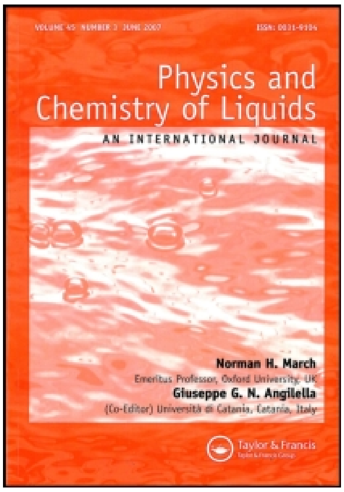

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Description of the Radial Distribution Function of Liquid Argon in the Quasi-Crystalline Model of Liquids

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(*Reveived May 25, 1978*)

It is shown that the radial distribution function (RDF) of liquid argon is described quantitatively in terms of the quasi-crystalline model of liquids (crystal lattice with the lattice sites smeared out by Gaussian distributions) under the following conditions:

1) The model is based on the BCC lattice.
2) The dispersion of the Gaussian distributions depends linearly on the radius of the coordination sphere.
3) The initial lattice is dilated isotropically with the exception of the first sphere.

Empirical methods of determination of the dispersion law are proposed which show that the dispersion law is not simple for liquid argon described on the basis of the FCC and HCP lattices. The regularities found allow one to treat liquid argon as an irregular atom packing with a random distribution of local compressions and expansions but with a regular alternation of the coordination spheres at large distances (packing order).

1 INTRODUCTION

The quasi-crystalline model of liquids proposed by Prins and Petersen in 1936 describes the spatial arrangement of particles as a result of smearing out the sites of a certain crystal lattice according to the Gaussian law. This model turns to be useful for interpretation of diffraction experiments on liquids and has been utilized in many works (e.g., see Refs. 1–8).

The quasi-crystalline model can be treated from two viewpoints. It can be considered as formal means for description of the experimental radial distribution functions (RDF) for liquids. In this case it is quite justified to compare the experimental and model RDFs at a qualitative or semi-qualitative level, in terms of similarity or difference, as it is done, e.g., in papers by Tsvetkov[1] and Dutchak.[2] The other viewpoint, more interesting for physics of liquids, is that the quasi-crystalline model is not only a formal scheme but reflects correctly certain features of the liquid structure. At present it is impossible to deduce this assumption from first physical principles, it is necessary to compare systematically calculation and experiment to justify it. It is natural that in this approach only a quantitative description of experiment is of value.

In this paper we shall describe quantitatively the experimental RDF of liquid argon on the basis of the quasi-crystalline model without setting a priori any requirements on the behaviour of parameters of the model except those which result necessarily from its mathematical formalism. This approach allows us to discuss the physical meaning of the parameters obtained and, we hope, offers a possibility to elicit from the RDF of liquids a certain information on the liquid structure.

2 FORMALISM OF THE QUASI-CRYSTALLINE MODEL

An adequate mathematical formulation of the model is of primary importance for quantitative description of the RDF. The basic concepts of the mathematical formalism of the quasi-crystalline model can be considered well determined due to works of various authors done during the last ten years. These consist in three points.

1) Franchetti[9] and Bagchi[10] found that in the quasi-crystalline model the RDF is described by the formula

$$D(R) = \frac{R}{\sqrt{2\pi}} \sum_{i=1}^{\infty} \frac{N_i}{R_i \sigma_i} \left\{ \exp\left[-\frac{(R-R_i)^2}{2\sigma_i^2} \right] - \exp\left[-\frac{(R+R_i)^2}{2\sigma_i^2} \right] \right\} \quad (1)$$

where the sum is over the coordination spheres of the lattice to be smeared out with R_i and N_i being the radius and coordination number of these spheres.

2) It follows from the general statistical considerations (see Ref. 11 and Section 6.2 of the present paper) that at sufficiently large distances the dispersions of the Gaussian distributions, σ_i^2, must obey the law of structural diffusion

$$\sigma_i^2 = \beta R_i. \quad (2)$$

This law is valid only asymptotically and reflects statistical independence of the displacements of the particles in the liquid relatively to each other at large distances. On the contrary, the displacements of neighbouring particles must be correlated, and one can expect a deviation from the law of structural diffusion (2) for several first coordination spheres.[3,6,10]

3) As was shown in our recent paper[12] quantities R_i and N_i in formula (1) cannot coincide exactly with the radii of the coordination spheres (R_i°) and the coordination numbers (N_i°) of any real crystal lattice. If such a coincidence took place, the asymptote of the RDF calculated by (1) with law (2) would be

$$D(R)_{R\to\infty} \sim 4\pi\rho(R^2 + \beta R).$$

In other words, the function $H(R) = D(R) - 4\pi\rho R^2$ would behave asymptotically as

$$H(R)_{R\to\infty} \sim 4\pi\rho\beta R, \tag{3}$$

whereas from physical considerations it must tend to zero. To remove this nonphysical behaviour of the asymptote, it is necessary to modify the crystal lattice before smearing out by varying the radii of its coordination spheres and the coordination numbers. Such a modification can be done in various modes. So, in the case of a linear dilatation of the lattice,

$$R_i = kR_i^\circ, \tag{4}$$

the coordination numbers must be varied by the law (Medvedev and Naberukhin)[12]

$$N_i = k^3N_i^\circ(1 - \beta/R_i)\rho_L/\rho_C. \tag{5}$$

Here ρ_L and ρ_C are the average densities of the liquid considered and of the initial crystal lattice, k is a constant coefficient.

All the three points of the mathematical formalism of the quasi-crystalline model have never been used simultaneously for a quantitative fitting of the model to experiment. In most of papers (especially in old ones) the basic formula for calculations is written intuitively. As a result, either the RDF, $D(R)$,[1–3] or the pair correlation function, $g(R) = D(R)/4\pi\rho R^2$ (Prins and Petersen)[13] is decomposed into the Gaussian distributions. As a matter of fact, formula (1) shows that it is the function $D(R)/R$ that is the sum of Gaussians. There are papers (e.g., see Ref. 3) where the law of structural diffusion (2) is neglected without any argumentations and the dispersions of all coordination spheres at large distances are considered to be the same. This violates the logics of the quasi-crystalline model and demands to introduce instead of (2) other suppositions which seem to be not obligatory. Bagchi[8] fits the model to experiment over a limited range of R by independent variation of all R_i and N_i. This approach can at best give a good formal description of the RDF, but from the very beginning it is not aimed at finding the regularities of the liquid structure and cannot be called a physical model.

The third point of the mathematical formalism of the quasi-crystalline model deserves particular attention. It is difficult to see the nonphysical behaviour of the asymptote if the RDF is calculated until small values of R, within the limits of the first 2–3 maxima, as it is done in a number of papers.[1,2,8] Moreover, it is more convenient to use the differential RDF, $H(R)$, to judge of the character of the asymptote, since according to (3) the mean line of oscillations of the function $H(R)$ systematically deviates from zero with growing R. This behaviour of the asymptote was observed by Franchetti and Mazza[5] when calculating the function $H(R)$ on the basis of the first two points of the formalism for liquefied noble gases till $R = 20$ Å. The deviation of the asymptote from zero, as we have specially tested,[12] is described perfectly well by formula (3). To correct the behaviour of the asymptote Franchetti and Mazza[5] proposed to dilate nonlinearly the initial crystal lattice. However, this recipe improves the behaviour only over a limited interval of R and does not result in a correct asymptote.[12] In more recent papers Franchetti[6,7] gives no analysis of the asymptote behaviour but calculates the function $g(R)$ where the effects in question cannot be observed visually.

We have mentioned not all suppositions made when realizing the quasicrystalline model. It is clear from the foregoing that so far there is no conventional method to determine the parameters of the model. Therefore, any existing calculation procedure is not free from arbitrary assumptions. As a result, it is not surprising that different authors come to different conclusions on the structure of one and the same liquid, e.g., according to Franchetti and Mazza[5] and Franchetti[6] the initial crystal lattice for liquid argon represents hexagonal close packing (HCP) whereas according to Bagchi (1972) it is similar to the face-centred cubic lattice.[8] On the other hand, we have shown[14] that asymptotic oscillations of the experimental RDF for liquid argon can be described by none of the three lattices, HCP, FCC and BCC (body-centred cubic), provided these are not modified.

The above three points of the mathematical formalism of the quasicrystalline model impose strong limitations on the parameters of the model and remove to a considerable extent arbitrariness in their selection. Nevertheless, these are not sufficient to develop a model on the whole. It is clear that to choose the crystal lattice is of primary importance for the model. However, the main aim of calculations is to determine the type of the lattice for a given liquid, and thus it must not be a point of the formalism of the model. We think there must be the following additional points of the formalism:

4) The dispersion law of the Gaussian distributions in the nearest coordination spheres and

5) the way of modification of the initial crystal lattice.

The following sections of the present paper are devoted to these problems.

3 DETERMINATION OF THE DISPERSION LAW FROM EXPERIMENT

The damping rate of RDF peaks is determined evidently by the law of dispersion change with the distance. Calculations show that using law (2) one obtains for the BCC lattice a rapid exponential damping of oscillations of the function $Rh(R) = R(g(R) - 1)$, and in the case of the Debye smearing (dispersion is the same for all spheres) the oscillations of this functions are not damped.[14] The functional dependence $\sigma^2(R)$ ensuring the same damping of the calculated and experimental RDFs can be found as follows. Suppose that the amplitude of each peak of the calculated RDF depends mainly on the dispersion value under this peak, i.e., only on the local dispersion, and is independent of the concrete form of the function $\sigma^2(R)$. This supposition is valid at least if the dispersion varies negligibly within an RDF peak. Calculating by formula (1) we can now plot "calibrating" curves, i.e., dependences of the amplitudes of various RDF peaks on the local dispersions. Then, with the obtained calibrating dependences, we define the values of the local dis-dispersions for each RDF peak from the amplitudes of the experimental peaks. These values plotted against the positions of the corresponding peaks of the experimental RDF give the desirable dependence of the dispersion on R, i.e., the dispersion law which is necessary to describe the amplitudes of the experimental RDF peaks.

The procedure described was realized first of all for the initial lattice of BCC type. To plot the calibrating dependences we calculated RDF in two ways: with the Debye law of dispersion, $\sigma_i^2 = \sigma_0^2 = \text{const}$, and with the law of structural diffusion (2) (taking into account formula (5) with $k = 1$). The calibrating curves were plotted for each maximum and minimum with varying σ_0 and β respectively. Figure 1 shows that the calibrating dependences are practically linear in coordinates $lg|Rh(r)|$ vs. σ^2 and almost similar for all extrema studied. However, a more important fact is that both ways of smearing the lattice result in similar dependences. This proves our supposition that the amplitudes of oscillations of the calculated RDF are determined mainly by the values of the local dispersions. With the calibrating dependences obtained and on the basis of the known values of the extrema of the experimental function $Rh(R)$ for liquid argon[15] we determined the local dispersions which are necessary to describe the corresponding extrema of the experimental function. Plotting these local dispersions versus the extremum positions we found the dispersion law which ensures the description of the experimental RDF. Dependences $\sigma^2(R)$ obtained are interpolated very well by the functions of type

$$\sigma^2(R^*) = \alpha + \beta R^* \tag{6}$$

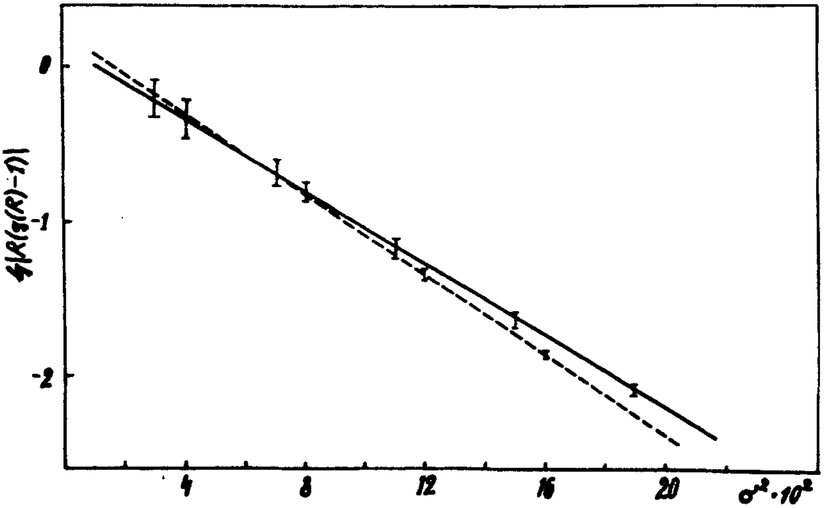

FIGURE 1 Calibrating curves for the BCC lattice. Calculations by the law of structural diffusion ($\sigma_i^2 = \beta R_i$) are given in solid line, those for the Debye smearing ($\sigma_i^2 = \sigma_0^2$) in dashed line. The curves plotted are averaged calibrating dependences for extrema starting from the second minimum and ending with the seventh maximum. Vertical bars show a maximum range of deviations of the dependences for separate extrema.

($R^* = R/R_1$). Calculation by the least squares method gives for the case of the Debye law of dispersion.

$$\alpha = -0.0090 \pm 0.0017, \qquad \beta = 0.0242 \pm 0.0004, \tag{7}$$

and for the law of structural diffusion

$$\alpha = -0.0157 \pm 0.0018, \qquad \beta = 0.0269 \pm 0.0004. \tag{8}$$

Functions $Rh(R)$ calculated by law (6) are compared with experiment in Figure 2. We see that, firstly, the functions corresponding to both sets, (7) and (8), of parameters α and β differ slightly. This proves the used procedure of determining $\sigma^2(R)$ to be reliable. Secondly, the calculated function (especially with parameters (8)) reproduces well the character of damping the experimental function. This allows us to state that law (6) is necessary for description of the RDF of liquid argon in the quasi-crystalline model.

Nevertheless, the fit of the model to experiment cannot be considered good since the positions of the calculated and experimental RDF peaks do not coincide (Figure 2). As we noted earlier[14] it is impossible to obtain coincidence of the peaks only by selecting the parameters in a given law of lattice smearing. Therefore, further modification of the radii of the coordination spheres, R_i, and the coordination numbers, N_i, of the initial lattice is required.

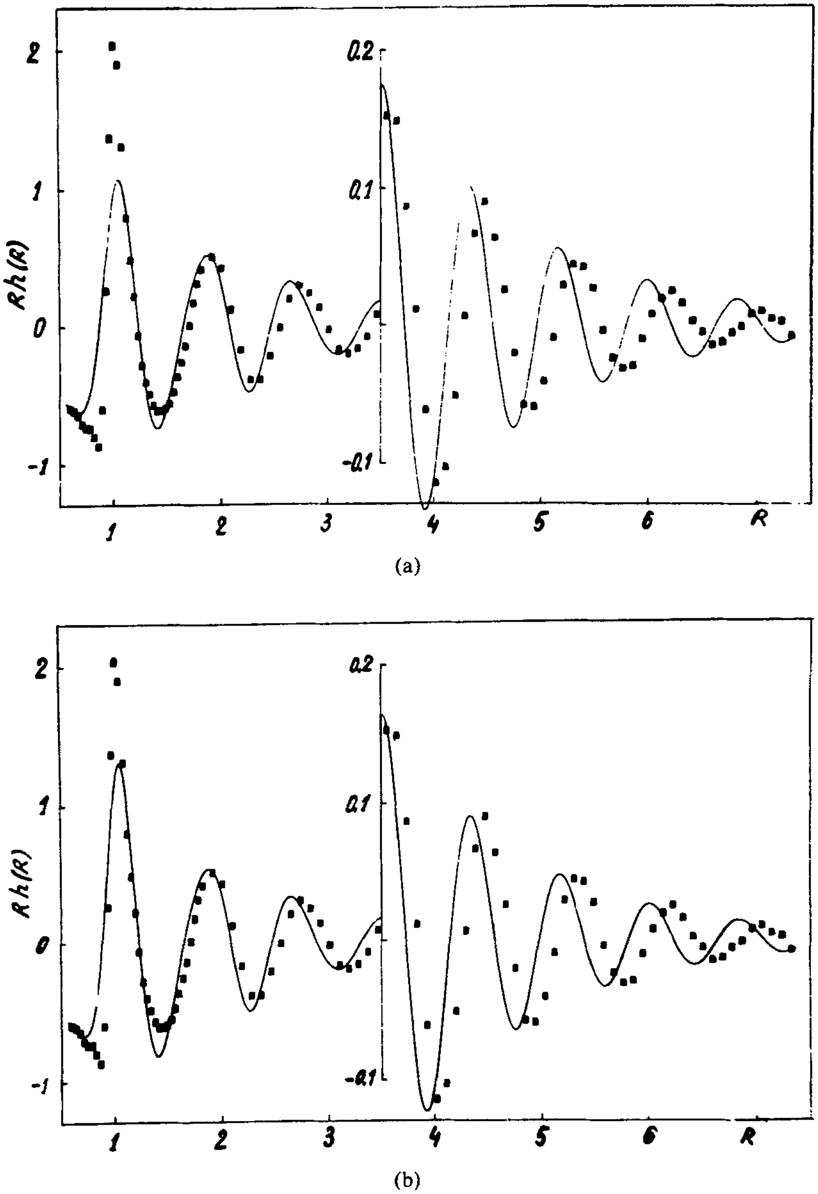

FIGURE 2 Comparison of the model function $Rh(R)$ with experiment. a) Calculations based on the BCC lattice with parameters (7). b) Calculations with parameters (8). Squares denote the function $Rh(R)$ for liquid argon according to Yarnell *et al.*,[15] with $R_1 = 3.71$ Å.

4 LATTICE DILATATION

A systematical shift of calculated RDF peaks relative to experiment manifests that distant coordination spheres of the lattice describing the structure of liquid argon have somewhat larger radii than the corresponding spheres of the BCC lattice. Consequently, to describe the RDF of liquid argon, we must change (dilate) the radii of the distant spheres of the lattice with respect to that of the first coordination sphere.

Figure 3 demonstrates that the difference of the extremum positions of the experimental and calculated RDFs (shown in Figure 2) turns out to be approximately proportional to the position of the corresponding extremum starting from the second peak. Hence, the radii of the coordination spheres of the BCC lattice must be linearly transformed starting from the spheres which determine the second peak of the RDF. According to Figure 3 one should take $R_i = 1.03R_i^\circ$. On the other hand, the radius of the first coordination sphere, R_i°, must remain constant since it has been initially chosen so that it describes correctly the position of the first peak of the experimental RDF. For the sake of definiteness we shall further assume that the dilatation affects all the coordination spheres except the first one, i.e.,

$$R_i = 1.03R_i^\circ (i > 1), \quad R_1 = R_1^\circ. \tag{9}$$

The RDF obtained on the basis of the BCC lattice dilated by law (9) well describes the extremum positions of the experimental RDF when law (6) is used with parameters (7) and (8). The fit of amplitudes becomes however somewhat worse. To find a more precise law of smearing the dilated lattice,

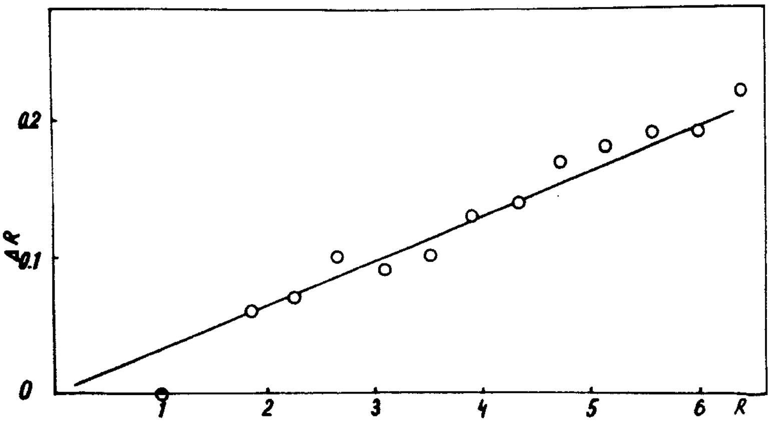

FIGURE 3 Differences of the extremum positions of the experimental and the model functions $Rh(R)$ plotted as a function of positions of corresponding extrema of the model function. The dependence corresponds to the functions shown in Figure 2b.

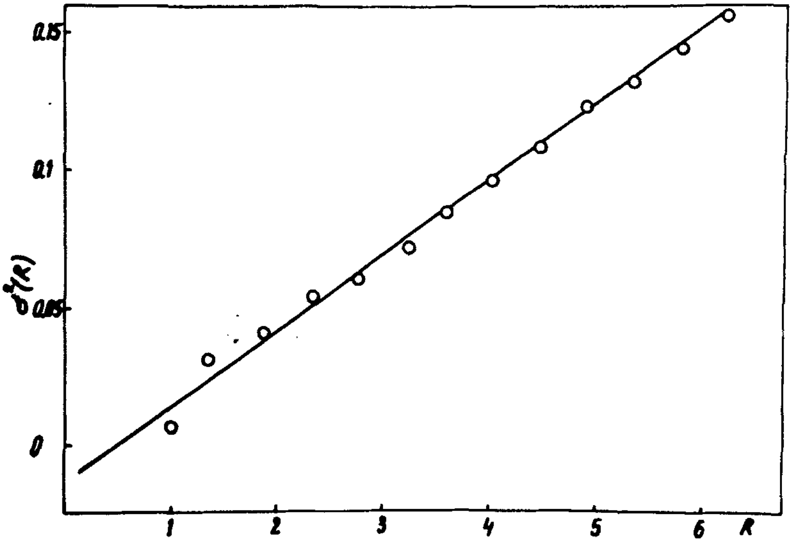

FIGURE 4 The local dispersions which give fitting the oscillation amplitudes of the model to the experimental functions $Rh(R)$ plotted against the positions of corresponding maxima. Calculations are based on the BCC lattice. The line corresponds to law (6) with parameters (10).

we used again the method described in Section 3, i.e., we plotted calibrating dependences of extrema of the calculated function $lg|Rh(R)|$ vs. the local dispersions. This time the BCC lattice was dilated by law (9), and the calculations were carried out with varying β in the law of structural diffusion (2).

Figure 4 demonstrates that the dispersion law obtained with the new calibrating dependences is described again by a linear function of type (6) with coefficients

$$\alpha = -0.015 \pm 0.003, \qquad \beta = 0.0279 \pm 0.0007. \tag{10}$$

More accurate definitions of the parameters α and β as given by sequence of three sets (7), (8) and (9) is essential for quantitative fit of the model to experiment.

The RDF calculated on the basis of the dilated by (9) BCC lattice using dispersion law (6) and set of parameters (10) well coincides now with the experimental RDF not only in the positions and amplitudes of the extrema but also in the overall behaviour in the interval from the second to the eighth maximum (Figure 5). The only exception is the first peak which needs particular discussion.

Figure 4 shows that the dispersion of the first peak does not obey law (6) which is valid for all following extrema. This means that the dispersion of the first coordination sphere must be expressed in a special way. According to Figure 4 the local dispersion in the first peak must be $\sigma_1^2 = 0.006$. For definiteness we assume that this dispersion corresponds to the first coordination sphere, and the dispersions of all other spheres starting from the second one obey the general law (6). In this case the calculated RDF gives the correct height of the first peak (Figures 5 and 6). As to the location of the first peak, Figure 6 shows clearly that the radius of the first sphere must not participate in the lattice dilatation, i.e., the necessity of law (9). If R_1 were increased like the radii of the distant spheres, not only the maximum but the entire peak would be shifted as compared to the experimental one.

A special choice of the position and dispersion of the first coordination sphere is not sufficient, however, to reproduce correctly the form of the first peak. The experimental peak is very asymmetrical. This fact, which has been often discussed in the literature[5-7,16,17] manifests the repulsive core of interatomic potential. It is perhaps impossible to obtain a peak with the desirable asymmetry within the model with the Gaussian smearing of the lattice sites. In this paper we shall not give a detailed description of the form of the first peak since we consider here general regularities of the quasi-crystalline model. The law of smearing the first coordination sphere is, though important, only one of these regularities.

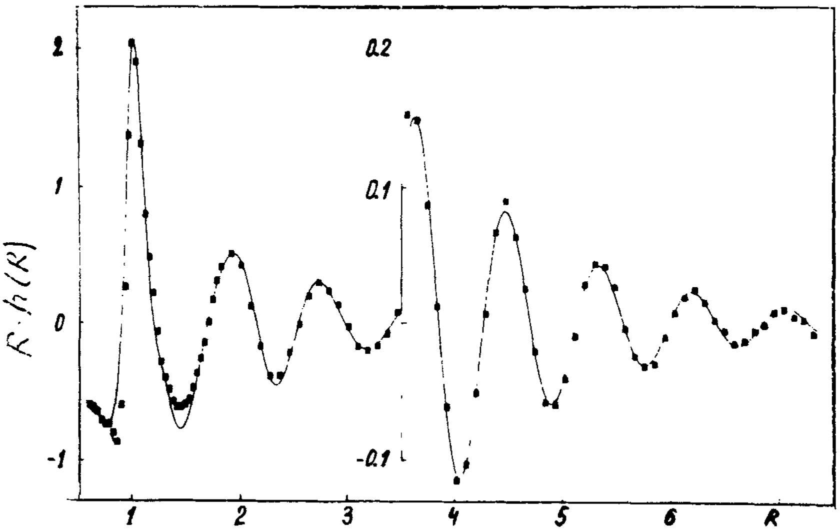

FIGURE 5 Comparison of the model and experimental (squares) functions $Rh(R)$. Calculations with parameters (10) are based on the BCC lattice dilated according to (9).

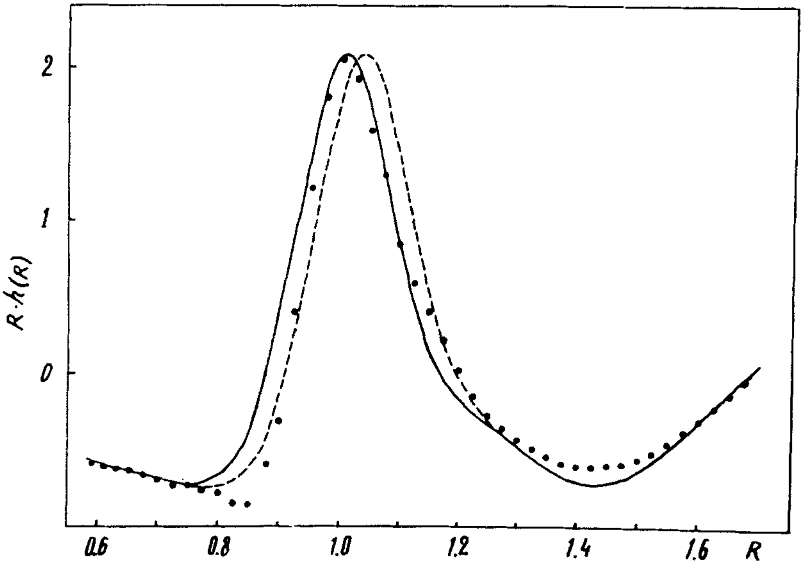

FIGURE 6 The first peak of the function $Rh(R)$. Squares—experiment for liquid argon according to Yarnell *et al.*[15] Solid line—calculations under the conditions given in Figure 5. Dashed line—calculations for the case when the first coordination sphere participates in the lattice dilatation by the law $R_i = 1.03R_i^\circ$.

5 RADIAL DISTRIBUTION FUNCTION FOR LIQUID ARGON DESCRIBED ON THE BASIS OF CLOSE-PACKED LATTICES

The calculations given in Section 3 and Section 4 for the BCC lattice were also made for the face-centred cubic (FCC) and hexagonal close packing (HCP) lattices. Both lattices are found to give much worse description of the RDF of liquid argon as compared to the BCC lattice. This conclusion correlates with our earlier result[14] that asymptotic oscillations of the RDF calculated by the quasi-crystalline model are well described by the Fisher formula[18] only for the BCC lattice and worse for the FCC and HCP lattices.

5.1 The FCC lattice

We showed[14] that the RDF calculated in the quasi-crystalline model with the law of structural diffusion (2) on the basis of the FCC lattice is described by the asymptotic Fisher formula only starting from $R \sim 5R_1$. Since the experimental RDF is described by this formula starting from $R \sim 2R_1$, one should not expect the smeared FCC lattice to describe satisfactory experiment at $R < 5R_1$. The linear dilatation of the lattice (9) and the modification of the law of structural diffusion by formula (6) do not save the situation in this case because the dispersion law, which is necessary for description of the values of experimental function $Rh(R)$ at the points of maxima and minima, deviates appreciably from linear function (6) (see Figure 7). Only for large R it is approximated by the straight line

$$\sigma_i^2 = -0.022 + 0.0266R_i. \tag{11}$$

The RDF calculated with this law and with an appropriate dilatation of the lattice,

$$R_i = 1.04R_i^\circ(i > 1), R_1 = R_1^\circ,$$

does resemble the experimental RDF in the region of the last three maxima (Figure 8). However, all less distant peaks are badly described by it. The calculated function gives too large shifts for the 4th and the 5th maxima and too small shift for the 2nd maximum. The amplitudes of near peaks are badly described by the dispersion law (11) too. In the region of the 2nd and the 3rd maxima the calculated and experimental RDFs differ considerably even in the form of their peaks. Calculations show that the experimental RDF values at the minima after the 2nd and the 3rd peaks cannot be obtained with any values of the local dispersions. Therefore, it is impossible to plot in Figure 7 the points corresponding to these extrema.

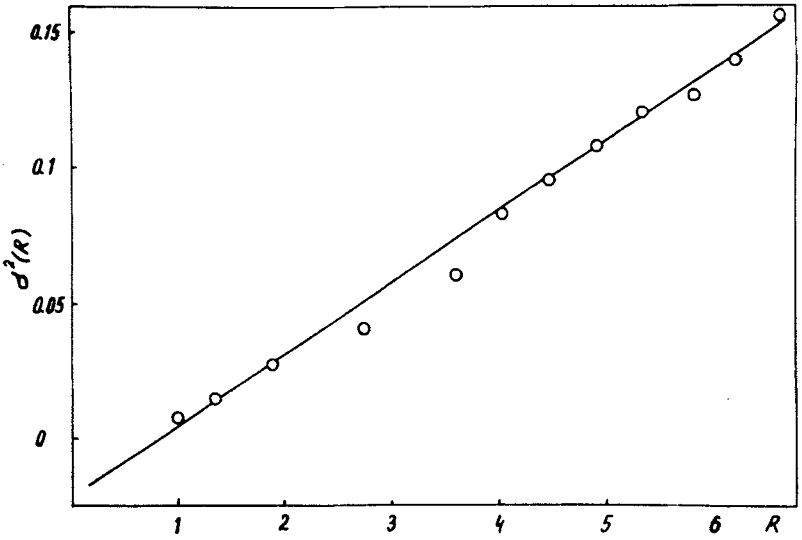

FIGURE 7 The local dispersions which are necessary to describe the amplitudes of oscillations of the experimental function $Rh(R)$ vs. the positions of corresponding extrema. Calculations are based on the FCC lattice. The line corresponds to dispersion law (11).

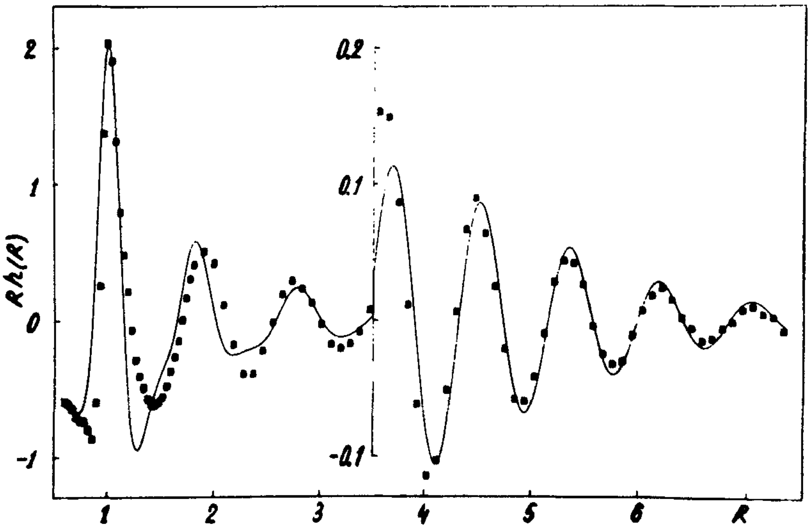

FIGURE 8 Experimental (squares) and model (line) functions $Rh(R)$ calculated with dilated FCC lattice and dispersion law (11) where $\sigma_1^2 = 0.009$.

Thus, it is impossible to describe the RDF of liquid argon on the basis of the FCC lattice over a wide range of R using the existing formalism of the quasi-crystalline model. There is however hope that this lattice can describe experiment at $R > 5R_1$ since it results here in a correct form of asymptote. However, at present it is impossible to verify this supposition since experimental data for $R > 7R_1$ are not available.

5.2 The HCP lattice

In contrast to the FCC lattice here it is possible to obtain the coincidence of the positions of the first six maxima with experiment (Figure 9) by choosing an appropriate dilatation of the lattice,

$$R_i = 1.14R_i^\circ - 0.14R_1^\circ. \tag{12}$$

However, the extremum amplitudes are badly described at any parameters of the linear law of dispersion (6). For example, at

$$\sigma_i^2 = -0.016 + 0.0262R_i \tag{13}$$

we overestimate the heights of the 2nd and the 7th peaks and underestimate the amplitudes of the maxima in between (Figure 9). This fact shows that the local dispersions, which are necessary to describe the heights of the extrema, behave irregularly with the radius (see Figure 10). Interesting is the fact that

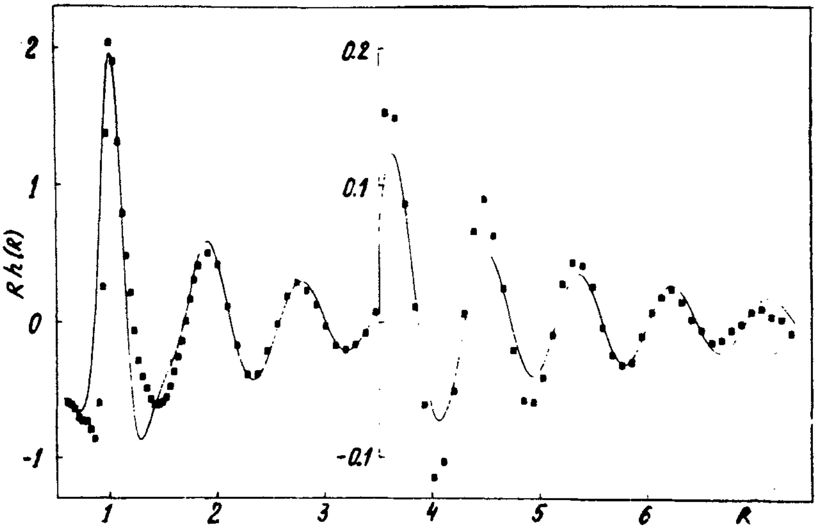

FIGURE 9 Experimental (squares) and model (line) functions $Rh(R)$ calculated on the basis of the HCP lattice dilated by (12) with dispersion law (13).

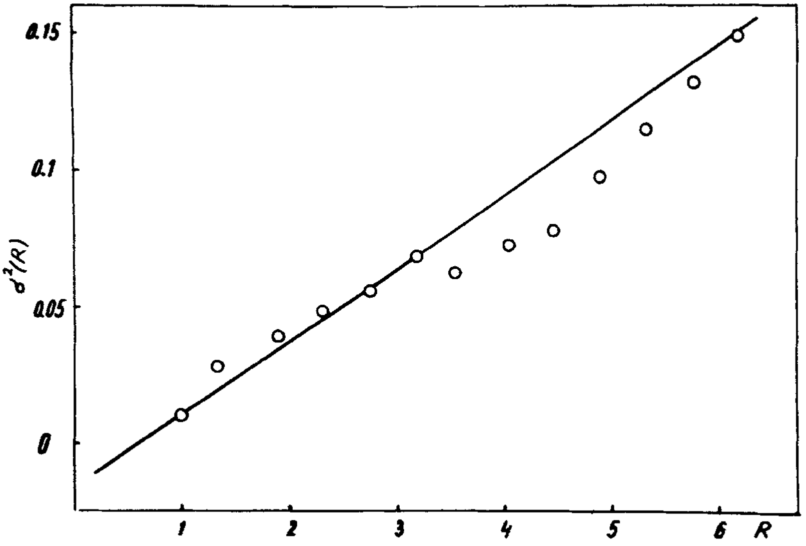

FIGURE 10 The local dispersions which are necessary to describe the amplitudes of experimental $Rh(R)$ for liquid argon. Calculations are based on the HCP lattice. The line corresponds to dispersion law (13).

the dilatation law (12) differs from (9) by the presence of a constant term. However, this law also leaves constant the position of the first sphere as in the case of the previous lattices.

Thus, the HCP lattice cannot be the basis for description of the RDF of liquid argon within the quasi-crystalline model either. To be applicable to the model this lattice as well as the FCC lattice demands some particular law of varying the dispersion with the distance which must differ from the simple linear law (6). However, if the model did not postulate an universal form of the dispersion law, it would lose its constructive content.

6 DISCUSSION

6.1 The lattice dilatation

The fact that the first coordination sphere does not participate in the general lattice dilatation, $R_i = kR_i^\circ$, is nontrivial for the transformation of the radii of the coordination spheres (9) needed to describe the RDF of liquid argon. If all the spheres, including the first one, participated in the dilatation, it would simply result in increasing the lattice constant without changing the lattice structure. This uniform dilatation of the initial lattice corresponds to the decrease in argon density on melting, and can be readily interpreted in terms of an additional free volume attained by each particle on melting. However, a proportional increase of the radii of all spheres would not result in relative shifts of the RDF maxima. Hence, the exclusion of the first coordination sphere from the process of thermal expansion is a necessary condition. This means that the packing in liquids differs essentially from that in crystals, i.e., the quasi-crystalline model must be based on a distorted crystal lattice.

The requirement of constancy of the first sphere radius found by us from the analysis of the experimental RDF in terms of the quasi-crystalline model is an analog of the well-known fact that the distance between next-neighbouring particles remains constant both on melting or heating the liquids in close-packed substances[3,19,20] including argon[21]. The contradiction between this fact and the mean expansion of a substance heated is usually ascribed to vacancies which occur in the liquid.† These vacancies, if any, cannot account for shifts of the RDF peaks since they influence only the coordination numbers but not the positions of the spheres. Therefore, another interpretation of the lattice distortions described by formula (9) must be proposed.

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† In terms of vacancies the term $k^3\rho_L/\rho_C$ in formula (5) is interpreted as $1 - x$ where x is the fraction of vacant sites in the quasi-lattice.[5,6] For our calculations of liquid argon based on the BCC lattice, $R_1^\circ = 3.71$ Å, $\rho_L = 0.02125$ Å^{-3},[15] $k = 1.03$, and $x = 0.087$.

Hence we are to consider that the free volume which occurs on melting is distributed neither evenly among the particles nor in the regions of molecular size (vacancies). It is irregularly distributed all over the volume of the specimen as local compressions and expansions. Hereat the separations between nearest neighbours remain approximately the same as those in the crystal but the packing becomes looser. The random distribution of the local expansions leads to an increase in the mean separations between long-distant atoms. Assuming this interpretation we must treat the success of our calculations as an evidence for the fact that the average positions of the distributions of the separations between distant particles correspond to the radii of the coordination spheres of the BCC lattice uniformly dilated. In other words, the local particle compressions and expansions can be represented as resulting from random displacements of the particles with a diameter R_1° from the sites of the dilated BCC lattice. The center of the distribution of the positions of nearest atoms will not coincide with the radius of the first coordination sphere of the dilated lattice because the displacements of the particles from the sites of this sphere must be correlated to ensure equal nearest distances between the particles. The picture described is close to the concept of liquid structure proposed by Bernal.[19,22] Bernal has shown that in an irregular close packing of spheres, which represents a model of the simple liquid structure, neighbouring atoms tend to join up to build pseudonuclei with the shortest interparticle distances being practically the same as those in crystal. The density of the atom packing in the pseudonuclei is even higher than that in close-packed crystals, though the pseudo-nuclei form loose packing so that the average density of the liquid is lower than that of the crystal. These arrangements of particles are irregular in principle, and Bernal considered that those are incompatible with the description by the quasi-crystalline model. We think however these two conceptions not to be alternative. The model of Bernal describes an *instantaneous* realization of the particle positions in the liquid, whereas the quasi-crystalline model deals with the distribution of the particle positions *averaged* over these realizations. It goes without saying that the quasi-crystalline model implies instantaneous realizations of the particle positions to be irregular though it proposes no way to describe these realizations.

It is worthy of note that the coordination number of the first sphere of the BCC lattice, 8, coincides with the mean number of neighbours in Bernal's random close packing, and the mean number of geometrical neighbours in this packing (i.e., the mean number of faces of Voronoi polyhedra), 13.6 (Bernal[22]), practically equals the number of atoms in the first two spheres of the BCC lattice, 14. This curious situation appears to throw some light on the fact that only the BCC lattice gives good description of liquid.

Thus, the law of lattice dilatation (9) obtained on the basis of formal analysis of the liquid argon RDF has a clear physical interpretation within the ideas being elaborated in the modern theory of liquids.

6.2 The modified law of structural diffusion

The linear law of dispersion, $\sigma_i^2 = \alpha + \beta R_i$, was often used in the literature. Franchetti[9] considered it merely as a possible formal generalization of the law of structural diffusion (2). Glauberman[23] has shown that this law is obtained from the supposition that the smearing of the lattice sites results from two independent processes—statistical fluctuations obeying formula (2) and Debye's atomic oscillations round instantaneous positions of the sites with dispersion σ_D^2. This interpretation was used by many authors (e.g., see Refs 1–3, 8). However, in this case $\alpha = \sigma_D^2$, i.e., $\alpha > 0$, that contradicts the condition $\alpha < 0$ which is necessary (as we have shown in Section 3 and Section 4) to describe the liquid argon RDF. To interprete the negative sign of α it is useful to consider in more detail the simplified derivation of the law of structural diffusion given by Frenkel (Ref. 11, Chapter III, Section 4).

Let us consider an ensemble of "trajectories" connecting a fixed atom at the origin with an atom at some distant coordination sphere which consists of s atoms "in contact," i.e., at the shortest distances from each other. The distance between these two atoms is

$$R_s = \sum_{i=1}^{s} d_i \tag{14}$$

where d_i are the separations between the atoms of the trajectory being projected on the direction connecting these particles. Averaging over all the trajectories of the ensemble, we have for the average distance

$$\bar{R}_s = \sum_{i=1}^{s} \bar{d}_i. \tag{15}$$

Supposing that the locations of neighbouring particles of the trajectory are not correlated, we obtain that

$$\sigma_s^2 = \sum_{i=1}^{s} \Delta\sigma_i^2 \tag{16}$$

is valid for the mean-square fluctuation of this distance. Here $\Delta\sigma_i^2$ is the dispersion of the distribution of the projection lengths of the i-th element of the trajectory. For simplicity, but without loss of generality (Frenkel[11]), suppose that the projections of the mean lengths and the dispersions of all elements of the trajectory are the same and equal d and $\Delta\sigma_0^2$ respectively. Then (15) is reduced to

$$R_s = sd, \tag{17}$$

and the law of structural diffusion (2) is obtained from (16) if we set $\beta = \Delta\sigma_0^2/d$.

This consideration can be readily generalized for the case when the locations of neighbouring particles are correlated. Then the dispersion of the first element of the trajectory will be less than those of the others,

$$\Delta\sigma_1^2 = \Delta\sigma_0^2(1 - \kappa) \qquad (0 < \kappa < 1). \tag{18}$$

The case when $\kappa = 1$ corresponds evidently to the total correlation. Substitute (18) into (16) and obtain

$$\sigma_s^2 = \Delta\sigma_1^2 + \sum_{i=2}^{s} \Delta\sigma_0^2 = s\Delta\sigma_0^2 - \kappa\Delta\sigma_0^2$$

Excluding s by (17) we get a linear law of dispersion,

$$\sigma_s^2 = \alpha + \beta R_s \tag{6}$$

with

$$\alpha = -\kappa\Delta\sigma_0^2 = -\kappa d\beta, \qquad \beta = \Delta\sigma_0^2/d.$$

Thus, the modified law of structural diffusion (6), as well as law (2), can be understood on the basis of very general statistical considerations. The negative magnitude of the parameter α obtained for liquid argon is indicative of an appreciable correlation in the displacements of its nearest atoms. The anomalously small value of the dispersion of the first coordination sphere, $\sigma_1^2 = 0.006$, obtained for argon in Section 4 provides one more evidence for this correlation.

6.3 Packing order

Before making structural conclusions from the data obtained, it should be noted that the conventional description of the liquid structure in terms of short-range and long-range order is not appropriate for this purpose. The absence of the long-range order in liquids is usually understood as the absence of the translational symmetry in the arrangements of their atoms. This property is however general for all liquids and its constatation for a given liquid, made by rapid damping of RDF maxima, gives no additional information. On the other hand, in liquids there is a short-range order, i.e., a certain law of arrangement of nearest neighbours which is manifested in the pronounced structure of the first RDF peak. However, as was shown in Section 4, the quasi-crystalline model in its simplest form fails to give a good description of the first peak shape. Thus, those features of the RDF of liquids which are well reproduced by the quasi-crystalline model, i.e., the character of oscillations beyond the first maximum, correspond to neither the short-range order nor the long-range order.

In this context it is useful to remember that the notion of short-range and long-range order was first introduced by Bethe[24] not for liquids but for *crystalline* binary alloys. In this case the long-range order has a quantitative characteristic which shows the fraction of atoms located in "proper" sites of the crystal lattice.[11,24] In liquids this measure of the long-range order is unacceptable, therefore the notion of long-range order itself loses its constructuve meaning.

The above considerations makes it expedient to introduce a special notion of *packing order* which, together with the notion of short-range order, is better adapted for description of the particle arrangement in liquids. The packing order is a certain quantitative regularity in the arrangement of long-distant particles resulting from their finite size and form (for complex molecules). The notion of packing order can be also applied to crystals where this is not identical with the notion of long-range order. Indeed, every crystal system is characterized by its own principle of particle interlocation which can be described quantitatively by, e.g., a set of values of the radii and the number of atoms in the successive coordination spheres, $\{R_i^\circ, N_i^\circ\}$, i.e., the very information on the crystal lattice which is assumed to be the basis of the quasi-crystalline model.† Packing order is a more general concept than long-range order since the former can exist in substances even when the latter cannot. In crystals the long-range order may be considered as a consequence of the packing order.

The existence of a packing order in liquids follows from the presence of oscillations in the radial distribution functions of real liquids over all experimentally available range of R. They are indicative of regular variations in the local density when moving away from any particle of the liquid. The quasi-crystalline model proposes a description of this behaviour of the local density. Our calculations have shown that this model gives a good description of the liquid argon structure only if it is based on the BCC lattice. Neither the FCC nor the HCP lattices are appropriate here. The possibility to distinguish between the initial lattices when describing the RDF at long distances is on no account trivial. The thing is that the average smearing of a coordination sphere at $R \sim 7R_1$ is $(\overline{\Delta Z^2})^{1/2} = \sigma(R) = 0.43R_1$ which is much larger than the distance between two neighbouring spheres ($<0.1R_1$)

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† Note that up to now no analytical expressions for R_i° and N_i° for various lattices are proposed and it is even unknown whether they exist. It is easy however to develop an algorithm for their calculation on the basis of the crystal elementary cell structure and the principle of long-range order.

and exceeds even the width of the RDF maximum. Therefore, the sensitivity of the description, provided by the quasi-crystalline model, to the type of the initial crystal lattice shows that the packing regularities (specific for each lattice) are preserved at long distances even at considerable smearing of the lattice. This fact illustrates very well the pithiness of the notion of packing order. It is the existence of packing order that predetermines the quasi-crystalline model being fruitful for interpretation of the RDF.

The fact that calculations based on the FCC and HCP lattices do not fit experiment, and the existence of the BCC lattice which describes experiment well cannot be considered occasional. It is more reasonable to suppose that the quasi-crystalline model reveals the real physical regularity of the packing order of liquid argon. Thus, we may hold that atom packing in liquid argon resembles that in the BCC lattice and that this packing order is preserved at long distances (at least up to $R \sim 7R_1$).

7 Conclusions

We take two points as an invariable basis of the formalism of the quasi-crystalline model: formula (1) for RDF calculations which expresses independent smearing of sites of the initial lattice by the Gaussian law, and the rule of modification of the coordination numbers (5) which ensures the proper form of the asymptote. The behaviour of the other parameters of the model was set not arbitrarily but was derived from the damping rate of the experimental RDF using the procedures developed in Section 3 and Section 4. The result is that the experimental RDF of liquid argon can be well described within the quasi-crystalline model under the following conditions:

1) The BCC lattice must be taken as initial, whereas the FCC and HCP lattices give worse descriptions;

2) The initial lattice must be dilated by law (9) except the first coordination sphere;

3) The law of structural diffusion must be modified by formula (6) where $\alpha < 0$.

The last two conditions have clear physical interpretation which is in agreement with general ideas on the structure of liquids. This allows us to hold that the quasi-crystalline model is not merely a formal scheme but is indeed a physical model reflecting real features of the structure of liquids. We called the regularities of particle arrangement in liquids, which are described by the quasi-crystalline model, a packing order.

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