

Methods of description of the structure of amorphous substances

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Abstract. Today to describe experimentally the structure of the amorphous substances the alternative methods are being sought actively. These methods must require only setting a small number of structural parameters of the atomic network easily sought experimentally. The best of such methods is the method that requires the least number of the initial a priori information about the system under study. The most of the above experimental methods are based on the use of the binary correlation functions of the mutual spatial location of atoms or other structural particles (or radial distribution function). As of today, the methods that will allow the structure of the whole macrosample to be described on the basis of the structure of its small fragments are being actively sought. The main problem of such approach is the optimal choice of the elementary minimal typical microregions of the amorphous atomic network, which demonstrate the properties that agree with the experimentally determined properties of the macrosample. The studies of the amorphous state must be based also on the clear distinguishing of the ideal disordered atomic network and its structural defects. The notion of the defective structural particles must be taken as a basis of such distinguishing. Their pointing out among the main structural particles may be based on the two conditions: a) the concentration of the defective particles must be much less than the atomic density of the substance; b) the relevant property or the physical and chemical parameter of the defective particle must lie beyond the limits of the distribution function of this property for the main structural particles.

Keywords: amorphous materials, disorder structure, amorphous structure defects

The structure of the crystal is considered known if the spatial symmetry group and the spatial distribution function of the electron density for the elementary cell of its spatial lattice are determined with sufficient accuracy [1]. For real amorphous substances the concept of the symmetry of the spatial groups, reverse space and wave vectors is not applicable in the form it is used for the crystals. To describe the structure of the amorphous state with the same accuracy one has to know the spatial coordinates of all atoms of the relevant sample volume. Therefore, of specific importance is the study of the amorphous structures in the real space [2].

The set N of the radius-vectors \vec{r}_k , the coordinates of which define the equilibrium positions of all the atoms in the space in the defined coordinate frame is taken as the most general characteristics of the structure of the whole macrosample comprising N atoms [3]. These vectors could be conveniently defined by the function of location of the centers of the structural units $A(\vec{r}) = \sum_{k=1}^N \delta(\vec{r} - \vec{r}_k)$.

The functions $A(\vec{r})$ are always discrete due to their physical nature. They can be strictly periodic (for the crystals) or non-periodic (for the amorphous substances).

The function $A(\vec{r})$ exists really for any condensed system, but for different structural states it is specified differently. For the ordered structures one may analytically strictly specify the location of any atom with respect to the given one. Their functions of location are called the first-kind functions (fig. 1 a). These functions describe totally determined functional order in the locations of atoms using, for example, the translation vectors of the elementary cell. For the infinite extended disordered locations of the structural particles, when there exist only certain correlations in the locations between the nearest neighbors and it is impossible to specify the locations of the distant structural particles, the functions of location are called the second-kind functions (fig. 1 b).

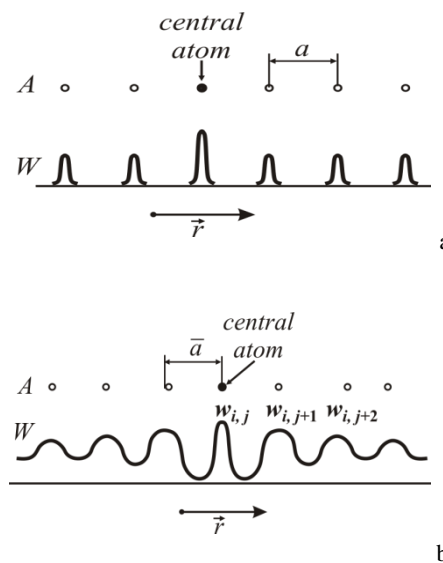


Fig. 1. Examples of setting the functions of location $A(\vec{r})$ and the binary correlation functions $W(\vec{r})$ of the first (a) and second (b) kind for the one-dimensional model of the substance

The function of location and, respectively, the structure of the crystal are defined by the spatial parameters of the elementary cell and the spatial group of its symmetry. Such description allows the geometric structure of the whole crystal to be determined using a small number of the structural parameters. Thus, the model concepts of the crystalline lattice enable the most complicated crystalline structures to be studied relatively easily.

For the amorphous substances there is no such simple setting of the functions of location and no structural description due to the lack of the spatial periodicity in the locations of atoms. To describe the amorphous state with the same accuracy as for the crystal, one has to specify the coordinates of all atoms of the sample. Unfortunately, it is impossible to do this for real objects experimentally [4].

Now such setting in a pure form is realized only for the theoretical amorphous structures calculated by computer modeling [5]. Therefore to describe experimentally the structure of the amorphous substances the alternative methods are being sought actively. These methods must require only setting a small number of structural parameters of the atomic network easily sought experimentally. The best of such methods is the method that requires the least number of the initial *a priori* information about the system under study [6].

The most of the above experimental methods are based on the use of the binary correlation functions of the mutual spatial location of atoms or other structural particles $W(\vec{r})$. The Patterson's functions for the crystals are a specific example. By definition, these functions result from the quadratic convolution (self-convolution) of the functions of location [7]:

$$W(\vec{r}) = \int A(\vec{r}')A(\vec{r}' - \vec{r}) dV \\ = N\delta(\vec{r} - 0) + \sum_{j=1}^N \sum_{k=1}^N \delta(\vec{r} - \vec{r}_{jk})$$

As seen, the Patterson's functions are the particular case of the first spatial correlation function $\Phi(\vec{x}) = \overline{P(\vec{r})P(\vec{r} + \vec{x})}$ of the discrete atomic system, where $P(\vec{r})$ is some spatial structural parameter of the atomic network.

At the origin of coordinates, the functions $W(\vec{r})$ have a peak of the N magnitude (N is the number of atoms in the system under study). For the disordered substances due to the existence of only probabilistic regularities in the mutual locations of atoms as well as due to averaging over the macrosample, $W(\vec{r})$ are set in a form of a series of peaks of almost Gaussian shape $W(\vec{r})$, each of them specifying the probabilities of the mutual locations of the atoms j and k at the distance \vec{r}_{jk} , i.e.:

$$W(\vec{r}) = \sum_{j,k} (\vec{r} - \vec{r}_{jk})$$

The binary correlation functions $W(\vec{r})$ of the crystals reflect those symmetry elements, which are typical for the corresponding crystalline lattices. For all amorphous substances, $W(\vec{r})$ have a point symmetry C_0^m , i.e. they are spherically symmetric. In addition, $W(\vec{r})$ in the amorphous state by their form and content reflect directly the probabilistic correlation type of ordering of the atomic network and are directly revealed in the diffractograms in a form of the smeared Gauss-like distributions of random quantities.

The functions $A(\vec{r})$ and $W(\vec{r})$ describe only the mutual locations of the structural particles. When it is necessary to know also the parameters of their mutual orientation in the space, what is important for the covalent substances, then the relevant multi-argument functions $A(\vec{r}, \alpha, \psi, \theta)$ and $W(\vec{r}, \alpha, \psi, \theta)$ are used, where α, ψ, θ – are the relevant Euler's angles, which specify the spatial orientation of the structural particles in the atomic system.

The function $W(\vec{r})$ is only one of the possible correlation functions of the disordered substances. According to the general statistical theory for such systems, their characteristics and behavior are completely specified by a set

of different correlation distribution functions Y_q . For the system of N atoms the function $Y_q(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_q)$ defines the probability of finding each of q atoms of selected group in the volume elements dV_1, dV_2, \dots, dV_q at the distances $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_q)$ from the origin of the coordinate frame at the random location of all other $(N-q)$ atoms, which do not belong to the selected group. By definition, this probability is:

$$dJ(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_q) = Y_q(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_q) \frac{dV_1, dV_2, \dots, dV_q}{V^q}$$

If the mutual location of the atoms of the system is totally chaotic (the case of the total disorder), then all correlation functions are constants not dependent of the particular set of the spatial coordinates, i.e. $Y_q(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_q) = c_q$. In the real condensed unordered systems, there exist the spatial correlations in the atomic locations. This means that the probability of the location of a certain atom of the system in the certain point of the space depends on the points, in which the other atoms are located. The character of such correlations is described by the set of correlation functions: unitary $Y_1(\vec{r}_1)$, binary $Y_2(\vec{r}_1, \vec{r}_2)$, ternary $Y_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ and so on.

The function $W(\vec{r})$, in fact, corresponds to the binary correlation distribution function $Y_2(\vec{r}_1, \vec{r}_2)$ and is its derivative. This function plays an important role in studying the structure of the amorphous substances. After averaging over the structural parameters of all structural particles with the allowance made for the spherical symmetry of the functions $W(\vec{r})$ for the amorphous substances, a new function $Y_2(|\vec{r}_1 - \vec{r}_2|)$ is obtained from the binary correlation function. It depends only on the distance between the two atoms under consideration $r = |\vec{r}_2 - \vec{r}_1|$ and does not depend on the mutual location of these atoms in the space. Thus, redefined binary correlation function $Y_2(|\vec{r}_1 - \vec{r}_2|)$ almost coincides with the radial distribution function $W(r)$, which is the scalar analog of the vector function $W(\vec{r})$. In scientific literature, $W(r)$ is called the radial distribution function (RDF) of corresponding structural particles [8]. Knowing this function and interatomic interaction potential for the monatomic liquids, one may calculate theoretically a series of parameters and characteristics [8]: the equation of state, the isothermic compressibility, the shear modulus, the internal energy and so on.

The radial distribution function $W(r)$ is the basic structural parameter for the amorphous solids, which can be determined experimentally. This function is the object of the diffraction studies in the amorphous substances. Its main task is to obtain the radial distribution function for corresponding scattering centers, which is unambiguously related to the correlation radial function $W(r)$ (fig. 2). On the basis of the geometric parameters of this function one may determine experimentally the averaged parameters of the short range order (SRO) structure. The positions of the RDF maxima R_1 and R_2 correspond to the predominant interatomic distances in the atomic network or the radii of the coordination spheres; the areas under the peaks S_1 and S_2 are related to the corresponding coordination numbers; the halfwidths of the peaks σ_1 and σ_2 define the mean-square displacements of the atoms in the amorphous struc-

ture with respect to the most probable ones. In some cases it becomes possible to make substantiated conclusions about the most probable geometry of location of the nearest neighbors in the atomic network and about the character of interatomic bonds between them. As of today, it is impossible to reproduce unambiguously the real spatial distributions of the atoms in the amorphous substance on the basis of RDF only. It also should be noted that in the general approach the disordered structure is described not by the separate SRO parameters, but by the whole RDF.

In the most cases the experimental studies relate not the complete structure of the condensed substances, but only the structure of its certain subsystem: nuclear, atomic, spin subsystems and so on. Respectively, in these cases the attention should be drawn to the separate specific subelements of the structure. It seems most expediently to specify the spatial distribution of the above subelements in a form of the special functions of the momentary local density $\rho(\vec{r}, t)$, where \vec{r} – is the radius-vector of the corresponding point of the space in the chosen coordinate frame. Thus, $\rho(\vec{r}, t)$ is the local density of a certain subelement of the structure in the spatial point with the radius-vector \vec{r} at the moment of time t . For the same object this may be the electron density, the atomic density, the nuclear density, the electric potential distribution, the spin density and so on. Not momentary, but measuring time-averaged microdistributions of the density $\rho(\vec{r})$ related directly to RDF are obtained experimentally.

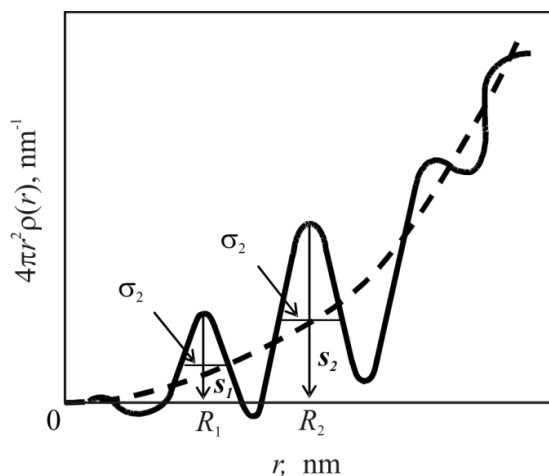


Fig. 2. Illustration of the RDF form for the amorphous substance and its principal parameters: R_i are the radii of the coordination sphere, S_i are the areas under the peaks that define CN, σ_i are the halfwidths of the peaks that define the dispersions of the chemical bond length distribution.

In the diffraction experiments, it appears convenient to take the objects, which serve the scattering centers of the probing radiation, as the microdistribution elements. The function $\rho(\vec{r}, t)$ can be set in the different forms depending on the peculiarities of the structure of the particular objects. Two representations of microdistribution $\rho(\vec{r}, t)$ are boundary: that in a form of the discrete functions, e.g., for the crystals, and that in a form of the continuous functions, if the substance is considered the permanent continuum.

The functions $A(\vec{r})$, $w(\vec{r})$ and $\rho(\vec{r})$ are the most general, but, at the same time, the most abstract structural

characteristics of the amorphous substances. As of today, the methods that will allow the structure of the whole macrosample to be described on the basis of the structure of its small fragments are being actively sought. The main problem of such approach is the optimal choice of the elementary minimal typical microregions of the amorphous atomic network, which demonstrate the properties that agree with the experimentally determined properties of the macrosample. The solution of this problem includes two stages [9]. The first stage is the optimal partitioning of the atomic network into a system of fragments with the definition of their structure and properties. It is preferably in this case to use chosen fragments in studying the atomic network of the amorphous substances of different chemical composition. On the second stage the relation between the structure and the properties of the whole sample and the properties of its separate fragments is found.

In Ref. [9], the strict observance of the additivity principle for the glasses is demonstrated on the basis of the first principles of quantum mechanics. Thus, the properties of the glasses can be formed of the properties of their primary component formations, i.e. certain structural fragments. The only task is to choose correctly the above formations and to determine their properties. The choice of the fragments is related to the boundaries that separate them. There are quite many variants of such partitioning and it is not easy to choose the best of them like in the case of crystals. In any case the basis of the choice of the partitioning method should be the additivity principle, whereas the specific choice must be determined by the kind of the problem to be solved using this partition.

The most comprehensive and fruitful method is that suggested in Ref [10]. This method is based on the consideration of the substance as the system of different interacting particles. As a result, the macrosystem of the atomic network is generally represented as that comprising a great number of macroscopic identical particles. The choice of the size of microscopic particles must ensure their quite large number in the macrosystem in accordance with the criterion of applicability of the statistical methods. This approach makes a basis of the above analysis of the problems of studying the amorphous state. The hypothetical structural particles introduced in the beginning, i.e. the certain associates of atoms that form the atomic network of the substance, are the basic ground of this approach. Let us analyze now in more detail the essence of the particle method.

There are many variants of introducing the different-type structural particles. According to Ref. [10], depending on what properties of the solid are considered, the following basic types of the particles can be distinguished: the chemical composition particles, the structural particles, the kinetic particles and the defective particles (see table). In general case they cannot be transformed to each other; they cannot be substituted by the universal particles applicable for the description of all characteristics of the substance simultaneously. The chemical composition particles are considered the main of them, whereas other particles can be considered as their derivatives. As a result, different substances and their different states are considered the sets of different particles with different regularities of their mutual combining.

Table. Basic types of the particles for describing the solids [10]

Particle type	Examples	Role of the particles
Chemical composition particles	Atoms, molecules, formula units	Specify the substance as the separate individual quantum-mechanical macrosystem
Structural particles	Individual groups of atoms	Describe the peculiarities of the structure of the substance and specify its all properties
Kinetic particles	Electrons, holes, phonons	Specify the kinetic properties of the substance
Defective particles	Impurities, vacancies, charge centers	May influence the most of the properties of the substance

The most stable in the substances are the chemical composition particles, for which the conservation law is obeyed, i.e. the quantitative and qualitative set of the chemical elements included in the substance is fixed. The structural particles are less fixed characteristic and in their case the conservation law may not be obeyed. For the amorphous substances the structural particles are the main elements of their disordered atomic network. The necessity to correspond to a certain chemical composition of the sample imposes serious restrictions onto the choice of certain microfragment of the structure of the amorphous solid as the structural particle. For example, provided the validity of the chemical composition conservation law for the $As_{30}S_{70}$ glass, the structural particle must include at least 10 atoms, while for the $As_{32}S_{68}$ compound – 25 atoms. The latter condition requires the development of the description of the fragment structure in the non-crystalline substances of rather large size, which is comparable by complexity with the description of the structure of the whole macrosample.

Pointing the structural particles out is often based on a clear differentiation of the interatomic interaction forces into the strong and weak ones. It is assumed here that strong interactions are revealed only inside the structural particles and at the sites of their linkage in the general atomic network. The structural particle is surrounded by a weak force field that characterizes its interaction with the neighbors. Thus, in general case, the structural particles are not independent of each other [10].

In the ideal case the use of the particle method must ensure the choice of the minimal number of the types of the structural particles sufficient to describe the maximal number of different substances and their states. Furthermore, such particles should desirably fill uniformly the whole space occupied by the substance, not leaving free volume residuals. In the amorphous substances, some difficulties arise in this respect. As a rule, it is necessary to introduce the particles of different types to describe the structure of the amorphous materials. As the amorphous materials have different chemical composition, different geometric 'shapes' and frequent deviations from multiple relations of different chemical element content, they fail to ensure the continuous complete filling of rather large macrovolume. Therefore, the presence of the free volume is typical for the most disordered substances [10].

In such approach, the real solid body should be considered the system of interacting different-type particles-microfragments of the atomic network with the volumes v_i that satisfy the condition $V = \sum n_i v_i + V$, where V is the sample volume, n_i is the number of the structural fragments of the i -th type, and ΔV is the free volume in the sample structure. In this case v_i must include, if possible, an integer number of the formula units.

In general form, the elementary cell of the crystalline lattice can be considered the main structural particle in the crystal. The disordered structure of the non-crystalline sol-

ids complicates pointing the structural particles out. However, with the development of the notions about SRO of their atomic network, it became also possible to point out the structural particles in them (as an example, one could mention the silicon-oxygen tetrahedrons in the silicate glasses). According to Ref. [10], the volume of these structural particles should not exceed that of the elementary cell of corresponding crystal of the same chemical composition.

Thus, the most general and typical for all non-crystalline solids feature, i.e. the presence of SRO in the atomic locations, makes a basis of dividing the amorphous substances into the structural particles. Therefore, the correct distinguishing of the structural particles must ensure the total description of SRO in the atomic network. Moreover, when choosing the structural particles in the amorphous substances one has to take into account the ordering in the IRO region and the presence of the mesoscopic structural peculiarities. This is mainly provided by the rules that make a basis of bonding the structural particles. In such conditions, the structural particles are the characteristics of both SRO and IRO simultaneously. The fruitfulness of such approach for the silica glasses is proven by, e.g., Ref. [11], where the character of the structure of their atomic network was found to define by the rules of combining the SiO_4 tetrahedrons according to the stishovite, colusite or quartz structure types. This also means that one can, using different laws of combining, obtain different amorphous structures of the same structural particles. This problem is analyzed in details in Refs. [9, 11, 12].

The peculiarities of the atomic network SRO indicate that the structural particles of the amorphous substances have certain elements of the spatial symmetry. This assumes the presence of any symmetry elements. In this context, the maximal symmetry of the structural particles can be an important criterion of their choice.

In the case of crystals, the knowledge of their elementary cell defines simultaneously the procedure of construction of the whole macrosample. In our opinion, the structural particles in the amorphous substances must play the role of the elementary cell of the crystalline lattices. This condition must also determine the procedure of their distinguishing in the disordered atomic network. Evidently, the procedure of constructing the macrofragment of the atomic network in the amorphous substances of the structural particles must use both the simplest (translation, rotation) and much more complicated rules of their mutual spatial combination. These rules were first introduced by Zachariassen for combining separate polyhedrons in the oxide glasses.

Many amorphous structural particles may be isomorphic, i.e. formally replaceable at the transition from one chemical composition to another one, e.g., for the case of the structural particles in $AsS_{3/2}$, $AsSe_{3/2}$, $AsTe_{3/2}$. At the total (unlimited) isomorphism of the structural particles, their correspondence by geometry, volume, shape and the rules of their combining with other structural particles is assumed. In the case of the presence of common atoms in

the neighboring structural particles, the conditions of their isomorphism must be especially rigorous. The use of the methodological approaches of stereochemistry and chemistry of polymers can be an important trend of the studies.

The structure of the particular structural particle may result from both the free manifestation of interatomic interactions and the 'binding' action of the surrounding atomic network with other types of the structural particles. Such binding may be of two types: the first, passive, when it leads only to a slight change of the parameters of the structural particle, which remains itself a stable structural formation. The second, a stronger, kind of binding occurs in the case, when the structural particles acquires under the influence of the surrounding matrix the other structure, which it fails to keep beyond the atomic network. In the crystals, such binding is possible only in the case when the number of the structural particles of binding component is much more than the number of the particles of non-typical component, since the non-typical structure will be quite stable only in the conditions of a strong influence of the main component. The example is the crystalline lattice structure in the region of occurrence of the impurity atoms or point defects. In the amorphous substances, the non-typical can be realized much easier, since in the disordered atomic network they can easily adopt for the structure of surrounding neighbors. The active 'binding' influence of certain structural particles on the structure of their neighbors and vice versa is a decisive peculiarity of the structure of the amorphous substances.

Thus, in the case of the amorphous substances, the structural particles must simultaneously satisfy some important conditions: the additivity conditions (i.e. the lack of overlapping) at the space filling; each their type must specify a certain part of the atomic network of the amorphous structure, they must have the maximal symmetry in the SRO region. Here an important requirement for the structural particles is excluded – to be the smallest possible part of the structure, which is due to the lack of long range order in the amorphous matrix. Combining the requirements of additivity of the structural particles at the volume filling with their maximal symmetry frequently leads automatically to the necessity to 'cut' the particles of the chemical composition of the substance when pointing out the structural particles (e.g., in the case of the $AsS_{3/2}$ structural units). Thus, the chemical composition of certain structural particles may not coincide with the general chemical composition of this amorphous substance. In the quantum-mechanical calculations, 'cutting' of the chemical composition particles for the creation of the additive units is not admitted, therefore, the other principles of the atomic network partitioning is used, which may not ensure the condition of maximal symmetry of distinguished structural particles.

Distinguished structural particles can have different spatial scale. On the lower step of their hierarchy there are the structural units (SU) widely used to describe the atomic structure of the amorphous substances. The original variant of the structural particles of the amorphous substances in a form of the bipyramids, which are the carriers of information about the SRO symmetry and satisfy the additivity condition, was suggested by Pinsker [13–16]. At their distinguishing the statistical scatter of the structural parameters of the bipyramids is allowed and they fill the space with the residual free volume.

The above approach is feasible if the introduced structural particles are reasonably independent, i.e. if it is possible to describe in the first approximation the certain structural parameter or the structurally-sensitive property P of the substance as:

$$P = \sum_{i=1}^N n_i p_i$$

where p_i is the relevant characteristics of the i -th particle, n_i is their concentration, and N is the number of the types of introduced particles.

It should be noted here that for the disordered substances it is reasonable to take as p_i not simply the individual characteristics of the separate microparticle, but the relevant distribution functions of this characteristic [16] over the ensemble of the introduced structural particles (fig. 3). In the simplified variant, the arithmetic average values of such distributions p_i may be used [17]. The quantitative criterion of applicability of the arithmetic average values may be, for example, the proportionality of the distribution function width Δp to the absolute error of measuring the parameter P . The narrower is the relevant distribution function of the particles over the value of given parameter, the better is the applicability of such approximation.

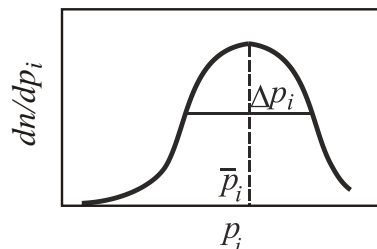


Fig. 3. Distribution function of the structural particles over the parameter p [17]

Up to this moment we analyzed dominantly the ideal crystals and the ideal amorphous solids. In both these states, different defects (foreign, abnormal, minor structural particles) including broken bonds should be absent. In the real amorphous solids, the presence of the defects of the atomic network is real like in the real crystals. The fact that the concentration of such defects in them can be considerably larger does not changes the situation, because definition of the terms of such rank must be based on the general qualitative distinctions, not on the separate quantitative ones.

The extended definition of any defect both for the crystals and for the amorphous solids covers, in fact, all violations manifested in the real atomic network as compared to the ideal one. In our opinion, this qualitative definition should be complemented by the quantitative criterion, namely, the concentration of the defects in the atomic network should be at least order of magnitude less than the atomic density of the substance. Here the typical situation for the real crystals is observed and the general physical sense of the notion of defect is kept. For the same reason different defects could not be responsible for all the properties of the amorphous substances, but for some of them only.

In such approach, one may introduce the quantitative criterion of pointing the defective particles out of the structural particles of the atomic network [18–20]. Besides those mentioned above, such criterion must include an important additional condition. It is related to the fact that certain

property p_i of any of the principal structural particles of the atomic network could not deviate from the average value more than by $\Delta p_i/2$ (fig. 3). It is evident that the relevant property p_i for the defective particles must lie beyond the limits of this distribution of a given property of the main structural particles (fig. 4). For example, if one considers the internal energy of the structural particles as the parameter P , then the defects will correspond to those of them, the energy of which differs largely from the average energy [16]. In this context, the defects of the amorphous substance are treated as the structural particles with relatively low concentration and with the properties, which differ substantially from the properties of the main structural particles. In other words, the local volume of the atomic network is the defect of the amorphous structure and the SRO parameters of it substantially differ from the statistically average SRO parameters of this network over the macro-volume. In addition, the model ideal amorphous systems having the atomic networks absolutely free of the defective structural particles can be used as the benchmark for the comparison with different real amorphous substances.

One may distinguish two basic types of the effectiveness of the amorphous substances: the defective particles with the chemical composition of the atomic network and the defective structural particles of the atomic network. For example, in the covalent substances, the 'broken' chemical bonds, which can be in different charge states, are one of the most common defects of the atomic network. In many cases they may interact with each other and, respectively, exist in a form of the pairs of even the complexes.

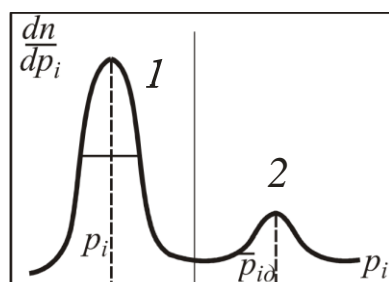


Fig. 4. Distribution function of the main (1) and defective (2) structural particles pointed out to describe the certain property P of the substance.

Elliot [21] also points out several types of defects in the amorphous substances:

1. Deformation defects related to the changes (deformations) of parameters of interatomic distances, valence and torsion angles of the atomic network.
2. Topological defects, e.g., the chains and rings with different number of atoms or structural polyhedrons.
3. Incorrect or homopolar bonds in the atomic network.
4. Defects of the chemical bonds.

If one accepts the above definitions of ideality of the amorphous atomic network and the criteria of distinguishing the defective particles, the first three of the above types of violations will not necessarily belong to the defects of the amorphous substances. This is due to the fact that the above distinguishing is based on the ideal benchmark in a form of the relevant crystalline lattice. As mentioned above, this approach to the studies of the atomic networks of the amorphous substances is not always feasible. How can we determine the value of deformations of the amorphous atomic network? Can we treat as the de-

fects any deformations of interatomic distances and valence angles? Perhaps the small deformations are inherent in the amorphous substances, whereas the large ones are the defects? How can we define the quantitative boundary between the large and small deformations? Can we consider the defects the 5-term and 7-term rings of the atomic network in the amorphous germanium, if they include about 15% of all atoms? What is the defect in the atomic network of the amorphous selenium – the rings or the chains? What chemical bonds should be considered correct, and what chemical bonds should be meant incorrect in the atomic network of the $As_{10}Se_{80}$ glass? What is the substance that includes 20% of the defects? Who will take courage to carry out serious researches in the crystals with such degree of 'defectiveness'?

In the above context, one may also note the known approach with a special emphasis made on the role of the charged structural defects of the atomic network in the revelation of the physical and chemical properties and structural inhomogeneities of the amorphous chalcogenides. Beyond all doubt, the important achievements in the studies of the photo-induced changes in the amorphous chalcogenides were obtained in this area, where the main emphasis is given to the change in the state of the defects. However, when studying these changes an appropriate attention was not always drawn to the local structural reconstructions and revelations of metastability of the amorphous atomic network, which manifest themselves via the collective (mesoscopic) rearrangements of the atoms. This especially concerns the studies of the anisotropic (vector) properties in the non-crystalline solids.

An attempt to revise some notions based on the estimates of the specific role of the charged defects of the atomic network in the revelation of the structural metastability of certain amorphous chalcogenides, in particular, As_2S_3 , was made in Ref. [22]. K. Tanaka developed the idea that the nature of so-called tails of weak absorption in these materials (Urbach edge) can be related not to the charged defects but to the presence in the atomic network of a certain part of homogeneous As-As-like atomic bonds, which form the energy states below the conduction band. The density of these states recalculated to the total number of atoms of the substance is at least ~1%, and this considerably exceeds the concentration of the charged defects according to the N. Mott's concepts [23]. Moreover, K. Tanaka challenges the decisive role of charged defects in the electron properties of the covalent amorphous chalcogenides. K. Tanaka's ideas are the object of intense discussions [24]. Nevertheless, they are quite substantiated and supported by the manifestation of different structural effects in the amorphous chalcogenides [25-26]. In our opinion, many of these controversial questions can be easily solved if one introduces generally accepted rule of constructing the ideal atomic networks and pointing out the defective structural particles in them. One of the possible variants was suggested by us above.

In this context, the differences between such notions as fluctuations and defects in the amorphous substances should be noted [27]. Gubanov was the first to estimate the parameters of fluctuations of the non-crystalline structure and related them to the existence of the localized states in the forbidden band. Statistically, the defects are also fluctuations, but they include mainly the stable discrete violations of the atomic network structure of quite large amplitude.

As a result, the defects are related to the strong changes of the nearest environment by only small number of separate atoms at almost constant environment of all other atoms. This allows several defects to be clearly and reliably identified in the structure of the solid. The fluctuations in the amorphous structure, unlike defects, are related not to the large discrete changes but to the continuum small change of the environment of some atoms with respect to the other ones.

Consider the model system of the ideal gas to clarify this question. From the point of view of the structure it is treated as extremely chaotic state with full absence of the structure. Nevertheless, such state has its own 'zero' and not completely unambiguous structure. The idea of the presence of equivocal structure of the ideal gas appears after the conditional execution of the operation of fixation of its structural particles in the space. The analysis of configurations of the particles in such momentary photograph shows that different structural particles have different environment and different local density of distribution. However, some average values of the structural parameters can be established, and the local deviations from them are called fluctuations, not defects. It is important that such deviations are not the characteristics of deviation of the ideal gas from ideality. Alternatively, the presence of the fluctuations in it is an integral intrinsic entity of the ideal gas state. Probably, such approach must make a basis for choosing the ideal

model for the amorphous solids as well. Then the model data can be different, including those, which do not require ordering, unambiguity and, at the same time, have fluctuations of the structural parameters. Unusual specific clearly defined local deviations of the amorphous structure from the ideal one, which we will call defects, must be revealed against the fluctuations of any of such ideal models.

In our opinion, the relatively small fluctuations of the structural parameters are revealed in the amorphous solids within the SRO limits at the transition from one equivalent atom to other. However, such fluctuations are the integral intrinsic entity of the ideal amorphous structure. The defects are realized against the fluctuations and are revealed in a form of quite strong violations of the structure of the atomic network.

Thus, similarly to the case of the crystals, the studies of the amorphous state must be based on the clear distinguishing of the ideal disordered atomic network and its structural defects. The notion of the defective structural particles must be taken as a basis of such distinguishing. Their pointing out among the main structural particles may be based on the two conditions: a) the concentration of the defective particles must be much less than the atomic density of the substance; b) the relevant property or the physical and chemical parameter of the defective particle must lie beyond the limits of the distribution function of this property for the main structural particles.

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