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SIMILARITY AND SHORT-RANGE ORDER PARAMETERS FOR LIQUIDS AND AMORPHOUS SOLIDS

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In the paper the pattern recognition method of the information theory has been adapted to three dimensional disordered structures to compare their short-range order, and a short-range order parameter has been introduced. Theoretical results were applied to the model as well as to the real liquid structures.

ПОДОБИЕ И ПАРАМЕТРЫ БЛИЖНЕГО ПОРЯДКА ДЛЯ ЖИДКОСТЕЙ И АМОРФНЫХ ТВЁРДЫХ ТЕЛ

В работе применён модифицированный метод структурного распознавания теории информации к трёхмерным неупорядоченным структурам с целью сравнения их ближнего порядка и введёния параметра ближнего порядка. Теоретические результаты применены к модели, а также к реальным жидким структурам.

I. INTRODUCTION

The crystalline state is characterized by the presence of a short-range as well as a long-range order. In non-crystalline matter (e.g. liquids or amorphous solids) only some short-range order (confirmed by the fact that both the interference and pair correlation functions have only a few diffuse maxima) is present. It is generally believed that the increasing height and sharpness of the peaks are due to an increased shortrange order. Sometimes, esp. in amorphous structures, it is very difficult or even impossible to compare short-range orders in various non-crystalline states even if the interference and pair correlation functions are known. It is therefore desirable to characterize the short-range order by a single parameter.

Several attempts have been made so far to define some ordering parameters. For instance, Frank [1] introduced an ordering parameter for real crystals simply as the ratio of the number of atoms in crystal lattice sites to the total number of atoms. Stevels [2] introduced the so-called repeatability number and suggested how to calculate it in model structures. A connection with the radial distribution function is mentioned but no mathematical correlation between them has been done.

A number of attempts to characterize the order of atoms has arisen with regard to the determination of the degree of crystallinity (e.g. in polymers) by means of intensity curves measured by X-ray diffraction [3, 4, 5].

In this paper we propose to compare the short-range order of various disordered structures by means of the so-called similarity parameter introduced in the theory of information for patern recognition. This parameter was used by McLachlan [6] in a method for testing the presence of a given atomic configuration in some organic structures. Here, we will introduce the short-range order (SRO) parameter in a similar manner.

In Chapter II we describe the principles of pattern recognition following McLachlan and the basic notions and relations of the structure analysis of disordered systems. Also, various similarity parameters are defined and a precise definition of the SRO-parameter is given.

In Chapter III the theory is verified by applying it to the Unger model and liquid He, Cs, and Pb at various temperatures.

II. THEORY

II. 1. Pattern recognition

The problem of pattern recognition is a very important one in the information theory. Most of the information-retrieval systems, the translation of languages, and the data processing are based on recognizing patterns.

Solving this problem requires to involve a mathematical function which is capable of expressing the identity of, or the similarity between, two patterns in a plane. Such a similarity function should recognize any given motif regardless of a) position in the plane, b) orientation, and c) size (or magnification) (c.f. Fig. 1.).

Next, we shall describe a similarity function which fulfils the requirements a) and b).

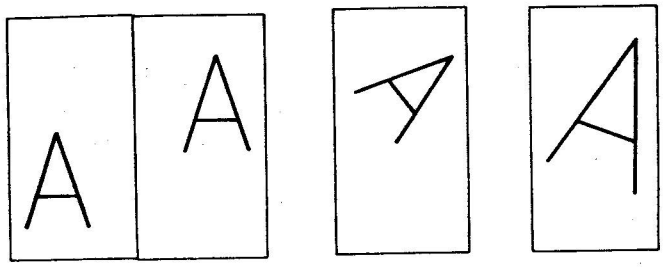

Fig. 1. The pattern *A* translated (a), rotated (b), and enlarged (c).

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The pattern in Fig. 1 can be represented by some characteristic function of the position $\varrho(x, y)$ (e.g. density, reflectivity, blanckness). It is clear that the quantity $\varrho(x, y)$ varies when passing from 1a to 1c. We can introduce the autocorrelation or Patterson function

$$A(u, v)=\frac{1}{ab}\int_0^a\int_0^b \varrho(x, y)\,\varrho(x+u, y+v)\,\mathrm{d}x\mathrm{d}y\,, \tag{1}$$

where a and b are the outer dimensions of a single pattern. This function is an invariant, independent of the position of the initial pattern. Then we can introduce the radial autocorrelation function of $\varrho(x, y)$ defined as

$$C(r)=\frac{1}{2\pi}\int_0^{2\pi} B(r, \Theta)\,\mathrm{d}\Theta\,, \tag{2}$$

where $B(r, \Theta)=A(u, v)$ (in polar coordinates).

The function $C(r)$ is one-dimensional, independent of both position and orientation of the pattern $\varrho(x, y)$. Next, we introduce the cross-correlation $D(s)$ of two radial autocorrelation functions $C(r)$ and $C'(r)$, derived from the patterns $\varrho(x, y)$ and $\varrho'(x, y)$, respectively. Let

$$D(s)=\frac{1}{R}\int_0^R C(r)\,C'(r+s)\,\mathrm{d}r\,, \tag{3}$$

where R is the maximum radius of the pattern. According to McLachlan [6], the integral

$$S_{\varrho\varrho'}=\frac{1}{R}\int_0^R D^2(s)\,\mathrm{d}s \tag{4}$$

is a number which has its greatest value when $\varrho(x, y)$ and $\varrho'(x, y)$ are identical, and it becomes smaller as they are dissimilar, regardless of positioning or orientation.

Now, let us consider Figs. 1a and 1c. If we require the similarity parameter to be independent of the magnification we must replace the radial Patterson function $C(r)$ by a magnification independent function. It is sufficient to find how the radial Patterson function varies with the magnification of a pattern (Fig. 1c). One can easily ascertain that in order to obtain $C_k(r)$ of a k-times larger pattern it is necessary to enlarge the variable r as well as its maximum value R k-times. This means that an appropriate re-scaling of $C(r)$ in r is sufficient even for a comparison of patterns with various magnifications.

II.2. Application to disordered structures

Let us take a real disordered structure for the pattern A of Fig. 1. It is clear that the coordinates of the individual atoms (or the actual atomic density function $\varrho(x, y, z)$) are not known and even if we knew them, we should not be able to calculate the corresponding Patterson function because of the large number of atoms. According to the theory of diffraction by disordered structures, the radial Patterson function $P_a(r)/V$ is a Fourier transform of the interference function $I(s)$ and this relation has the form

$$sI(s)=2\int_0^\infty r\,\frac{P_a(r)}{V\varrho_0}\sin(2\pi sr)\,\mathrm{d}r\,, \tag{5}$$

$$r\,\frac{P_a(r)}{V\varrho_0}=2\int_0^\infty sI(s)\sin(2\pi sr)\,\mathrm{d}s\,. \tag{6}$$

However, this Patterson function is not obtainable from $I(s)$ because the integral of (6) does not exist. Looking back to Sect. I. we can see that the radial Patterson function was introduced as independent of translation and orientation of the pattern. These requirements are fulfilled not only by the radial Patterson function but by the radial distribution function (RDF) and the pair correlation function $g(r)$ and $g(r)-1$, as well.

The Fourier transform between the pair correlation function $g(r)-1$ and the interference function $I(s)-1$ has the form

$$s[I(s)-1]=2\int_0^\infty \varrho_0[g(r)-1]\,r\sin(2\pi sr)\,\mathrm{d}r\,, \tag{7}$$

$$r\varrho_0[g(r)-1]=2\int_0^\infty s[I(s)-1]\sin(2\pi sr)\,\mathrm{d}s\,, \tag{8}$$

where ϱ_0 is the average number density of atoms, $s=2\sin\Theta/\lambda$ is the magnitude of the reciprocal space vector s (Θ and λ being the diffraction angle and wavelength of the applied X-rays, respectively) and r is a distance in real space [7].

The integral (8) can be easily calculated, as the function $I(s)-1$ tends to zero for large s. After a re-scaling (analogical to that mentioned at the end of Section II.), the pair correlation function $g(r)-1$ will not depend on the size of atoms and can be used instead of the radial Patterson function. Considering two structures, if we take $g(r)-1$ and $g'(r)-1$ for $C(r)$ and $C'(r)$, respectively, from the square of their crosscorrelation according to Section II.1., we obtain a number which decreases with a decreasing similarity between the structures. This similarity parameter will be largest when $\varrho'(r)=\varrho(r)$.

II.3. Short-range order parameter

So far we have considered disordered structures only. These can be gained for example by disordering crystalline structures. The amount or degree of such a disorder can be characterized by the method of the similarity parameter,as can be seen in Section III.2., where model structures gained by the disordering of a simple cubic lattice are dealt with.

From the structure analysis and geometrical considerations it is known that the face centred cubic and hexagonal close packed structures are the most ordered ones. If we take as the reference function $C(r)$ (the first of the two cross-correlated functions) the pair correlation function of such a structure and fix the limits of integration, the resulting parameter will depend only on $C'(r)$.

Let us denote $C(r)=g(r)-1$ of the fcc structure $\varrho(x, y, z)$ and $C'(r)=g'(r)-1$ derived from a model or from an experiment ($\varrho'(x, y, z)$). Perform re-scaling so that the first maxima are at position $r=1$. Each of these re-scaled pair correlation functions is invariant of translation, orientation, size of atoms and their average density.

The cross-correlation has the form

$$D(s)=\int_0^R C(r)\, C'(r+s)\, \mathrm{d}r\,, \tag{9}$$

where we take R to equal the distance in atomic diameters up to which the short-range order is being examined (usually from 5 to 10). The normalization coefficient $1/R$ from Section II.1. is not used. The similarity parameter SP is written in the form

$$SP=S_{\varrho\varrho'}=\int_0^R D^2(s)\, \mathrm{d}s\,. \tag{10}$$

The larger the obtained value, the more similar the examined structure ϱ' will be to the fcc structure ϱ. The parameter can be useful for disordered structures that have a tendency to crystalize into a fcc structure (most metals). We denote it as SP_{fcc}. Having used the $C(r)=g(r)-1$ of a simple cubic lattice, we denote it as SP_{sc}.

In a similar way we could introduce similarity parameters comparing a given disordered structure with the other lattices. In order to avoid comparing with the reference structure, we propose to introduce a mathematically simpler but not so instructive parameter characterizing the short-range order, simply defining

$$C(r)=C'(r)=g'(r)-1 \tag{11}$$

in a cross-correlation (9). The corresponding $S_{\varrho\varrho'}$ is denoted as the SRO-parameter. It can be considered a result of a mathematical processing of a pair correlation function as a whole. This single number depends on the number and height of peaks, as well as on their relative positions.

III. APPLICATIONS

III.1. Some technical notes

Computation of the similarity parameter (SP) defined in Section II.3 requires a pair correlation function $g(r)-1$ of a simple cubic lattice (Section III.2) and of a face centered cubic lattice (Section III.3). Both functions can be easily computed. After generating coordinates of atoms in a sufficiently large area of the fcc latice we choose an atom near the centre and the distance of all other atoms from this one and the number of atoms $N(r)$ corresponding to the distance r are calculated.

It is clear that

$$N(r)=4\pi r^2\, \varrho_0 g(r)\Delta r\,, \tag{12}$$

where ϱ_0 is the mean number density of atoms and Δr is the step by which $g(r)$ is to be calculated.

Putting R to be the distance up to which the order is investigated, we let $g(r)-1=0$ for r greater than R.

In Table 1 the calculated distances r and the corresponding number of atoms $N(r)$ are shown, by an asterisk are denoted the values of a simple cubic case.

Computation of the SRO parameter is much simpler because it does not need any special reference function.

Since correlations between atoms in liquid and amorphous states are perceptible only at several atomic diameters, all integrations were performed with an upper limit equal to 5 (in atomic separation units).

Table 1

Distances r and the corresponding numbers of atoms $N(r)$ for a face centred cubic lattice

r	1.00	1.41	1.73	2.00	2.24	2.45	2.65	2.83	3.00
$N(r)$	12	*6	24	*12	24	*8	48	*6	36
r	3.16	3.32	3.46	3.61	3.87	4.00	4.12	4.24	4.36
$N(r)$	*24	24	*24	72	48	*12	48	*30	72
r	4.47	4.58	4.69	4.80	4.90	5.00	5.10	5.20	5.29
$N(r)$	24	48	24	48	8	84	24	96	48
r	5.39	5.57	5.66						
$N(r)$	24	96	6						

III.2. Unger's model

The theory introduced in the first part of this paper was tested with a structural model of a disordered system of atoms proposed by Unger [9]. We have restricted ourselves to structures which transform to a simple cubic lattice at a vanishing disorder. Starting from such a lattice, Unger's model may be built up step by step

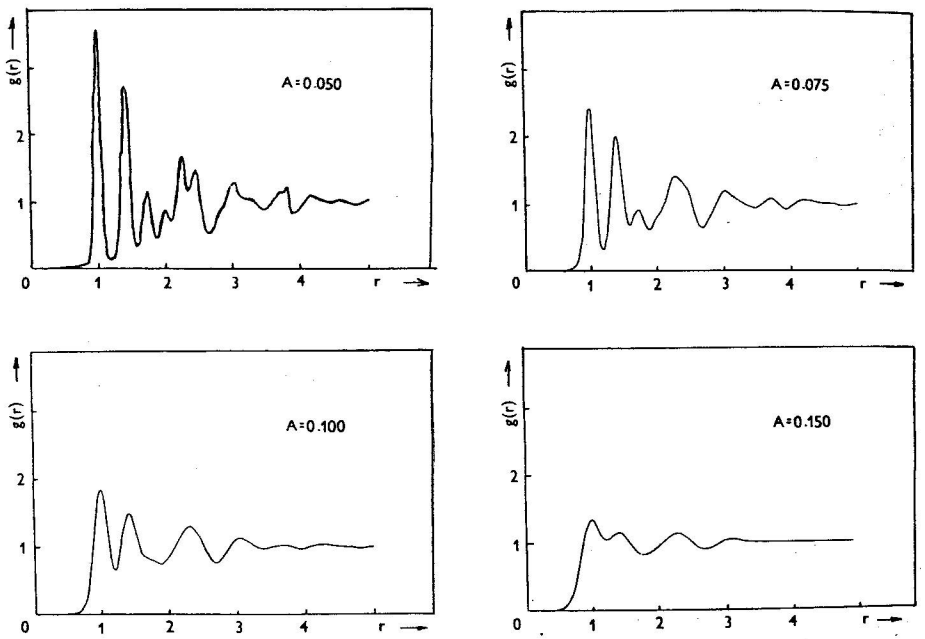

Fig. 2. The pair correlation functions $g(r)$ for Unger's model. (a) $A = 0.050$, (b) $A = 0.075$, (c) $A = 0.100$, (d) $A = 0.150$.

by adding further atoms to the existing cluster at random positions in such a way that the short-range order of the crystal is only slightly disordered. The loss of the longrange order in such a structure is connected with the increase of distortion as one proceeds away from the origin site.

Unger obtained a simple analytical expression for the pair correlation function, namely

$$g(r)=\frac{1}{4\pi\varrho_0}\sum_{i,j,k}[f(r-a_{ijk}, v^2A^2)-f(r+a_{ijk}, v^2A^2)]\,. \tag{13}$$

This formula contains only the adjustable parameter A, which decreases with

Table 2

Values of the SP_{sc} and the SRO-parameter for several values of $A(a = 0.090)$.

A	SP_{sc}	SRO
0.050	0.513 525	0.244 099
0.075	0.245 475	0.135 500
0.100	0.149 950	0.105 131
0.150	0.093 147	0.079 031

Table 3

Values of the SP_{sc} and the SRO-parameter for several values of A ($a = 0.095$).

A	SP_{sc}	SRO
0.050	0.503 556	0.238 220
0.075	0.241 794	0.133 646
0.100	0.148 288	0.104 217
0.150	0.092 621	0.078 589

Table 4

Values of the SP_{sc} and the SRO-parameter for several values of A ($a = 0.100$).

A	SP_{sc}	SRO
0.050	0.494 008	0.232 683
0.075	0.238 258	0.131 880
0.100	0.146 685	0.103 332
0.150	0.092 107	0.078 153

a decreasing disorder (in the crystalline state $A = 0$). *The* v^2 denotes the reduced width tabulated in [9], a_{ijk} is the distance of the atom with the coordinates i, j, k from the atom at the origin, and f is a Gaussian-like function

$$f(x, y)=\frac{1}{\sqrt{2\pi y^2}}\exp\left(-\frac{x^2}{2y^2}\right). \tag{14}$$

The pair correlation functions for such structures (for various values of A) are shown in Fig. 2. Since the author used relatively small groups of atoms, $g(r)$ does not approach unity for higher values of r but it slowly decreases down to zero. In

order to suppress this tendency we have imposed an exponential factor $\exp(-ar^2)$ on $g(r)-1$ which, in turn, lowers the ordering. The eight initial peaks of $g(r)-1$ in the simple cubic lattice were used as a reference function $C(r)$ in cross-correlation.

The resulting SP_{sc} and SRO parameters for various values of the coefficients a and A are summarized in Tables 2, 3 and 4. Using these Tables one can see that with an increasing disorder (increasing a and A) both the SP_{sc} and the SRO-parameter decrease. The magnitude of SP_{sc} is higher than that of the SRO-parameter.

III.3. Liquid helium, caesium, and lead

Mozer et al. [10] published the interference functions for liquid ^{4}He at various temperatures. These functions can be Fourier transformed to the pair correlation functions $g(r)$. Brostow and Sochanski [11] found an analytical expression that fits the $g(r)$'s. In Fig. 3 two of them (after re-scaling for the first peaks) are shown.

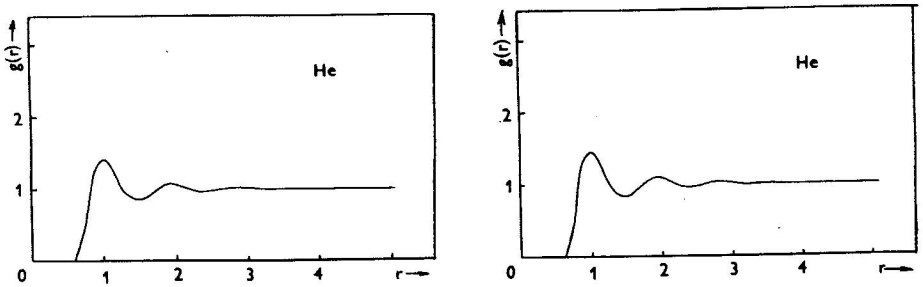

Fig. 3. Pair correlation functions $g(r)$ for liquid ^{4}He with a mean density of 0.1528 gcm^{-3} at temperatures (a) 2.05 K, (b) 2.84 K.

Huijben and van der Lugt [12] measured the interference functions for liquid caesium at four temperatures. The interference functions of liquid lead of three temperatures were measured by Steffen and Hosemann [13].

We have applied the Fourier transform

$$g(r)=1+\frac{1}{2\pi^2 r\varrho_0}\int_0^\infty k[I(k)-1]\sin kr\,\mathrm{d}k\,, \qquad (15)$$

where $k=4\pi\sin\Theta/\lambda$, to their data in order to obtain the corresponding pair correlation functions $g(r)$. The results are shown in Figs. 4 and 5.

The similarity parameter SP_{fcc} and the SRO-parameter were computed. The

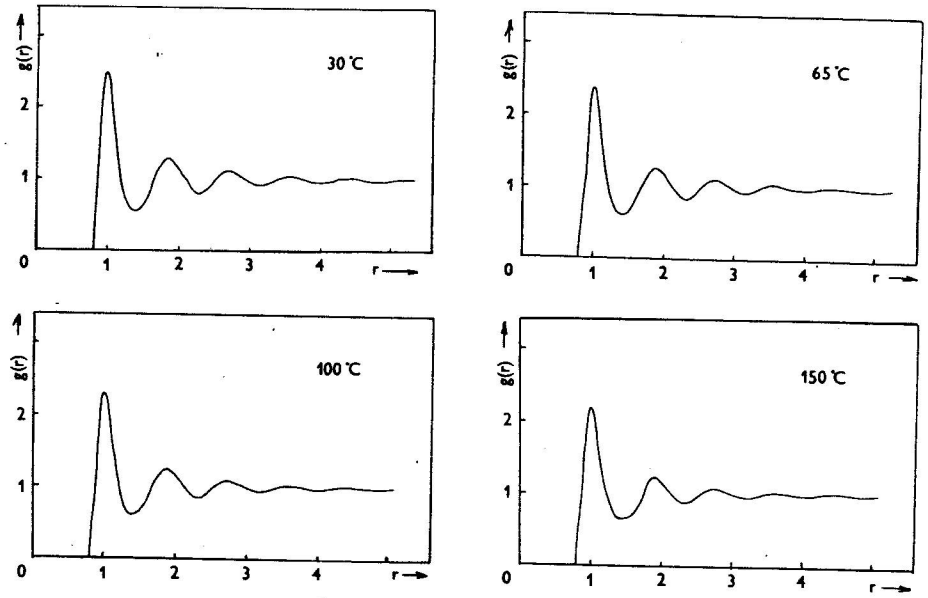

Fig. 4. Pair correlation functions $g(r)$ for liquid caesium at temperatures (a) 30 °C, (b) 65 °C, (c) 100 °C, (d) 150 °C.

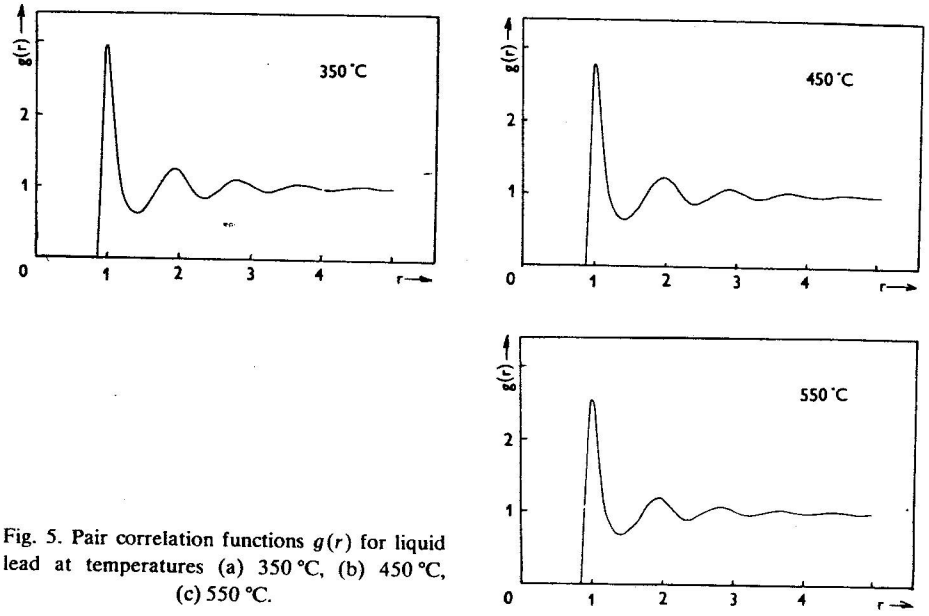

Fig. 5. Pair correlation functions $g(r)$ for liquid lead at temperatures (a) 350 °C, (b) 450 °C, (c) 550 °C.

Table 5

Values of the SP_{fcc} and the SRO-parameter for liquid helium

ϱ_0 [atA^{-3}]	T[K]	SP_{fcc}	SRO
0.0230	2.05	0.123 856	0.097 792
0.0230	2.84	0.128 291	0.101 047

Table 6

Values of the SP_{fcc} and the SRO-parameter for liquid ceasium

T[°C]	ϱ_0 [atA^{-3}]	SP_{fcc}	SRO
30	0.008304	0.302 250	0.170 250
65	0.008217	0.273 012	0.159 750
100	0.008129	0.265 639	0.156 375
150	0.008005	0.247 247	0.148 625

Table 7

Values of the SP_{fcc} and the SRO-parameter for liquid lead

T[°C]	ϱ_0 [atA^{-3}]	SP_{fcc}	SRO
350	0.0310	0.354 124	0.179 818
450	0.0306	0.323 120	0.171 829
550	0.0310	0.289 829	0.164 501

results are given in Tables 5, 6 and 7. It can be seen that both the SP_{fcc} and the SRO-parameter decrease with increasing temperature.

IV. DISCUSSION

There was published a great number of diffraction data (X-ray, neutron, electron) for liquids and amorphous solids with a consequent radial distribution analysis. When comparing the structures, various parameters are taken into account in order to distinguish their short-range order, e.g. location, the heights and widths of the peaks of the interference, the pair correlation, and the radial distribution functions, the mean number density, coordination numbers, and the packing fraction. This work brings the possibility of a direct mathematical comparison of amorphous structures with each other, or with the crystalline structure (SP_{fcc} and SP_{sc}) and introduces the SRO-parameter which characterizes the short-range order in disordered structures.

Our method was tested both in model and real structures or liquid caesium, helium, and lead. The parameter SP requires the pair correlation function $g(r)-1$ of a face centred cubic or a simple cubic lattice as an "internal standard", the SRO-parameter uses $C(r)=C'(r)$, where $C'(r)$ is equal to the $g'(r)-1$ of the considered structure.

The method makes it possible to characterize quantitatively the short-range order not only for the same material (e.g. caesium at various temperatures) but, furthermore, it enables to compare the short-range order of different materials (e.g. liquid lead and caesium). From Tables 6 and 7 it can be easily found that lead at 450 °C is more ordered than caesium at 30 °C (it has a greater SRO-parameter) though such a decision cannot be made using the Figures 4 and 5 only. From Table 5 can be seen that liquid helium is far less ordered than liquid lead or caesium are.

In [8] we discussed the possibility of computing the SRO-parameter straightforward from the interference functions. This is, however, beyond the aim of this paper.

It is necessary to note that it is not quite evident that the rescaling of the pair correlation functions for the 1st peak is fully correct in connection with their use in the integral of (9).

In this paper we have considered one-component materials only. However, there is no problem to extend the SRO-parameter to more-component materials provided that the corresponding partial pair correlation functions were known.

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REFERENCES

[1] Frank, F. C.: Proc. Roy. Soc. *A 170* (1939), 182.
[2] Stevels, J. M.: J. Non-Cryst. Solids *6* (1971), 307.
[3] Klug, H. P., Alexander, L. E.: *X-Ray Diffraction Procedures.* J. Wiley and Sons. New York 1959.
[4] Clark, G. L. (ed.): *The Encyclopedia of X-Rays and Gama Rays.* Reinhold Publ. corp. New York 1963.
[5] Červinka, L., Dusil, J.: J. Non-Cryst. Solids *21* (1976), 125.
[6] McLachlan Dan, Jr.: in [4], p. 495.
[7] Guinier, A.: *X-Ray Diffraction.* W. H. Freeman and Co. San Francisco and London 1963.
[8] Korytár, D.: *Thesis.* Inst. of Phys. Slov. Acad. Sci. 1977.
[9] Unger, H. J.: Phys. Stat. Sol. *(a) 76* (1976), 207.
[10] Mozer, B., De Graaf, L. A., Le Neindre, B.: Phys. Rev. *A 9* (1974), 448.
[11] Brostow, W., Sochanski, J. S.: Phys. Rev. *A 13* (1976), 882.
[12] Huijben, M. J., van der Lugt, W.: J. Phys. F. Metal Phys. *6* (1976), L 225.
[13] Steffen, B.: Phys. Rev. *B 13* (1976), 3227.

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