of static systems and its geometric/topological characteristics may be averaged according to the corresponding characteristics of the systems from the ensemble. When local characteristics of isolated points of a system (*e.g.* geometry and topology of the first coordination sphere) are of interest, it is sufficient to consider only one system from the ensemble if the number of points is large enough. The algorithm of generation must provide ‘randomness’ of this system, *i.e.* it must not lay any additional limits on the system configuration except those that are given by the evolution law of the corresponding dynamic system. It is clear that large cardinality of such Delauney systems, which will be called ‘random’, provides realization of one of the most probable configurations of a dynamic system and if the evolution law supposes that in these configurations corresponding characteristics of a system are similar then the proposed approach is quite justified from the statistical point of view.

The suggested assumption is correct for the majority of real systems with many particles in equilibrium (in this case characteristics of a random system are close to ensemble averages). Therefore, the described method is wisely used for investigation of noncrystalline con-

densed phases (Bernal, 1964; Tanaka, 1986*a,b*) as a principal tool of statistical geometry of a set of points (Bernal, 1964). The above-mentioned papers are devoted to research into the atomic arrangement in liquids and amorphous solids to which dynamic Delaunay systems with the evolution law assuming conservation of short-range order in mutual arrangement of points correspond. At the same time, there are no systematic investigations of the influence of change of the evolution law on topology of a dynamic Delaunay system, which at first causes appearance of short-range and then long-range order in atomic arrangements and corresponds to phase transitions gas-liquid-crystal. The influence of cardinality of a random Delaunay system on reliability of obtained statistical characteristics was not investigated either. The goal of our research is to solve the above-mentioned problems as far as possible.

It is natural to introduce the conception of a dynamic VDP [$\Pi^D(\mathbf{p}_i)$] to characterize geometric/topological properties of the nearest arrangement of a point \mathbf{p}_i in a dynamic Delaunay system. $\Pi^D(\mathbf{p}_i)$ is defined as a set $\{\Pi_k(\mathbf{p}_i)\}$ (*i.e.* a set of static VDPs) from the ensemble of static Delaunay systems and the weight ω_k is equal to the probability that the $\Pi_k(\mathbf{p}_i)$ realization in a dynamic system correspond to each $\Pi_k(\mathbf{p}_i)$. Thus, $\Pi^D(\mathbf{p}_i)$ is a VDP, averaged on all VDPs that are realized for \mathbf{p}_i when the system moves within the considered time interval. Further, we shall use the abbreviation VDP for static Voronoi-Dirichlet polyhedra.

Let the maximum ω_k value (ω_{\max}) be called a $\Pi^D(\mathbf{p}_i)$ degree of stability and $\Pi^D(\mathbf{p}_i)$ with $\omega_{\max} = 1$ be called a stable dynamic VDP. It is clear that a stable $\Pi^D(\mathbf{p}_i)$ can be realized only in solids, in which there is practically no translational motion of atoms and a set $\{\Pi_k(\mathbf{p}_i)\}$ possesses limited cardinality. In this case, the degree of $\Pi^D(\mathbf{p}_i)$ stability depends on the presence or absence of small edges and faces in $\Pi_k(\mathbf{p}_i)$ with ω_{\max} [$\Pi_{\max}(\mathbf{p}_i)$], identified with regard to the value of amplitude of atomic thermal oscillations. We note that $\Pi_{\max}(\mathbf{p}_i)$ may usually be calculated from atomic positions obtained as a result of structural experiments. However, if an atom \mathbf{p}_i occupies a special position, then the calculated static VDP [$\Pi_{X\text{-ray}}(\mathbf{p}_i)$] may be a result of 'averaging' of some $\Pi_{\max}(\mathbf{p}_i)$. A typical example of this is the VDP of an atom in a f.c.c. lattice (rhombododecahedron).

In liquids, gases and plasma, cardinality of $\{\Pi_k(\mathbf{p}_i)\}$ is not generally limited but when the system reaches thermodynamic equilibrium significant stability of dynamic VDPs can appear. When the system is ergodic (*i.e.* there are no prohibited domains in its configuration space) and possesses large cardinality (m), $\Pi^D(\mathbf{p}_i)$ may be evaluated from the set of all $\{\Pi_k(\mathbf{p}_i)\}$, $i = 1-m$, of any static system of the corresponding ensemble. $\Pi^D(\mathbf{p}_i)$ may be generated for crystal systems, starting from $\Pi_{X\text{-ray}}(\mathbf{p}_i)$ and taking

into account atomic oscillating motion. Initially, two 'extreme' $\Pi(\mathbf{p}_i)$ may be obtained to generate $\{\Pi_k(\mathbf{p}_i)\}$. The first one ['bottom', $\Pi_b(\mathbf{p}_i)$] is formed from $\Pi_{\max}(\mathbf{p}_i)$ by the contraction of all edges, whose length is less than double the amplitude of atomic oscillations (2α) (Fig. 1) and the other ['top', $\Pi_t(\mathbf{p}_i)$] is constructed by means of the common 'gift wrapping' procedure (Blatov, Shevchenko & Serezhkin, 1995) after shifting all atoms forming no $\Pi_{X\text{-ray}}(\mathbf{p}_i)$ towards \mathbf{p}_i also with amplitude 2α . The rest of the VDPs from $\{\Pi_k(\mathbf{p}_i)\}$ may be obtained by exhaustion of all variants of 'splitting' all vertices of $\Pi_b(\mathbf{p}_i)$ with degree $v > 3$, as is demonstrated in Fig. 1, followed by rejection of additional [in comparison with $\Pi_{X\text{-ray}}(\mathbf{p}_i)$] faces of $\Pi_t(\mathbf{p}_i)$. It should be noted that, with regard to system dynamics, in dynamic VDPs the probability of occurrence of $\Pi_k(\mathbf{p}_i)$, which have vertices with $v > 3$, is very small and the $\Pi_k(\mathbf{p}_i)$ cannot be taken into account, although $\Pi_{X\text{-ray}}(\mathbf{p}_i)$ can be one of them as in the example mentioned above.

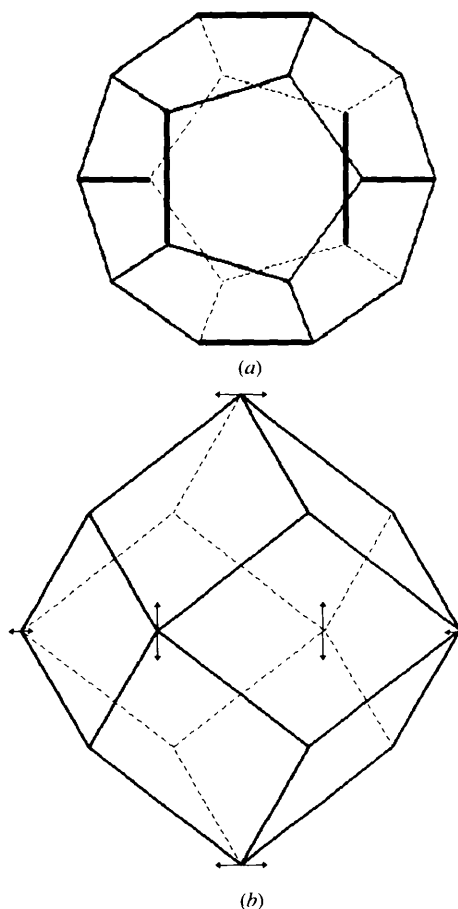


Fig. 1. Transformation of a VDP pentagonal dodecahedron (a) into a rhombododecahedron (b) by means of 'tightening' small edges indicated by bold lines. The rhombododecahedron can be transformed into a pentagonal dodecahedron by means of 'splitting' all vertices with degree $v = 4$ (shown by arrows).

3. Topological criteria for the presence and type of order in Delaunay system

At present, it is evident that the only distinct criterion for the presence of short-range or long-range order in Delaunay system is the existence of site or space symmetry in a mutual arrangement of points. This criterion, connected with metrics of a system, may be called the 'geometric' criterion. At the same time, it is clear that the order in a system can be observed when symmetry is absent. Therefore, new criteria must be searched. In the present paper, 'topological' criteria of order based on the analysis of Voronoi-Dirichlet tessellation (VDT) of a system are proposed and tested. We note that, as long as a dynamic system is ergodic, its VDT is completely characterized by arbitrary $\Pi^D(\mathbf{p}_i)$. For non-ergodic systems (e.g. crystal lattices), all $\Pi^D(\mathbf{p}_i)$ should be considered, $i = 1 - Z$, where Z is the number of non-equivalent atoms in a unit cell. Since a dynamic VDP characterizes the nearest environment of a point in a dynamic Delaunay system, it is natural to use its characteristics to investigate short-range order in the mutual arrangement of points in a system. Among such characteristics, we have chosen the distribution of a dynamic VDP on the number of faces f [$F_{\text{VDP}}(f)$] and on combinatorially topological types and also the view of relationship between a solid angle Ω of the face of a dynamic VDP and a distance r_{at} between the corresponding pair of points. As was shown by Blatov, Shevchenko & Serezhkin (1995), in a static VDP, Ω can be a measure of the intensity of the interatomic interaction, which causes the appearance of short-range order. Therefore, the choice of this characteristic seems to be perfectly justified. We note that this set of characteristics is not complete, since theoretically any parameter of a dynamic VDP can characterize short-range order to a certain degree. When crystal substances with small cardinality of a symmetrically independent part of a Delaunay system are analyzed, the above-mentioned parameters must be averaged on dynamic VDPs of different structures, and as a result the obtained conclusions may be spread over the whole class of investigated substances if we abstract partially or completely from their chemical nature.

At the same time, it is not known *a priori* whether one can form an opinion about the presence, absence or degree of long-range order in a system using the view of a dynamic VDP. The present paper is devoted to the investigation of this problem too.

Henceforth, the results are given of the investigation of the model, which is analogous to the 'ideal gas' system without both long-range and short-range order in the mutual arrangement of atoms, considered by Tanaka (1986a), of crystal lattices of chemical compounds, where both types of order take place, of model multiregular systems of points only with long-range order and of systems possessing only short-range order.

Among the latter, there are Lennard-Jones systems with the potential

$$E(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

where attractive forces make the primary contribution to the energy of a system under the condition that the interatomic distance is $r < \sigma$, and also one-component Coulomb systems consisting of particles with the same sign of charge and characterized by Coulomb potential caused only by repulsive forces. Evolution laws of the corresponding dynamic Delaunay system are determined by the system of Newton equations with regard to the above-mentioned potentials. It should be noted that, strictly speaking, a dynamic Delaunay system of the 'ideal gas' type is characterized by zero value of r_{min} and by the absence of prohibited domains in configuration space. However, in the scientific literature, the term 'ideal gas' is also used for systems with $r_{\text{min}} > 0$, which are analogous to systems of hard non-interacting spheres with radius $r_{\text{min}}/2$ (Tanaka, 1986a). In Lennard-Jones and Coulomb systems, formally $r_{\text{min}} = 0$ but r_{min} is actually determined by the repulsive part of the potential.

All calculations were done by means of the program package *TOPOS* in accordance with the previously described methods (Blatov, Shevchenko & Serezhkin, 1995).

4. Presence of short-range and long-range order. Crystal lattices

In this section, the results of the analysis of combinatorially topological organization of lattices of complexing atoms, which are accepted as centers of the corresponding complex groups in structures of coordination compounds of Ti, Zr, Hf, Mo, Th, U and Np, are presented.

We used information from the Cambridge Structural Database and the crystal database on actinide compounds (Blatov & Serezhkin, 1989). The structures of 4124 compounds of Ti (724), Zr (567), Hf (104), Mo (1719), Th (107), U (863) and Np (40) were investigated.

In Table 1, the results of the calculation of the $\Pi_{\text{X-ray}}(\mathbf{p}_i)$ distribution in accordance with the number of faces are given. It is notable that the number of structural groups following the Belov 12-neighbors rule (Belov, 1976), which $\Pi_{\text{X-ray}}(\mathbf{p}_i)$ in the form of a dodecahedron corresponds to, is relatively small and does not exceed 6% in all cases except uranium compounds, whereas the number of tetradecahedra varies within a wider range and is minimal for VDPs of uranium and neptunium atoms. Only the last two samples demonstrate pure inorganic (*i.e.* containing no organic carbon) compounds, among them uranates, neptunates and uranium oxides with a significant ionic

Table 1. Amount of VDPs with n faces in percentage of the total number

Element	Amount (n) of VDP faces							Other VDPs*	Volume of sample†
	12	13	14	15	16	17	18		
Ti	4.1	5.6	58.7	9.9	14.1	2.7	3.3	1.6	958
Zr	2.7	3.8	64.0	7.5	13.3	3.4	3.7	1.6	709
Hf	6.0	3.4	66.4	5.2	13.8	-	2.6	2.6	116
Mo	4.1	2.2	71.4	3.9	13.4	0.9	2.5	1.6	1877
Th	2.4	2.4	74.6	4.0	8.7	0.8	4.0	3.1	126
U	11.5	3.4	57.3	5.8	9.6	2.1	2.7	7.6	1060
Np	6.0	-	56.0	14.0	6.0	4.0	10.0	4.0	50

* Values of n for these VDPs vary from 6 to 11 and from 19 to 22.

† The data for each crystallographic type of atom, which is given in the first column, are taken into account.

contribution in the bond, belong only to the last two samples. To explain this fact, let us consider the model of a crystal structure as a packing of spherical structural units of different rigidity (deformability). The Belov 12-neighbors rule corresponds to close packing of hard spheres (Fig. 2a). Soft spheres, mutually deforming and trying to fill the whole space, transform to VDPs (Fig. 2c). Figs. 2(b), (c) show that the value of sphere deformation during construction of the tessellation is proportional to the volume of overlapping of spheres (V_o), forming the corresponding space covering. It is clear that V_o per sphere (V_{os}) is

$$V_{os} = V_s - V_{VDP} \quad (1)$$

and

$$V_{os} = V_{VDP}(K_c - 1), \quad (2)$$

where V_s is the volume of a sphere, $K_c = V_s/V_{VDP}$ is the coefficient of space covering.

The variants of close packing of spheres in three-dimensional space are well known to crystal chemists and explain the realization of the 12-neighbors rule for structures of compounds containing rigid structural

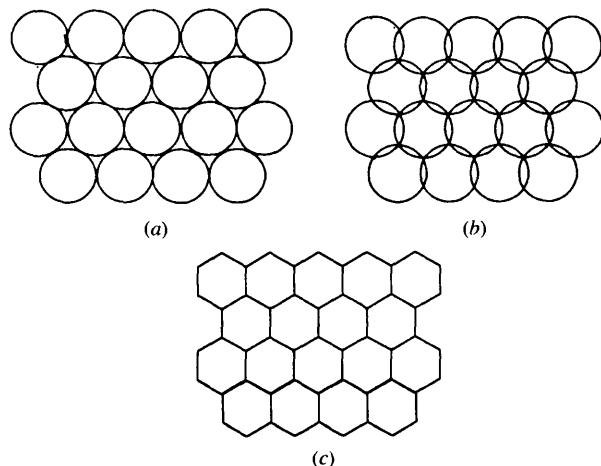


Fig. 2. (a) Packing, (b) tessellation and (c) covering of the plane.

groups (corresponding VDPs of atoms are rhombododecahedra). However, the model of the rarest covering of three-dimensional space by spheres has not so far been covered in the theory of solids. At the same time, it is known (Conway & Sloane, 1988) that in three-dimensional space only a b.c.c. lattice with the minimal value $K_c = 1.46$ satisfies such a covering. We note for comparison that $K_c = 2.09$ corresponds to the distribution of centers of spheres on the lattice of any close packing.

Thus, if soft spherical or quasi-spherical structural groups tend to achieve the maximum density of packing (in the case of absolutely soft groups, they tend to fill the whole space) in accordance with the principle of maximum filling (Vainshtein, Fridkin & Indenbom, 1983) and the centers of the spheres are distributed on the b.c.c. lattice, then, taking (2) into account, their total deformation will be minimal. With this condition, a VDP has the form of a Fedorov cuboctahedron and the number of groups surrounding the given one is equal to 14, *i.e.* for structures of coordination compounds, containing easily deformable structural groups, the '14-neighbors rule' must be realized. It should be noted that, if separate atoms are the structural units, then the greater their 'softness' the higher is their ability to overlap outer electronic shells when a chemical bond is formed. In such a case, the model of crossing spheres has a direct physical meaning.

In Fig. 3, histograms of distributions of uranium-containing VDPs, depending on the nature of the compounds, are given. As is shown in Fig. 3, together with the change of the composition of compounds in the sequence Fig. 3(a)→(b)→(c), the relative amount of VDP dodecahedra increases and that of VDP tetradecahedra decreases in the sample. Within the sug-

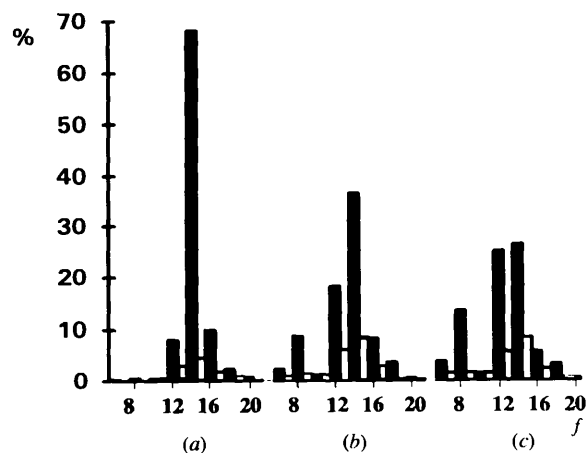


Fig. 3. Distribution of VDPs on the number of faces (f) in percent of the total size of samples, including m uranium compounds. (a) Containing organic molecules and ions ($m = 579$); (b) containing only inorganic, including multiautomic, groups ($m = 284$); (c) containing only inorganic mono- and quasimonoatomic (*e.g.* OH^- , H_2O , H_3O^+) ions and molecules ($m = 155$).

Table 2. Amount of VDPs with the determined combinatorial properties in percentage of the total number in the investigated samples

The types of VDPs with frequency >3%, at least for any sample of those considered, are given only. In the description of the VDP type, the numerator is equal to the number of angles of the face of a polyhedron and the denominator is equal to the number of faces of the given sort in a polyhedron. The numbers after the braces allow differentiation of combinatorially different polyhedra, which have identical designation of the type.

N	Type of VDP	Ti	Zr	Hf	Mo	Th	U	Np
I	{4/6 6/8}	27.1	29.5	36.2	37.2	45.2	32.3	32.0
II	{4/4 5/4 6/6} - 1	11.6	12.0	13.8	15.4	16.7	10.4	16.0
III	{4/4 5/4 6/6} - 2	8.4	8.6	5.2	9.1	5.6	4.5	4.0
IV	{4/3 5/6 6/5} - 1	4.8	4.5	4.3	4.9	3.2	1.9	-
V	{4/3 5/6 6/5} - 2	2.0	3.2	5.2	2.9	2.4	1.7	2.0
VI	{3/4 4/2 5/4 6/2 8/4}	2.2	1.8	1.7	3.4	3.2	2.0	2.0
VII	{4/8 6/4}	1.9	1.7	1.7	2.6	2.4	5.1	2.0
VIII	{4/6 6/2}	0.1	0.1	-	0.3	0.8	3.6	2.0

gested model of deformable spheres, this fact indicates that the rigidity of complex groups increases symbatly. Actually, complex particles, surrounded by the 'fur' of multiatomic organic ligands (L) are deformable owing to both the lability of coordination bonds $U \cdots L$ and the conformational mobility of molecules L themselves. At the same time, UO_6^{6-} groups, for example, in uranates possess stable geometry (Blatov & Serezhkin, 1991) and are distortable only to some degree, mainly owing to the deformation of the electron shells of oxo ligands.

Let us consider the tendency of the number of VDPs in the form of octahedra and hexahedra (*i.e.* hexagonal prisms and parallelepipeds, respectively) to increase in structures of uranium inorganic compounds (Figs. 3b, c). Analysis of the composition and structure of complex uranium-containing groups in these samples shows that VDPs in the form of hexagonal prisms are realized in substances where structural groups possess only two-dimensional (in a plane) deformability and are closely connected in a direction that is orthogonal to the plane (*e.g.* chain fluorouranylates and some uranates). At the same time, both absolutely rigid and deformable groups will be packed according to the same law because the optimal packing and covering of two-dimensional space are topologically equivalent (Figs. 2a, b). If 'rigid' bonds $U-L$ are directed to the vertices of an octahedron (as in the majority of uranates), then VDPs mainly in the form of hexahedra are realized.

The data in Table 2 show the existence of VDPs, which are 'intermediate' between the Fedorov cuboctahedron and rhombododecahedron. Among them there are four types of tetradecahedra and a hexadecahedron (II-VI, Table 2). It should be mentioned that the presence of rhombododecahedra is not typical for the samples considered; dodecahedra with hexagonal faces (VII, Table 2), which belong to the set of well known

Fedorov parallelohedra together with rhombododecahedron and cuboctahedron, occur much more frequently. However, this fact does not contradict the 12-neighbors rule because, when it was formulated by Belov (1976), the topology of the packing was not taken into consideration. If one constructs a scale of rigidity of structural groups, where a VDP in the form of a rhombododecahedron is unity and a VDP in the form of a Fedorov cuboctahedron is -1, then 'intermediate' VDPs will correspond to points within this interval or, in other words, to structural groups with intermediate rigidity, but verification of this hypothesis requires additional investigations.

In Fig. 4, the dependence of $\Omega(R_{U-O})$ on R_{U-O} for $\Pi_{X\text{-ray}}(\mathbf{p}_i)$, where \mathbf{p}_i are uranium(VI) atoms in 276 oxygen-containing compounds, is given. Apart from abnormally long distances $R_{U-O} \geq 3 \text{ \AA}$, the values of R_{U-O} that correspond to strong chemical bonds (covalent or ionic covalent) in the classical description of the structure of U^{VI} compounds occur on a straight line, which may be described by the following r.m.s. equations:

$$\Omega(R_{U-O}) = 51.2(1) - 16.79(5)R_{U-O} \quad (3)$$

or

$$\ln \Omega(R_{U-O}) = 5.08(1) - 1.130(5)R_{U-O} \quad (4)$$

with correlation coefficients 0.99 and 0.98, respectively, for 2525 experimental points with $R_{U-O} < 3 \text{ \AA}$. In (3) and (4) and in Fig. 4, $\Omega(R_{U-O})$ are expressed in percent of the total solid angle $4\pi \text{ sr}$ and R_{U-O} in \AA . It should be noted that (4) is analogous to the well known Pauling dependence of bond length-bond strength, if one considers Ω as an analog of bond strength as was proposed by Blatov, Shevchenko & Serezhkin (1995). The presence of the functional dependence $\Omega(R_{U-O})$ reflects the existence of strong $U-O$ chemical bonds

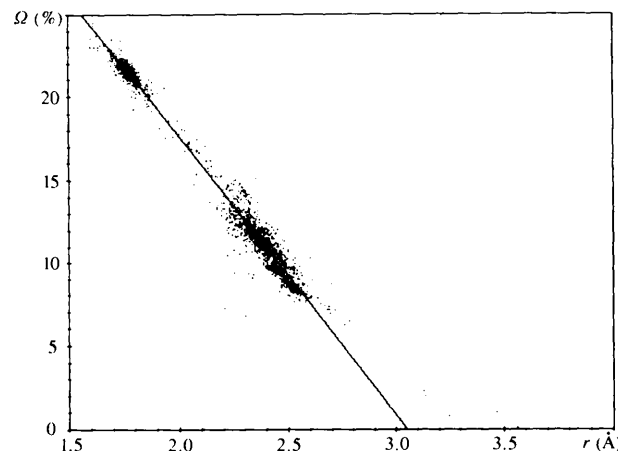


Fig. 4. $\Omega(R_{U-O})$ dependence for VDPs of U atoms in oxygen-containing compounds.

and, in our opinion, is the effect of short-range order in the first coordination sphere of U atoms.

5. 'Absence' of short-range order. The 'ideal gas' system

For the above-mentioned reasons, we used an ensemble consisting of three random Delauney systems with large cardinality to investigate the topology of the atomic arrangement in 'ideal gas' systems. In order to generate every random system from the ensemble, we applied an algorithm that is analogous to the one used by Tanaka (1986a). In a cubic box with fixed dimensions (the edge of the cube is 40–100 Å), we generated points with pseudo-random coordinates until the average volume per point of the Delauney system reached a given value while r_{\min} was varied from 0 to 3.8 Å. The maximum density of space filling for the corresponding system of hard spheres was approximately 37%, which is greater than the density of crystal lattices in the majority of chemical substances (in particular, for coordination compounds, the density of space filling for sublattices of complexing atoms is not more than 30%). In this case, the cardinality of the system reaches 10 000 points and r_{\min}/R_{\max} varies from 0 to 1. The further increase in the density of the system is connected with the extreme increase of the generation time. The above-mentioned range of r/R value variation is typical for the majority of static Delauney systems, which correspond to crystal lattices of chemical compounds, except for some simple substances [in particular, for lattices of close-packed metals, $r/R = 1.41$, and the maximum value $r/R = 1.55$ for lattices in three-dimensional space is reached in the case of b.c.c. metals (Galiulin, 1984)].

The typical view of $F_{\text{VDP}}(f)$ for the 'ideal gas' system ($m = 10\,000$, $r_{\min} = 3.8$ Å) is given in Fig. 5. The spread of all characteristics of $F_{\text{VDP}}(f)$, averaging over the ensemble, when $m \geq 1000$ did not exceed 2%. The results of the calculation of more than 200 000 VDPs allow the following conclusions to be made:

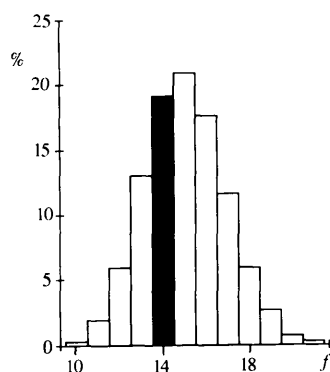


Fig. 5. $F_{\text{VDP}}(f)$ for the 'ideal gas' system.

(i) In all investigated samples, $F_{\text{VDP}}(f)$ is close to a normal distribution (more exactly to a polynomial one, taking into account its discreteness) with a small positive skewness [$\alpha > 3\sigma(\alpha)$] because its flatness is $\varepsilon = 0$ within the tripled standard deviation $\sigma(\varepsilon)$.

(ii) When $m \geq 1000$, independently of r_{\min} , the value of the distribution mode (M_F) firmly corresponds to pentadecahedra ($M_F = 15$), whose relative amount increases with increase of m .

(iii) With increase of cardinality of the Delauney system with the given r_{\min} , the value of G_3 (Blatov, Shevchenko & Serezhkin, 1995) decreases regularly (e.g. if $r_{\min} = 3.8$ Å then G_3 varies from 0.113 at $m = 100$ to 0.0865 at $m = 10\,000$). This fact indicates increase of system uniformity, which, however, remains sufficiently low even at $m = 10\,000$. Note that, for the most uniform three-dimensional periodic system (b.c.c. lattice), $G_3 = 0.0785$ (Conway & Sloane, 1988), and, for structures of elementary substances mainly with non-directional interactions, $G_3 < 0.082$ (Blatov, Shevchenko & Serezhkin, 1995).

(iv) Increase of r_{\min} for systems with identical cardinality causes regular increase of system uniformity (e.g. at $m = 10\,000$, for $r_{\min} = 0$, $G_3 = 0.115$, and, for $r_{\min} = 3.8$ Å, $G_3 = 0.0865$), appearing in particular in a decrease skewness and span of distribution of $F_{\text{VDP}}(f)$ [at $r_{\min} = 0$, the left and right limits of $F_{\text{VDP}}(f)$ are respectively $f_{\min} = 6$ and $f_{\max} = 29$, at $r_{\min} = 3.8$ Å, $f_{\min} = 8$ and $f_{\max} = 23$].

Altogether, the calculation results indicate that the increase of density of the 'ideal gas' system and the corresponding decrease of $\langle R \rangle$ at $m \geq 1000$ influence its topological characteristics insignificantly. At the same time, when an aperiodic system has small cardinality ($m < 1000$), rules (ii) and (iii), generally speaking, are not realized, and oscillations in the values of M_F and G_3 are observed. In our opinion, it indicates the influence of periodic boundary conditions on the topology of the system at the mentioned m values.

In our opinion, in order to explain the data obtained, one can propose the following model of change of $\Pi^D(\mathbf{p}_i)$ combinatorial properties, where \mathbf{p}_i is any point ('atom') of a dynamic Delauney 'ideal gas' system. Let us consider an arbitrary VDP from $\Pi^D(\mathbf{p}_i)$. At some instant, this VDP unambiguously determines the first coordination sphere and coordination polyhedron of \mathbf{p}_i [$\text{CP}(\mathbf{p}_i)$], which is dual to VDP. In this case, the terms 'coordination sphere' and 'coordination polyhedron' have a formal meaning because the interaction between atoms is absent. In particular, it is a result of the duality of VDP and CP that the number of CP faces is equal to the number of VDP vertices. It should be noted that the analysis of combinatorial properties of $\Pi^D(\mathbf{p}_i)$, characterizing the topology of the 'ideal gas' system, reveals the unambiguous dependence between the number of VDP faces (CP vertices) (f) and the number of VDP vertices (CP faces) (v):

$$v = 2f - 4, \quad (5)$$

indicating that degrees of vertices in all VDPs have the minimal possible value, which is 3. In this case, the number of edges (e) of the VDP is connected with the number of vertices by the formula $e = 3v/2$ and, using Euler's theorem, it is not difficult to get (5). This property of the VDP is stipulated by the fact that all considered VDPs are common (Shtogrin, 1973), *i.e.* they do not change their combinatorial properties during sufficiently small motion of the system. Thus, the corresponding CPs possess only triangular faces.

Assuming that CP can be approached by spheres and CP faces have approximately equal sizes, let us consider atoms of the second coordination sphere. We note that the program *DIRICHLET* from the program package *TOPOS* (Blatov, Shevchenko & Serezhkin, 1995) allows one to determine the composition of the n th arbitrary coordination sphere by constructing a VDP of the ' n th degree'. Let us call a VDP in the definition of Blatov, Shevchenko & Serezhkin (1995) a VDP of the first degree. Then, a VDP of the n th degree is constructed analogously but atoms taking part in forming all VDPs until the $(n - 1)$ th degree inclusively are not taken into account during the 'gift wrapping' procedure. Henceforth, we shall use 'VDP' for the designation of a VDP of the first degree. Each atom of the second coordination sphere belongs to at least one CP surrounding the central one. If all CPs have approximately equal size, then up to 13 analogous groups can be arranged around the central CP (*i.e.* the arrangement of 12 equal spheres around the central one always leaves additional free space and in the considered model the boundaries of CPs can be intersected). In the proposed model, the most probable mechanism of acquisition of the additional face by the VDP includes penetration of an atom from the second coordination sphere into the first one through one of the CP faces. The face conforming to this atom 'cuts' the

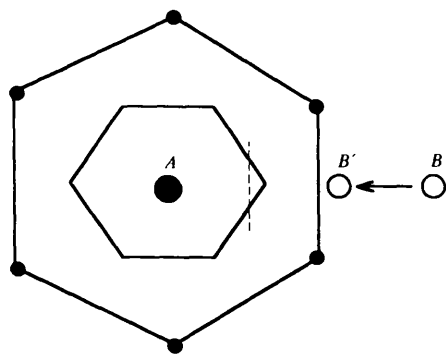


Fig. 6. Scheme demonstrating the mechanism of change of combinatorial properties of the VDP of atom A during the penetration of outer atom B through the CP face into the first coordination sphere of atom A . The dashed line indicates the VDP face appearing while moving atom B to position B' .

VDP vertex, corresponding to the CP face, through which the attack has been made. For a two-dimensional case, an example of the described process is shown in Fig. 6.

An attacking atom can belong to one of the 13 CPs surrounding the central one. It can be supposed that each of the mentioned CPs possesses one 'active' atom, which is capable of attacking the nearest face of the central CP. In the most probable state of the considered system, all 13 'active' faces of the central CP (if $v \geq 13$) can be attacked. On the other hand, its 'inactive' faces can disappear, pushing out atoms to the second coordination sphere and, since all CP faces are triangular, elimination of even one atom causes the loss of a face. One can assume that CPs with the number of active faces, which is equal to the number of inactive faces and to 13, will be the most statistically stable. For these CPs, $v = 26$ and VDPs, which are dual to them, according to (5) will be pentadecahedra and this is observed in practice (Fig. 5).

Using the proposed model, one can predict the bottom (v_b) and top (v_t) limits of the typical number of CP faces for the 'ideal gas' system. It is clear that $v_b = 13$ but, since the number of CP faces can only be even, according to (5), $v_b = 12$ or 14 fits the threshold value. The corresponding VDPs have eight or nine faces and this is in good agreement with the data obtained (only seven heptahedra were found among more than 200 000 investigated VDPs). One can evaluate v_t , taking into account that the maximum number of atoms that are capable of penetrating into the first coordination sphere of an atom, characterized by the most stable VDP with $f = 15$, is equal to the number of active faces of the corresponding CP, *i.e.* to 13. Then, $v_t = 15 + 13 = 28$, which also fits the obtained data (we did not find any VDP with $f > 28$ among the investigated ones).

'Absence' of short-range order also reflects absence of the expressed functional dependence $\Omega(R_{at})$, where R_{at} is the distance between points in a system (Fig. 7) in contrast to systems with strong interatomic interactions (Fig. 4). During increase of R_{at} , the spread in $\Omega(R_{at})$ values quickly increases and $\Omega(R_{at})$ looks like the typical shape of a 'tail of a flying up rocket'. However,

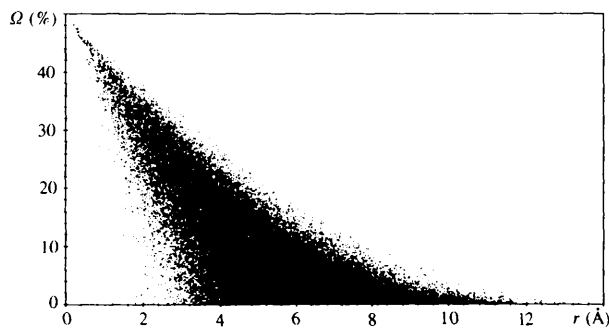


Fig. 7. $\Omega(R_{at})$ dependence for the 'ideal gas' system ($n = 155398$).

absolute chaos is not observed in the distribution of points on the plot (the correlation coefficient is equal to 0.75 for 155 398 points). This fact indicates correlation in the atomic arrangements in the system. It is clear that this correlation is caused by the presence of short-range order of a ‘thermodynamic’ type related to the tendency of S_{conf} to go to a maximum. In our opinion, the type of $\Omega(R_{\text{at}})$ dependence permits one to distinguish such a type of order from one stipulated by a force field.

In our opinion, the obtained results allow formulation of the 15-neighbors rule for dynamic Delaunay ‘ideal gas’ systems in addition to the 12- and 14-neighbors rules. According to this rule, on condition that long-range and short-range order are absent in a dynamic Delaunay system, the most probable number of points in the first coordination sphere of an arbitrary point of the system is 15 and the most frequent polyhedron type in the system VDT is a pentadecahedron. It may be supposed that the 12- and 14-neighbors rules are the effect of interatomic and intermolecular interactions, providing at least short-range order in the corresponding dynamic Delaunay system.

6. Presence of short-range order

6.1. Lennard-Jones systems

Dynamic Delaunay systems with short-range order were generated by the molecular dynamics method using the *HyperChem* program (Autodesk Inc., 1992) in a cubic box with edge 20 Å and periodic boundary

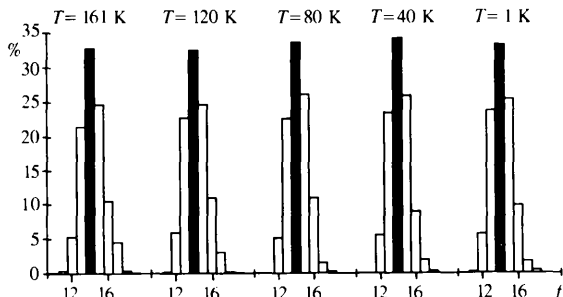


Fig. 8. $F_{\text{VDP}}(f)$ for the ‘liquid xenon’ system.

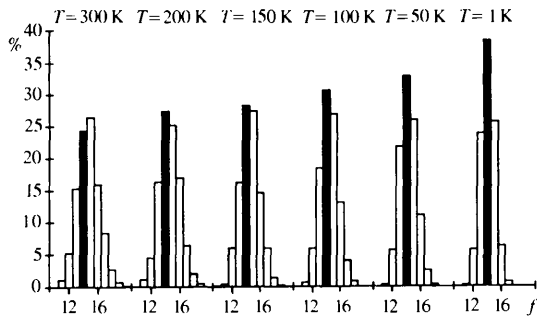


Fig. 9. $F_{\text{VDP}}(f)$ for the ‘atomic hydrogen’ system.

conditions. The relaxation time of the systems varied from 1 to 2.5 ps with a step of 0.002 ps.

In Figs. 8 and 9, the results are shown of the topological analysis of aperiodic systems, modeling liquid xenon at the temperature of crystallization (161 K) and during quenching down to 1 K ($\sigma = 4.06 \text{ \AA}$, $\epsilon = 2.07 \text{ kJ mol}^{-1}$) and atomic hydrogen ($\sigma = 0.891 \text{ \AA}$, $\epsilon = 0.084 \text{ kJ mol}^{-1}$, $T = 1\text{--}300 \text{ K}$), whose cardinalities were 1000 and 2160 atoms, respectively, which allow the influence of boundary conditions on the topological properties of VDT to be neglected, as has been mentioned in §5. During decrease of temperature, the density of the ‘liquid xenon’ system was linearly increased up to the value that is typical for crystalline xenon.

As is shown in Figs. 8 and 9, the VDTs of liquid xenon and atomic hydrogen (at $T \leq 200 \text{ K}$) are characterized by the predominance of tetradekahedra

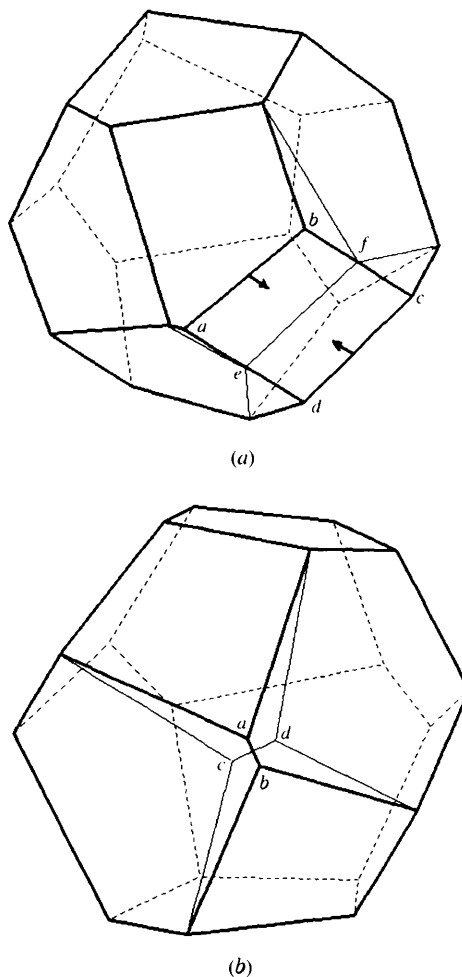


Fig. 10. Transformation into pentagonal dodecahedron {5/12} of (a) tridecahedron {4/1 5/10 6/2} by means of ‘tightening’ face [abcd] to edge [ef]; (b) dodecahedron {4/2 5/8 6/2} by means of ‘reversing’ edge [ab] into edge [cd]. The transformed parts of the polyhedra are shown as thin lines.

Table 3. *Distribution of the most frequent combinatorially topological types of VDPs, depending on the temperature, of the 'liquid xenon' and 'atomic hydrogen' systems*

Type of VDP*	Relation-ship†	'Liquid xenon' system ($m = 1000$)					'Atomic hydrogen' system ($m = 2160$)					
		Amount of VDPs (%)					Amount of VDPs (%)					
		161 K	120 K	80 K	40 K	1 K	300 K	200 K	150 K	100 K	50 K	1 K
{4/1 5/10 6/2}‡	pd	4.1	4.7	3.7	5.2	4.8	0.8	1.0	1.2	2.3	3.7	5.4
{4/3 5/6 6/4} - 1	in	2.6	3.2	2.8	2.7	2.6	0.8	0.8	1.8	2.2	2.9	4.0
{4/3 5/6 6/5} - 1	in	2.0	1.7	2.4	2.9	2.0	0.4	0.6	0.9	1.8	2.0	4.0
{4/3 5/6 6/4} - 2	in	1.6	2.3	2.7	2.7	3.3	0.6	0.5	0.9	1.2	2.0	2.5
{4/1 5/10 6/3}	pd	1.5	2.1	1.5	1.5	1.9	0.5	0.2	0.7	1.3	2.1	2.3
{4/2 5/8 6/4} - 2	pd	1.4	1.8	2.3	1.6	2.0	0.3	0.6	0.9	0.9	1.9	3.0
{4/2 5/8 6/2}‡	pd	1.4	1.3	1.4	1.7	1.8	0.6	0.6	0.7	1.3	1.7	1.9
{5/12}	pd	1.4	1.3	1.5	1.9	1.8	0.1	0.1	0.5	0.5	1.2	1.9
{4/2 5/8 6/4} - 1	pd	1.3	1.5	1.5	2.2	2.5	0.3	0.5	0.7	0.8	1.1	1.9
{4/4 5/4 6/6} - 2	fc	0.9	1.0	1.1	1.9	1.4	0.2	0.4	0.3	0.4	0.6	1.7
{3/1 5/9 6/3}	pd	0.5	1.2	1.8	1.0	0.8	0.1	0.3	0.3	0.3	1.1	1.1
{3/1 4/2 5/6 6/3 7/1}	in	0.4	1.7	1.4	1.1	1.1	0.4	0.2	0.4	0.5	1.1	0.6
{4/3 5/6 6/5} - 2	in	0.6	0.8	0.9	0.7	0.9	0.2	0.3	0.2	0.5	0.5	1.9
{4/4 5/4 6/6} - 3	in	0.5	0.8	0.8	0.8	0.9	0.1	0.2	0.1	0.2	0.5	2.5
{4/4 5/4 6/7}	in	0.2	0.8	0.8	0.9	0.9	0.1	0.1	0.2	0.1	0.5	1.8
{4/4 5/4 6/6} - 1	in	0.6	1.0	1.2	1.0	1.3	0.2	0.2	0.5	0.5	0.7	1.6
Total amount of the indicated types of VDP (%)		21.0	27.2	27.8	29.8	30.0	5.7	6.6	10.3	14.8	23.6	38.1
Total amount of VDP types		575	525	484	450	456	1068	1059	1442	1032	699	510

* Combinatorially topological types, the number of which compose no less than 1.5% from cardinality (m) of the system, at least for some state, are given. † Combinatorially topological relationship: pd with pentagonal dodecahedron; fc with the Fedorov cuboctahedron; in intermediate VDPs. ‡ Shown in Fig. 10.

because the mode $M_F = 14$ while $F_{VDP}(f)$ is close to normal distribution with small positive skewness. Thus, if the 15-neighbors rule is typical for systems without both short-range and long-range order, then the 14-neighbors rule, which is especially clear in periodic systems with long-range order, begins to be fulfilled, when short-range order appears in the atomic arrangement. It should be noted that the analogous view of $F_{VDP}(f)$ was observed in the other explored Lennard-Jones systems – in liquid noble gases, metals and close-packed spheres (Finney, 1970; Tanemura, Hiwatari, Matsuda, Ogawa, Ogita & Ueda, 1977; Yamamoto & Doyama, 1979; Tanaka, 1986a,b).

At the same time, the detailed analysis of VDT topology shows that the most frequent combinatorially topological types in a dynamic VDP are tridecahedra with ten pentagonal faces (Fig. 10a, Table 3), which are topologically similar to a pentagonal dodecahedron. Further, we shall consider topologically similar VDPs or VDPs possessing a combinatorially topological relationship in a Delauney system, which can be transformed into combinatorially equal polyhedra by a sufficiently small motion of the system, changing their combinatorial properties through the transformation of only one of the hyperfaces (*i.e.* vertex edge or face) belonging to these polyhedra into a hyperface with different dimensionality or topology.

Let us call the mentioned elementary act of the change of combinatorial properties of a VDP a 'transformation step'. For example, the VDP shown in Fig. 10(a) transforms into a pentagonal dodecahedron by means of 'tightening' a quadrangular face $[abcd]$ into

an edge $[ef]$ (shown by arrows), *i.e.* by one step. It is clear that, during the search of combinatorially topological relationships, one-step transformations of two VDPs into a combinatorially equal polyhedron can be placed by a two-step transformation of one polyhedron into another. For example, the VDP in Fig. 10(b) can be transformed into a pentagonal dodecahedron by 'reversing' the separated edge $[ab]$. This is equivalent to a two-step transformation (first, the $[ab]$ edge is 'tightened' into a vertex, then the vertex 'splits' into the $[cd]$ edge shown by a thin line). As will be shown further, besides VDPs related to a pentagonal dodecahedron, polyhedra, which are topologically equal to a Fedorov cuboctahedron, play an important role in VDT of the considered aperiodic systems. We shall call other VDPs, for the transformation of which into one of two mentioned 'basic' types of polyhedra more than two steps are necessary, as intermediate ones.

It should be noted that, for the 'liquid xenon' system, variation of temperature and density of the system does not influence the $F_{VDP}(f)$ (Fig. 8). Whereas, for the 'atomic hydrogen' system at 300 K, $M_F = 15$, $F_{VDP}(f)$ is similar to the distribution that is typical for the 'ideal gas' system (Fig. 5), and with the decrease of temperature and the corresponding increase of short-range order in the system, the maximum of $F_{VDP}(f)$ smoothly shifts to the left (Fig. 9) and at $T = 1$ K $F_{VDP}(f)$ is practically symmetric, $M_F = 14$. The shape of $\Omega(R_{at})$ dependence (Fig. 11) also changes appreciably for the 'atomic hydrogen' system, and the growth of short-range order is shown in the decrease of the spread of $\Omega(R_{at})$ values with the decrease of tempera-

ture (the value of the correlation coefficient increases from 0.89 at $T = 300$ K to 0.95 at $T = 1$ K).

The above-mentioned differences in the behavior of the systems during the quenching process may be explained by the small mass of H atoms in comparison with Xe atoms. At the same time, according to the data in Table 3, the combinatorial properties of a dynamic VDP change during the quenching process for systems of both types, while a significant increase of the part of VDPs that are topologically similar to a pentagonal dodecahedron is observed. Since the mentioned VDPs can be transformed into each other even by relatively small motions of the system (Fig. 10), the change of frequency of each type of VDPs separately with variation of temperature is not monotonous on the

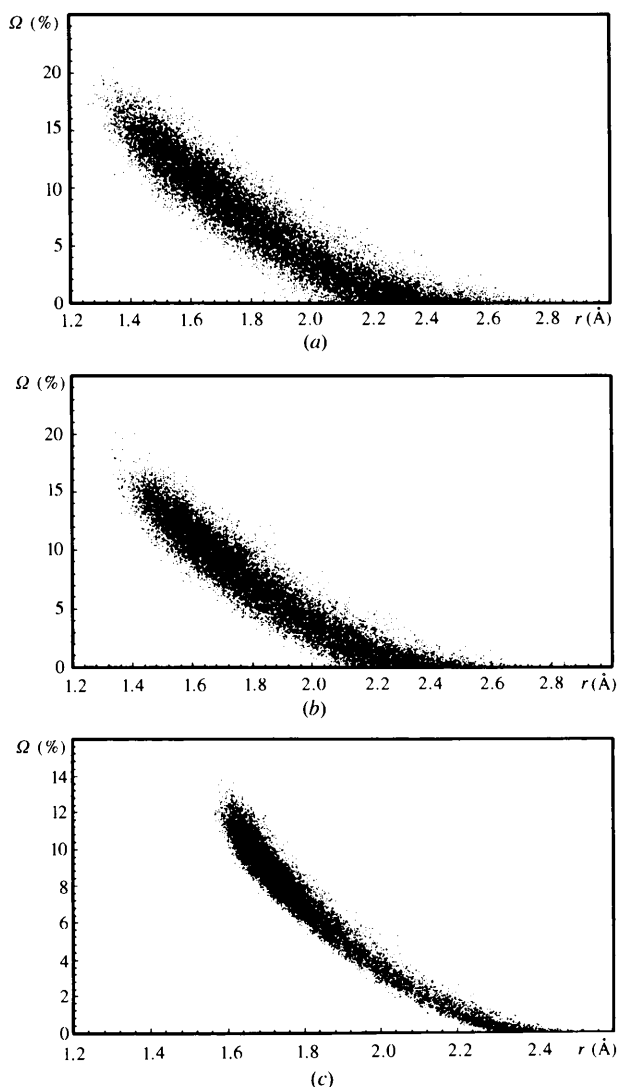


Fig. 11. Change of $\Omega(R_{at})$ dependence during temperature decrease in the 'atomic hydrogen' system: (a) $T = 300$ K, $n = 31\,796$; (b) $T = 150$ K, $n = 31\,348$; (c) $T = 1$ K, $n = 30\,332$.

whole (Table 3). At the same time, the decrease of the temperature of systems causes a regular increase in the total number of all frequent types of VDPs in a dynamic VDP of systems and a decrease in the total number of combinatorially topological types. This fact can be considered as a decrease of the 'combinatorial' component of the system entropy. Simultaneously, the regular increase of global uniformity of the system proceeds. Fig. 12 graphically demonstrates the growth of the number of VDPs that are topologically similar to a pentagonal dodecahedron during quenching of the 'atomic hydrogen' system, where the distribution of VDP faces on the number of angles is shown. Fig. 12 shows that a decrease of temperature causes the increase of weight of VDPs with pentagonal faces in the system VDT and it corresponds to the data (Finney, 1970; Tanemura, Hiwatari, Matsuda, Ogawa, Ogita & Ueda, 1977; Yamomoto & Doyama, 1979; Tanaka, 1986*a,b*). It should be emphasized that, in periodic systems (Fig. 12*h*), pentagonal faces do not conform to a distribution mode because the most frequent type of VDPs in the VDT of a crystal lattice (Fedorov cuboctahedron) contains only tetragonal and hexagonal faces.

Thus, for the considered systems, short-range order in the mutual arrangement of atoms is expressed first of all in the tendency to icosahedral encirclement of the central atom by other atoms in the first coordination sphere (because the CP of the central atom is dual to the corresponding VDP); this was also mentioned by Tanaka (1986*a,b*). In our opinion, the seeming contradiction between the 14-neighbors rule, which is typical for the system as a whole, and the tendency of each atom to icosahedral coordination may be solved within a statistical model of change of combinatorial properties of a dynamic VDP described in §5. It may be supposed that short-range order must be observed not only in the arrangement of separate atoms but also in the location of quasi-spherical CPs of these atoms relative to each

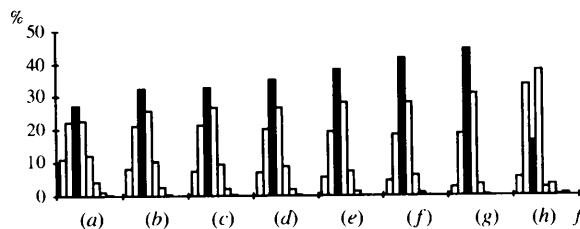


Fig. 12. Frequency of VDP faces with the given number of vertices in percent of the total size of sample (n). (a) For the 'ideal gas' system ($n = 155\,398$). For the 'atomic hydrogen' system (b) at 300 K ($n = 31\,796$), (c) at 200 K ($n = 31\,538$), (d) at 150 K ($n = 31\,348$), (e) at 100 K ($n = 31\,028$), (f) at 50 K ($n = 30\,740$), (g) at 1 K ($n = 30\,332$). (h) For the sample containing VDPs of complexing atoms in sublattices of crystal structures of coordination compounds, considered in §4 ($n = 72\,416$). For each of the eight histograms, the value of a step at the x axis corresponds to the change of the number of edges of a VDP face for a unit. The columns corresponding to pentagonal faces are indicated as black.

Table 4. Distribution of the most frequent combinatorially topological types of VDPs, depending on the density of the 'atomic hydrogen' system ($T = 50\text{ K}$, $m = 2160$)

Type of VDP*	Relation-ship*	Amount of VDPs (%) at the density (g cm^{-3})				
		0.295	0.448	0.545	0.850	0.295†
{4/3 5/6 6/5} - 1	in	0.1	2.0	3.0	5.0	3.5
{4/1 5/10 6/2}	pd	0.8	3.7	5.6	4.1	5.4
{4/3 5/6 6/4} - 1	in	0.8	2.9	3.5	3.7	3.0
{4/3 5/6 6/4} - 2	in	0.4	2.0	2.7	3.0	2.3
{4/2 5/8 6/4} - 1	pd	0.2	1.1	2.9	3.0	2.1
{4/2 5/8 6/4} - 2	pd	0.6	1.9	4.0	2.7	2.3
{4/4 5/4 6/6} - 1	in	0.2	0.7	1.3	2.5	1.1
{4/4 5/4 6/6} - 3	in	†	0.5	1.8	2.5	0.9
{4/4 5/4 6/6} - 2	fc	0.2	0.6	1.5	2.2	1.5
{4/4 5/4 6/7}	in	†	0.5	0.9	1.8	1.1
{4/2 5/8 6/3}	pd	0.2	1.3	1.5	1.7	1.2
{5/12}	pd	0.2	1.2	2.2	1.5	2.4
{4/2 5/8 6/2}	pd	0.6	1.7	1.4	1.5	1.4
{4/1 5/10 6/3}	pd	0.1	2.1	2.2	1.5	2.4
{3/1 5/9 6/3}	pd	0.1	1.1	1.3	0.8	1.8
$G_3 \times 10^3$		82.9	80.3	79.6	79.3	79.5
Total amount of the indicated types of VDP (%)		4.5	23.3	35.8	37.5	32.4
Total amount of VDP types		1086	699	524	479	569

* See footnotes to Table 3. † The value $\varepsilon = 84\text{ kJ mol}^{-1}$ conforms to the model of packing of 'hard spheres', for other columns of the table, $\varepsilon = 0.084\text{ kJ mol}^{-1}$. ‡ $< 0.1\%$.

other. Such short-range order of the 'second degree' results in the fact that only 12 analogous groups will mainly surround the central CP but not 13, as in the 'ideal gas' system. In this case, according to the mentioned model, the central CP will possess 12 'active' faces and CPs with equal numbers of 'active' and 'inactive' faces amounting to 24 will be statistically the most stable. The analysis of combinatorial properties of VDPs shows the correctness of (5) for them. According to this formula, a dual VDP with 24 vertices and 14 faces must fit to statistically the most stable CP with 24 faces and this is actually observed.

The increase of density of the 'atomic hydrogen' system, modeled by its isothermal compression at 50 K, causes an essential change of the combinatorially topological organization of a dynamic VDP (Table 4). The decrease of 'combinatorial' entropy is accompanied by an appreciable increase in the part of combinatorial (equal to Fedorov) cuboctahedra and intermediate tetradecahedra and by a reduction of the amount of VDPs of pentagonal dodecahedral type. If one links to each point in a Lennard-Jones system a van der Waals sphere with radius $R = \frac{1}{2}2^{1/6}\sigma$, where $2R$ is the equilibrium interatomic distance, then the sphere hardness k , which is proportional to the curvature of $E(r)$ in the minimum point $k \propto [d^2E(r)/dr^2]_{2R}$, will be determined by the relation ε/R^2 . Thus, varying the ε value at constant R , one can model the system of deformable

spheres with variable hardness. Since in the considered 'atomic hydrogen' system ε is sufficiently small [the potential energy of the system is comparable with the energy of thermal motion at 50 K ($\sim 1465\text{ kJ mol}^{-1}$) and equal to about 2100 kJ mol^{-1} when the density is 0.448 g cm^{-3}] and, thus, van der Waals spheres are 'soft', the above-mentioned influence of compression of the system on the topology of its VDT fits the qualitative model described in §4. At the same time, the calculations show that at small deformations short-range order of an 'icosahedral' type is more profitable. This fact allows the supposition that the minimum of the total overlapping of spheres at the incomplete filling of space will be reached at such an arrangement of centers of spheres, which VDT, characterized by pentagonal dodecahedra or by VDPs combinatorially equal to them, corresponds to. Modeling the packing of hard spheres ($\varepsilon = 84\text{ kJ mol}^{-1}$, Table 4) shows that the total decrease of combinatorial entropy and the increase of the system uniformity in contrast to the system of soft spheres ($\varepsilon = 0.084\text{ kJ mol}^{-1}$, Table 4) causes the appearance of the aperiodic system, in whose VDT VDPs related to pentagonal dodecahedron predominate.

6.2. One-component Coulomb systems

We considered the systems consisting of protons at $m = 2160$ and $T = 1\text{--}300\text{ K}$. The data obtained show that the 14-neighbors rule and the similarity of $F_{\text{VDP}}(f)$ and normal distribution are also typical for one-component Coulomb systems. However, the relative amount of tetradecahedra in VDT in contrast to the 'atomic hydrogen' system slightly depends on the temperature change. This fact may be explained by the small value of the energy of thermal motion ($\sim 27.2\text{ kJ mol}^{-1}$) in comparison with the energy of Coulomb interaction ($\sim 27.2\text{ GJ mol}^{-1}$). The results of the calculation of the VDT topology are given in Table 5. Table 5 shows that the most frequent combinatorially topological type of VDPs in dynamic VDPs of one-component Coulomb systems is a Fedorov cuboctahedron, while some types of VDP are combinatorially similar to it and can be easily transformed into it, e.g. by 'splitting' (Fig. 13a) or by 'reversing' an edge (Fig. 13b). The primary realization of the mentioned VDP type is explained by taking into account both the model of deformable spheres and the principle of uniformity (Blatov, Shevchenko & Serezhkin, 1995) because, in the presence of long-range central repulsion forces, the system tends to global uniformity in the mutual arrangement of particles. As was shown by Blatov, Shevchenko & Serezhkin (1995), VDTs, which are characterized by VDPs in the form of Fedorov cuboctahedra, fit with the maximum uniformity of the system. It should be noted that the presence of short-range van der Waals forces in Lennard-Jones systems causes growth of local uniformity because G_3 is less for

Table 5. Distribution of the most frequent combinatorially topological types of VDPs, depending on the charge of H atoms in the 'atomic hydrogen' system ($T = 1\text{ K}$, $\rho = 0.448\text{ g cm}^{-3}$, $m = 2160$)

Type of VDP*	Relationship*	Charge of H atoms		
		0.1	0.5	1.0
{4/6 6/8}	fc	0.4	1.3	6.7
{4/3 5/6 6/5} - 1	in	2.9	5.2	5.7
{4/4 5/4 6/6} - 1	in	1.2	2.7	5.6
{4/4 5/4 6/6} - 2†	fc	1.8	3.3	4.9
{4/3 5/6 6/4} - 1	in	2.9	4.0	4.4
{4/3 5/6 6/4} - 2	in	2.2	3.2	4.1
{4/4 5/4 6/6} - 3	in	1.9	2.8	3.4
{4/1 5/10 6/2}	pd	4.2	5.5	3.0
{4/2 5/8 6/4} - 2	pd	3.0	4.2	2.6
{4/2 5/8 6/4} - 1	pd	2.0	2.9	2.5
{4/5 5/2 6/6}†	fc	0.7	1.1	2.5
{4/4 5/4 6/7}	in	1.3	1.2	2.0
{4/5 5/2 6/8}	fc	0.5	1.0	2.0
{4/1 5/10 6/3}	pd	2.4	2.3	1.3
$G_3 \times 10^3$		79.9	79.3	79.1
Total amount of the indicated types of VDP (%)		27.4	40.7	50.7
Total amount of VDP types		583	403	383

* See footnotes to Table 3. † Shown in Fig. 13.

pentagonal dodecahedra (0.07813) than for Fedorov cuboctahedra (0.07854), but global uniformity remains less than in one-component Coulomb systems even at high density (Tables 4 and 5). It seems that the great amount of CPs of an 'icosahedral' type in Lennard-Jones systems even at high density and also in packing of hard spheres is explained by the short-range character of van der Waals interactions.

6.3. Intermediate systems

In order to investigate the features of competitive influence of attractive and repulsive forces on the topology of VDTs of an aperiodic system, we considered the systems consisting of 2160 H ions with positive charge $0 < Q_H < 1$ at 1 K, while the forces of interatomic attraction were modeled by a Lennard-Jones potential. Tables 4 and 5 show that the mentioned systems are topologically intermediate between Coulomb and Lennard-Jones systems. It should be noted that the most significant characteristic, reflecting the degree of similarity of an intermediate system to one of extreme systems, is the part of the Fedorov cuboctahedra in its dynamic VDP, regularly increasing with the increase of Q_H . Other types of VDP are rather frequently realized in all investigated systems but, during the increase of Q_H values and repulsive forces, tetradecahedra that are combinatorially similar to Fedorov cuboctahedra begin to predominate among combinatorially topological types, although VDPs combinatorially related to pentagonal dodecahedra are also stored as a significant part in a dynamic VDP of the system. It seems to be normal that intermediate

tetradecahedra are sufficiently frequent at any Q_H value. It should be noted that they (in particular II and IV, Table 2) also compose a significant part in the VDTs of crystal lattices.

Realization of the 14-neighbors rule of the aperiodic dynamic Delauney system indicates the presence of interatomic interaction whose energy is comparable at least with the energy of atomic thermal motion. When interatomic interaction is strengthened, the number of tetradecahedra in the VDT system increases and becomes greatest when long-range order and crystal structure appear, as is shown in Fig. 9. The predominance of Fedorov cuboctahedra in VDTs of crystal lattices should be interpreted as a result of the strong deformation of structural groups under the influence of interatomic attractive forces or as a result of packing of slightly deformable structural units in the presence of repulsive forces with long-range character. Other types

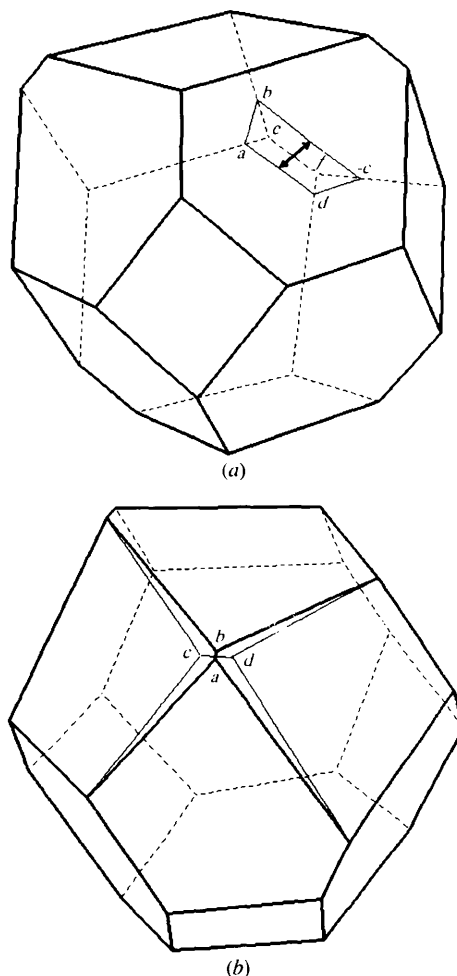


Fig. 13. Transformation into Fedorov cuboctahedron {4/6 6/8} of (a) tridecahedron {4/5 5/2 6/6} by means of 'splitting' edge [ef] into face [abcd]; (b) tetradecahedron {4/4 5/4 6/6} - 2 by means of 'reversing' edge [ab] to edge [cd]. The transformed parts of the polyhedra are shown as thin lines.

Table 6. Cardinality (m) of the independent part of the Delauney system and n_{sym} value, depending on the mode of VDP distribution on the number of faces f for space groups of the monoclinic system

Space group	ω_i^*	$M_F(1)$	m or n_{sym}^\dagger	Mode (M_F) of VDP distribution on the number of faces										
				8	9	10	11	12	13	14	15	16		
$P2$	27	8	m	-	-	-	-	-	-	-	-	20	2	
$P2_1$	3502	14	n_{sym}	-	-	-	-	-	-	2	6.7	4	0.84	
			m	-	-	-	-	-	-	-	-	2.8	-	
$C2$	619	14	n_{sym}	-	-	-	-	-	-	-	-	10	1.0	
			m	-	-	-	-	-	-	-	-	1500	7.5	
Pm	14	8	m	2	-	3	10	20	40	400	1500	-	-	
			n_{sym}	5.0	-	3.6	1.6	1.1	0.86	0.40	0.25	-	-	
Pc	270	14	m	-	-	-	-	-	-	4	5	2	-	
			n_{sym}	-	-	-	-	-	-	3.1	2.4	6.7	-	
Cm	110	8	m	-	-	-	2	20	30	90	1000	-	-	
			n_{sym}	-	-	-	4.9	0.95	0.78	0.50	0.23	-	-	
Cc	745	14	m	-	-	-	-	-	-	-	10	2	-	
			n_{sym}	-	-	-	-	-	-	-	0.32	7.2	-	
$P2/m$	88	8	m	2	-	3	4	10	20	90	500	-	-	
			n_{sym}	5.4	-	4.2	3.5	2.1	1.4	0.74	0.35	-	-	
$P2_1/m$	794	8	m	-	-	-	2	20	40	200	500	-	-	
			n_{sym}	-	-	-	4.9	1.0	0.81	0.42	0.30	-	-	
$C2/m$	1434	8	m	-	-	-	2	3	30	40	1500	-	-	
			n_{sym}	-	-	-	5.7	4.2	0.93	0.81	0.18	-	-	
$P2/c$	460	14	m	-	-	-	-	-	-	-	3	2	-	
			n_{sym}	-	-	-	-	-	-	-	5.0	7.5	-	
$P2_1/c$	21712	14	m	-	-	-	-	-	-	2	3	-	-	
			n_{sym}	-	-	-	-	-	-	7.1	4.2	-	-	
$C2/c$	4911	16	m	-	-	-	-	-	-	-	4	2	-	
			n_{sym}	-	-	-	-	-	-	-	2.7	6.7	-	

* Frequency of space groups [in accordance with Baur & Kassner (1992)]. $\dagger n_{\text{sym}}$ is the average number of points that are symmetrically equivalent to the central point of the VDP and take part in its formation; m_{lim} conforms to m at $M_F = 15$.

of tetradecahedron can appear in the VDTs of systems containing slightly deformable particles connected by short-range interactions. The fact that tridecahedra, which are typical for aperiodic systems, do not exist in crystal structures seems to be a result of geometrical/topological problems, appearing at the realization of CPs of an 'icosahedral' type in periodic systems.

7. Presence of long-range order and 'absence' of short-range order

7.1. Multiregular systems

Apparently, the realization of long-range order, on condition that short-range order is absent, is impossible in systems with many particles. At the same time, in any system with long-range order (e.g. in crystal lattices), one can always isolate a subsystem (i.e. sublattice), where particles are arranged at distances that are sufficiently large to neglect their immediate interaction. In such a system, short-range order may be absent. Investigation of topological features of such subsystems may be useful for the crystal-chemical analysis of structures of chemical substances, since, in particular, it permits the evaluation of radii of interatomic interaction.

As an example, we chose space groups of the monoclinic system, which are the most frequent in

structures of chemical substances. In order to generate random multiregular Delauney systems, we used the generation algorithm for the 'ideal gas' system. The differences were in accounting for non-translation space symmetry and for variation of the form of the unit cell

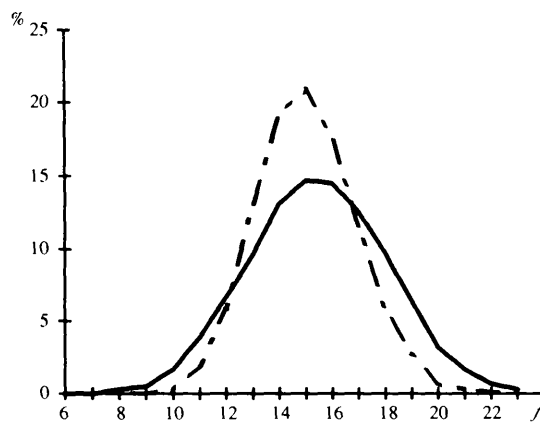


Fig. 14. Frequency of VDPs with the given number of faces (f) in percent from the cardinality (n) of the 'ideal gas' system ($n = 10000$, dashed line) and from the size of the sample containing VDPs of points in 2500 random multiregular Delauney systems with $m = 3$ for space group $P2_1/c$ ($n = 7500$, solid line; $F_{\text{VDP}}(f)/f$ values: 0.3/8; 0.5/9; 1.7/10; 3.9/11; 6.7/12; 9.7/13; 13.1/14; 14.7/15; 14.5/16; 12.6/17; 9.8/18; 6.5/19; 3.2/20; 1.7/21; 0.7/22; 0.3/23).

Table 7. Classification of space groups in accordance with the change of features of VDT topology during increase of cardinality of the independent part of the corresponding multiregular system

Type	Space group	m_{\min}	ΔM_F^*	Mode of $F_{VDP}(f)^\dagger$								Symmetry ‡			
				8	9	10	11	12	13	14	15		16		
A1	$P2_1/c$	3	1												VC
A2	$P2_1$	4	1									●	→		VC
B	$C2/c$	4	1										←	●	VC
C	$C2; Cc; P2/c$	3-10	2									●	←	←	C
D	Pc	5	2									●	←	←	C
E	$P2$	20	8	●	→	→	→	→	→	→	→	→	→	→	IC
F	$Pm; Cm; P2/m;$ $P2_1/m; C2/m$	500- 1500	7	●	→	→	→	→	→	→	→	→	→	→	IC

* $\Delta M_F = M_{F(\max)} - M_{F(\min)}$. † The change of M_F value from $M_F(1)$ to $M_F(m_{\lim})$ is shown by arrows. ‡ Label indicates that symmetry of the given group is 'very convenient' (VC), 'convenient' (C) or 'inconvenient' (IC) for provision of topology transformation of space of condensed state during the phase transition liquid \longleftrightarrow crystal.

within the considered crystal system. With regard to the data obtained on the practical independence of the considered topological properties of VDTs from the value of the discreteness parameter, r_{\min} was taken equal to 0. Cardinality of the generated systems was varied within the range from 2 to 2500 independent atoms, a varying step was taken as 1 at $m < 10$, 10 at $m < 100$, 100 at $m < 500$ and 500 at $m > 500$. Some independent systems were parallelly generated, whose total cardinality was 7000-8000 points for each space group.

The results of the calculations show that at $m \geq 200$ the topology of a random multiregular Delaunay system is practically independent of its metric and density [the deviation in the $F_{VDP}(f)$ values was not more than 1%]. Therefore, in the following calculations, all systems with $m \geq 200$ were generated in a pseudocubic unit cell with a specific volume of 500 \AA^3 per point. For systems with $m < 200$, the metric of the unit cell and the system density were varied randomly within the range, which is typical for sublattices of complexing atoms in structures explored in §4 (parameters of the monoclinic unit cell and the specific volume value were varied in the ranges $5\text{-}25 \text{ \AA}$ and $100\text{-}2000 \text{ \AA}^3$, respectively).

The results obtained (Table 6) indicate that for all considered space groups, starting from some limiting m value (m_{\lim}), the corresponding $F_{VDP}(f)$ are similar to a distribution that is typical for an ideal gas. So, all $F_{VDP}(f)$ at $m \geq m_{\lim}$ were found close to a polynomial distribution with slightly positive skewness and mode $M_F = 15$, while the distribution of a dynamic VDP on combinatorially topological types does not contain polyhedra with a frequency of more than 0.5% in all cases. For comparison, in Fig. 14, $F_{VDP}(f)$ for an ideal gas and for the most frequent space group $P2_1/c$ with $m_{\lim} = 3$ are given. Some discrepancies in the $F_{VDP}(f)$ shape (Fig. 14), in accordance with the conclusions given in §5, are explained by the influence of space symmetry, remaining at $m < 1000$, which is insignificant at $m \geq m_{\lim}$. It should be noted that the error of the found m_{\lim} values (Table 6) is determined

by the above-mentioned values of the step variation of the system cardinality at the given m .

Thus, at $m \geq m_{\lim}$, space symmetry practically does not influence the topology of a dynamic VDP of the system, for which the 15-neighbors rule begins to be performed. Since m_{\lim} is essentially dependent on the considered space group (Table 6), it should be noted that it is not practically associated with the $F_{VDP}(f)$ mode in the case of the monosystem basis [$M_F(1)$]. Thus, for space groups $P2$ and Pm , $M_F(1) = 8$, but m_{\lim} values (20 and 1500, respectively) significantly differ from each other. The obligatory condition of the large value $m_{\lim} \geq 500$ realization is the existence of mirror planes of symmetry in a space group. At the same time, the influence of other closed elements of symmetry on m_{\lim} is insignificant and it is especially clearly seen in $P2/c$ and $C2/c$ groups (Table 6).

It should be noted that the presence of closed elements of symmetry strongly influences the view of $M_F(m)$ dependence, realizing in the considered space groups. Thus, for groups containing mirror planes, the monotonous increase of $M_F(m)$ during the growth of m from $M_F(1) = 8$ up to $M_F(m_{\lim}) = 15$ is typical. Then, the transition $m \rightarrow m_{\lim}$ is accompanied by the decrease in the average number of points (n_{sym}) that are symmetrically equivalent to the central point of the VDP and take part in forming it, from 8 at $m = 1$, to 4.9-5.7 (i.e. about one half of the total number of VDP faces) at $m = 2$ and down to 0.18-0.35 at $m = m_{\lim}$.

For all monoclinic groups containing no m planes but including rotation axes 2 ($C2/c$ and its subgroups), independent of the $M_F(1)$ value, $M_F(2) = 16$, i.e. the attainment of $M_F(m_{\lim})$ is realized through the intermediate VDT, containing mainly hexadecahedra. It is notable that in groups containing mirror planes there is no distribution with $M_F = 16$ at any values of the cardinality of the corresponding multiregular Delaunay system, and as was mentioned above, hexadecahedra compose a significant part of the VDT for sublattices of complexing atoms in the structures of chemical compounds.

For regular systems of points of the most frequent (frequency $\omega_i > 1000$) space groups of the monoclinic system, the value $n_{\text{sym}}(m_{\text{lim}}) = 2.7\text{--}4.2$ is higher than for groups containing mirror planes. It is clear that the mentioned large $n_{\text{sym}}(m_{\text{lim}})$ values indicate the absence of essential limits on the nearest environment of \mathbf{p}_i point by the corresponding space symmetry. The above-mentioned features of the dependence of the topology of the considered multiregular systems are given schematically in Table 7, where all investigated space groups are divided into six types depending on the m_{lim} value, the difference (ΔM_F) between the maximally and minimally possible values of the distribution mode ($M_{F(\text{max})}$ and $M_{F(\text{min})}$, respectively) and also on the way of achieving $M_F = 15$ while m increases.

The n_{sym} value can serve as a quantitative evaluation of the space symmetry contribution to forming the nearest environment of point \mathbf{p}_i in the considered Delauney system (*i.e.* a set of points in the sphere with radius $2R$ and the center at \mathbf{p}_i , where R is the radius of the sphere described around the VDP of \mathbf{p}_i). Thus, the data of Table 7 show that for frequent groups the space symmetry does not prevent the mutual chaotic arrangement of points, which is typical for an ideal gas, *i.e.* in this case the presence of long-range order in the system does not forbid the presence of short-range thermodynamic disorder.

The results obtained allow consideration of the problem of causes of different frequencies of monoclinic groups, taking into account not only the number of degrees of freedom, which are given to a separate packing structural unit within the corresponding space symmetry, as has been done previously (Kitaigorodskii, 1971; Wilson, 1988), but also with regard to providing the greatest convenience in the change of space topology on the whole during crystallization. Actually, for the most frequent space groups, which belong to *A* and *B* types (Table 7), small values $m_{\text{lim}} = 3\text{--}4$ are typical, while for rare groups of *F* type, $m_{\text{lim}} = 500\text{--}1500$. In other words, even with 3–4 atoms in a unit cell, groups of *A* and *B* types allow the space topology that is typical for a liquid (because the topology of the VDT of the 'ideal gas' system is similar to the topology of a liquid with a small interparticle interaction). If the phase transition liquid \rightarrow crystal is considered as the process for the appearance of additional (to those already existing in a liquid) correlations in the atomic arrangement, then the results given above show that, for the formation of a crystal whose symmetry is described by one of the frequent symmetry groups, a significant smaller number of such correlations (and, therefore, decrease of system entropy is smaller in this case) than for a crystal with a rare space group is necessary. Thus, global topological properties of both liquid and crystal space prove to be immediately connected with phase-

transition thermodynamics. Similarly, the process that is the reverse of crystallization may be considered. Melting a crystal that belongs to a rare space group is possible only after the preliminary increase of m up to m_{lim} and it may be considered as the process of amorphization or after the intermediate phase transition with a symmetry change to one of the groups that are 'convenient' for further melting. At the same time, a transition from a crystal that belongs to a group with a small m_{lim} to a liquid does not require, in principle, intermediate amorphization and deep reconstruction of the structure. This fact is also reflected by small ΔM_F values, which are typical for such groups. According to the data of Table 7, the groups relating to *A* and *B* types with $\Delta M_F = 1$ and $m_{\text{lim}} = 3\text{--}4$, in our opinion, may be considered to be most 'convenient' ones in the above-mentioned sense, the groups with $\Delta M_F = 2$ and $m_{\text{lim}} = 3\text{--}10$ (*C* and *D* types) are rather 'convenient' ones, whereas *E* and *F* types ($\Delta M_F = 7\text{--}8$ and $m_{\text{lim}} = 20\text{--}1500$) include the groups whose symmetry does not provide gradual transformation of the space topology during a change of the aggregation state of a substance. It is notable that only $P2_1/c$ has the most optimal values of ΔM_F and m_{lim} criteria and it is the absolute leader in frequency of occurrence of all 230 space groups (in Table 7, it is isolated to a separate *A1* subtype). The above-mentioned facts specify the principal meaning of the known fifth Pauling rule (Pauling, 1929), according to which, in a crystal lattice, the number of crystallographically independent but chemically the same type of structural components tends to a minimum. We note that the fifth Pauling rule does not contradict the recent experimental data (Chernikova, Bel'skii & Zorkii, 1990), according to which the number of crystallographically different structural units is usually no more than 2–3.

It is shown in Table 7 that several relatively rare space groups (in particular *Pc* and $P2/c$) are 'convenient' and, on the other hand, the frequent $C2/m$ group belongs to the 'inconvenient' *F* type. This fact indicates that the considered criteria of similarity of crystal and liquid spaces ($\Delta M_F = 1\text{--}2$ and $m_{\text{lim}} = 3\text{--}10$) are only a relevant condition of the frequent realization of a space group on the condition of localization of structural groups in common positions and should be used together with the local criterion of convenience of mutual packing of structure-forming units (Blatov, Shevchenko & Serezhkin, 1993). In particular, $P2/c$ does not satisfy the packing criteria formulated by Blatov, Shevchenko & Serezhkin (1993). *Pc* fits them only on condition that compounds with rigid structural groups are crystallized in it and the frequent realization of $C2/m$ may be explained by the fact that mainly substances with structural units with non-trivial symmetry crystallized in this group (Blatov, Shevchenko & Serezhkin, 1993).

7.2. Atomic sublattices in crystals

In Fig. 15, the dependence of $F_{VDP}(f)$ for sublattices of O atoms in structures of 323 oxygen-containing uranium compounds with the mean value $\langle m \rangle = 10.7$ is given. Its shape is typical for $F_{VDP}(f)$ at $m \geq m_{lim}$, considered above, with a single difference: its M_F is

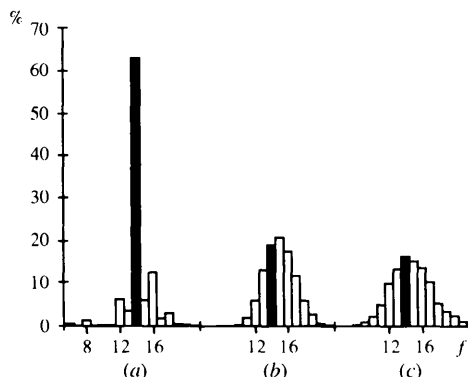


Fig. 15. Frequency of VDPs with the given number of faces (f) in percent from the cardinality (n) of the sample containing VDPs of O atoms in the structures of 323 oxygen-containing uranium compounds ($n = 3464$).

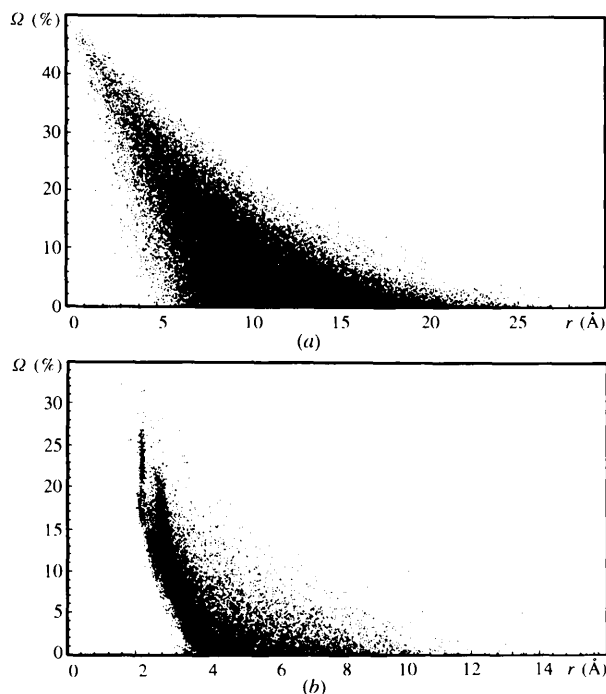


Fig. 16. $\Omega(R_{at})$ dependence (a) for the sample containing VDPs of 7500 points in 2500 random multiregular Delauney systems with $m = 3$ for space group $P2_1/c$ ($n = 115677$); (b) for the sample containing VDPs of 3464 O atoms in sublattices of crystal structures of oxygen-containing uranium coordination compounds ($n = 50179$).

equal to 14, although the mean value of faces $\langle f \rangle = 15$ coincides with the value of M_F for the 'ideal gas' system (Fig. 5). At the mentioned (m) value (because compounds are crystallized in one of the frequent space groups, as a rule), one can disregard the influence of space symmetry, in accordance with the conclusions given in §§5 and 6. This fact indicates that the sublattice of O atoms in the structure of uranium coordination compounds is topologically similar to a liquid with sufficiently weak forces (of van der Waals type) of interatomic interaction. We note that the shape of the relationship $\Omega(R_{at})$ for the mentioned systems (Fig. 16) is similar to the analogous dependence for the 'ideal gas' system (Fig. 7). This fact also indicates the absence of interatomic interaction and 'non-thermodynamic' short-range order in oxygen sublattices.

8. Conclusions

The data obtained show that by means of VDPs the topological analysis of systems with many particles allows conclusions to be made about the presence or absence of short-range or long-range order in the system. In some cases, one can also detect what caused the correlation in the mutual atomic arrangement. At the same time, the mechanisms connecting the space topology of the system with the features of the force field having formed it remain indistinct. In order to find them, an intensified crystal chemical analysis of the topology of structures of chemical substances with a different type of interparticle interaction is required. This is the objective of our further research.

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