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The Calculation of Liquid Structures by Paracrystalline Distortions

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The atomic structure of solids and the atomic distance distribution in gases have been known for a long time, but the real structure of liquids is unknown up to this moment. There exist several structural models of liquids which are based on the so-called radial distribution function (RDF)

$$4\pi r^2(\rho - \rho_0) = \frac{2r}{\pi}\int_0^\infty s\, i(s) \sin (sr)\, ds, \quad s = 4\pi \sin \theta/\lambda$$

ρ is the convolution square (pair-correlation function) of the centers of the atoms, ρ_0 is related to the macroscopic density of the liquid and s is the absolute value of the distance vector in Fourier space. $4\pi r^2 \rho$ therefore gives the mean number of neighbors, the coordination number, at a distance r of a randomly chosen reference atom in the liquid. This function is calculated from the scattering intensity of X-rays or electrons or neutrons from liquids by Fourier-transform.[13]

In this report I'll restrict myself for simplicity to the liquid elements which crystallize in highest symmetry, that means in a hexagonal-close-packed (hcp), face-centred-cubic (fcc) or body-centered-cubic (bcc) lattice. These are the normal metals and the inert gases.

The RDF's of this liquid elements calculated from the measurements, mostly show 3 almost equidistant maxima, which lie above the curve of the mean density ($4\pi r_2 \rho_0$) in the liquid (Fig. 1). From the shape of the curve there arises the question, whether this is the picture of a crystal-like order in the liquid. In the literature there exist mainly 3 different structure proposals of the liquid.

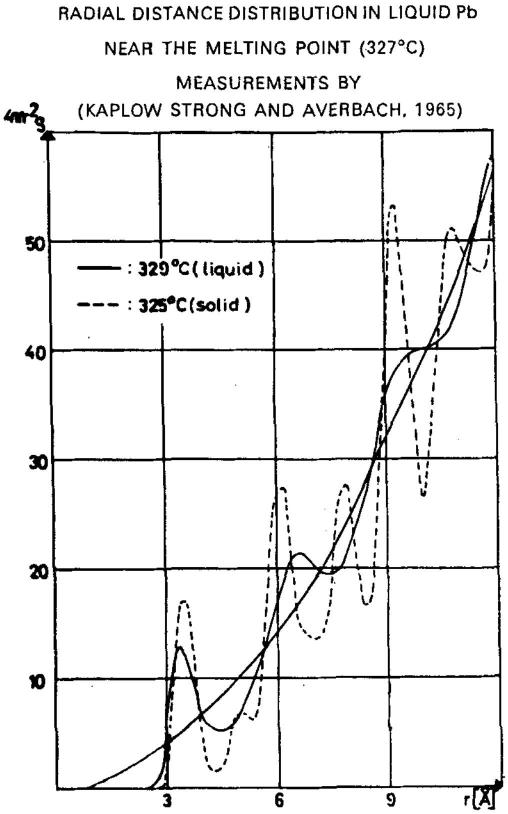


Figure 1

1. Many authors believe[3,6] that the melt is a distorted crystal of the same lattice type as in the solid state. In Fig. 1 you see the comparison of the RDF of lead 2 °C above and below the melting point. There are 3 maxima at about 5, 8 and 11 Å in the function of the fcc lattice of solid lead, which in the curve of liquid lead are absent. Therefore the statement of the same structure in the solid and liquid states is doubtful.

2. Other scientists, especially Bernal, Steeb, and Kruh[1,7,11] believe, that in monatomic liquids, there exists no crystal-like order, not even in a distorted manner. They base their arguments on the fact that in metallic melts the $\sqrt{3}r_1$-distance is absent (r_1 = mean distance of nearest neighbor atoms) which in solid metals exists with a high coordination number. The coordination number is the number N_m of neighbors at a definite distance r_m. But the statistical and geometrical model of Bernal gives a mean density ρ_0, which for most elements is much smaller than that ρ_0 which was experimentally found in most monatomic liquids. Therefore Bernal's model cannot be taken as the model of structure of liquids.
3. A third possibility is, and this is our opinion too, that the structure of the melts might be crystal-like and might be of another structure type than that in the solid state. For most elements it is found, that at the melting point, there is a decrease in density and an increase in coordination number to about 10. Those elements, which crystallize close packed show at the melting point a decrease in density and coordination number. Moreover in most cases the distance of next neighbor atoms in the melt is slightly less than in the solid state. There seems to be the tendency for the melting elements to turn over to a state of higher crystalline symmetry.

The experimental and mathematical methods to determine the structure of liquids from the scattering experiments are numerous and difficult and therefore uncertain to a high extent. These difficulties are not easily removed. By comparing literature RDF's of the same elements at almost the same temperature there are found some discrepancies between these curves (Fig. 2), especially in the range of the second maximum. This shows that there must still be much more effort to develop better experimental and mathematical methods to get clearer results.

If the individual atoms oscillate in a crystalline lattice under the influence of the temperature-movement about their lattice centers, the long-range order of the lattice is not destroyed. The mean

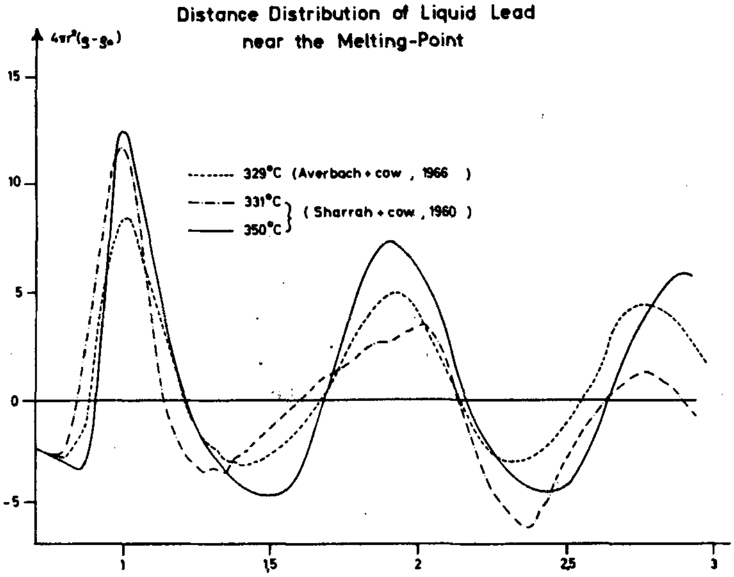


Figure 2

square fluctuation of this oscillation is calculated by the Debye–Waller factor and the characteristic temperature.

At the melting point the crystalline lattice is destroyed and there appears a second kind of lattice distortions. These are called liquid-like or paracrystalline. Here the long-range order is destroyed *and only a short-range order remains.* Every individual lattice particle now no longer knows its ideal periodic place in the crystalline lattice, but oscillates in its distances statistically and relative only to the instantaneous position of its nearest neighbors.

Averbach[6] believes too, that it is impossible to explain the RDF of liquids by lattice distortions of the first kind alone, this means by the temperature-movement inside a solid at that temperature. These additional distortions were called diffusive displacements by Averbach and Scheil[9].

By the theory of the paracrystal of Hosemann[5] it is possible to calculate the lattice distortions of the 2nd kind quantitatively, which was impossible up to date with the other liquid structure models.

The distance statistics between second neighbors H_2 and further statistics H_j are calculated by a repeated mathematical convolution of the distance statistic of next neighbors H_1 with themselves. The degree of the convolution power (i) is determined by the position of the considered particle relative to the reference atom in the distorted three-dimensional crystal.

$$H_j = \overset{(i-1)\text{times}}{\overparen{H_1}\overparen{H_1} \ldots \overparen{H_1}} = H_1^{(i)} \tag{1}$$

$$\overparen{H_1(r) H_1}(r) = \int H_1(y) H_1(r-y)\, dy \tag{2}$$

$$\int H_1(r)\, dv = 1.$$

In this way a synthetic RDF is calculated by summing up the lattice distances, which were broadened by lattice distortions of 1st and 2nd kind.

$$(4\pi r^2 \rho)_{\text{1st}+\text{2nd kind}} = \overparen{H_{\text{1st kind}}\,}\overparen{H_{\text{1st kind}}\left(\sum_{j=1}^{n} K_j H_j(r - s_j)\right)} \tag{3}$$

The result is to be compared with the experimentally determined RDF. K_j and s_j are coordination number and the center of the jth distance statistic.

For a successful fit of the synthetic to the experimental RDF there are some conditions to be fulfilled simultaneously:

1. The mean density of packing particles of the synthetic RDF must be compatible with the macroscopically determined density of the liquid ρ_0 and must satisfy the equation between the coordination number K_1 and the mean distance s_1 of the next neighbors and the macroscopic density ρ_0. C depends on the type of lattice:

$$K_1 = C \rho_0 s_1^3 \tag{4}$$

2. The distance statistic of next neighbors $K_1 H_1$, by which the further distance statistics will be calculated, must be chosen

asymmetric. Otherwise one never can fit the folding polynomial (3) with the experimental RDF at distances $r > 3$ Å.

3. A further parameter is the lattice type, which must be chosen to get the best fit to the experimental curve. In all cases under investigation the bcc and fcc lattice can be excluded. The lattice found its hcp with a minor amount of stacking faults ($\lesssim 30\%$).

4. The amount of lattice distortions of the first and the second kind must be found. Some evidence for the distortions of first kind is given by the characteristic temperature, but the values published in the literature differ very much.

The calculations were made by an electronic computer. From calculation to calculation the variable parameters as the lattice type, the portion of the lattice distortions of 1st and 2nd kind and the shape and the position of the distance statistic of next neighbors were varied as long as an optimal fit to the experimental curve is received.

The 1st asymmetric distance-statistic can be divided into 2 partial statistics. The center of the second lies at about 0.8 Å greater distances and has about 20% of the coordination number of the first symmetric statistic.

This is the same value which Eyring[14] found for the hole-volume in his hole theory of liquids.

From this asymmetry of the first statistic there comes the conception that in the liquid exist greater particles with crystal-like order inside. These particles, which we have called paracrystallites, probably have only a short lifetime. By means of the diffusive movement of the atoms in the liquid there is a permanent creation and decomposition of the paracrystallites. These two partial statistics of K_1H_1 can be explained by two different types of distances between next neighbors. The shorter distances are those between the atoms inside the paracrystallites and the about 0.8 Å greater ones are the distances between neighboring atoms belonging to different paracrystallites. The mean diameter of these particles is calculated near the melting point to be about

30 Å and decreases slowly with temperature and corresponds to the critical correlation distance of Averbach.[6]

In order to select the correct lattice type there were calculated synthetic RDF's for the hcp-, the fcc- and the bcc-lattice (Fig. 3). The first distance statistic, which was used for this calculation, is assumed to be of the Gaussian-type and its integral width is varied. The relative distance fluctuation of next neighbors g have 8, 10.7 and 13.2%. With increasing g-value the differences between the individual lattice types diminish. The comparison of these curves for $g = 8$ and 10.7% show that the fcc-lattice can clearly be distinguished from the hcp in the region of the second maximum and minimum.

The bcc-lattice always must be excluded, because on fitting eq. (3) to the experimental curves the coordination number of the symmetric part of the first peak must be taken to be about 10 which contradicts $K_1 = 8$ of the bcc-lattice.

In the experimental RDF of liquid elements, which were measured near the melting point, the g-value is determined to be 10 to 11%. At higher temperatures, this means 100 °C above the melting point and more, the relative distance fluctuations have values of 13% and more. In this case as it is seen from Fig. 3 it is no longer possible to analyze a definite lattice in the liquid. As the synthetic curves of $g = 13.2\%$ show, the 3 lattices become more and more similar with increasing g-value.

Figures 4 and 5 show the results of our investigation on some RDF's of liquid-elements published by different authors. The RDF's of all elements, which crystallize in a h.c.p.-, an f.c.c.- or a b.c.c.-lattice can be explained by a polyparacrystalline structure with about 20 to 50 Å large paracrystallites. Their lattice type is a distorted hexagonal-close-packing with 10 to 30% stacking faults. This large region of uncertainty is because of the still poor experimental curves.

Fig. 4a shows the best possible fit of a calculated synthetic RDF with an fcc-lattice to the experimental curve of liquid silver,[8] which in the solid state is fcc. It can be seen that it is impossible to fit the second minimum with an fcc-lattice. Figure 4b shows the

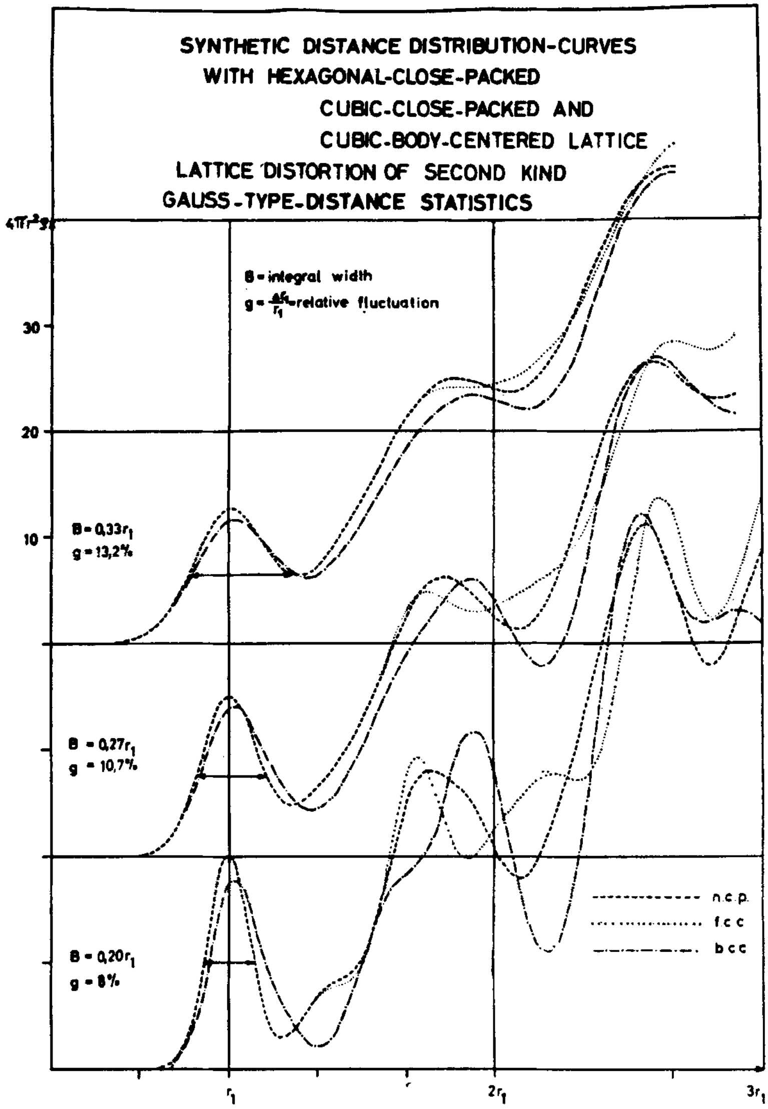
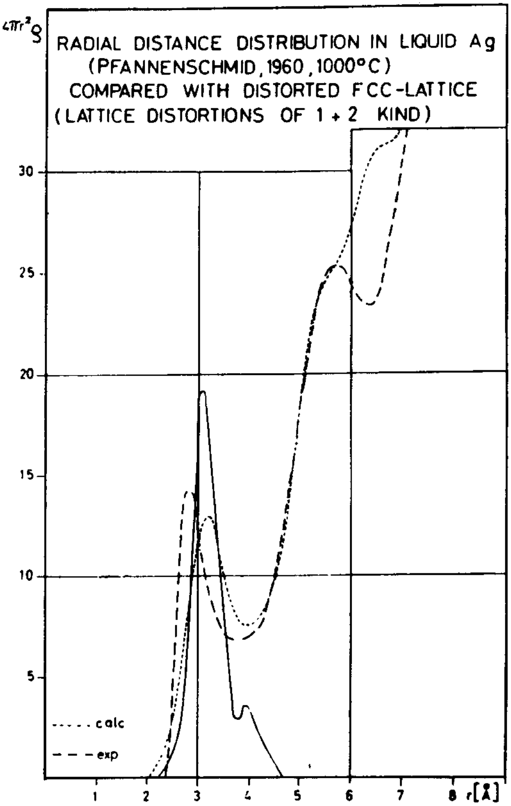

SYNTHETIC DISTANCE DISTRIBUTION-CURVES
WITH HEXAGONAL-CLOSE-PACKED
CUBIC-CLOSE-PACKED AND
CUBIC-BODY-CENTERED LATTICE
LATTICE DISTORTION OF SECOND KIND
GAUSS-TYPE-DISTANCE STATISTICS
$4\pi r^2 g$
B = integral width
$g = \frac{\Delta r_1}{r_1}$ = relative fluctuation
30
20
10
B = 0,33r_1
g = 13,2%
B = 0,27r_1
g = 10,7%
B = 0,20r_1
g = 8%
n.c.p.
f.c.c.
b.c.c.
r_1
$2r_1$
$3r_1$

Figure 3



$4\pi r^2 \rho$
RADIAL DISTANCE DISTRIBUTION IN LIQUID Ag
(PFANNENSCHMID, 1960, 1000°C)
COMPARED WITH DISTORTED FCC-LATTICE
(LATTICE DISTORTIONS OF 1 + 2 KIND)
30
25
20
15
10
5
calc
exp
1
2
3
4
5
6
7
8
r [Å]

Figure 4a

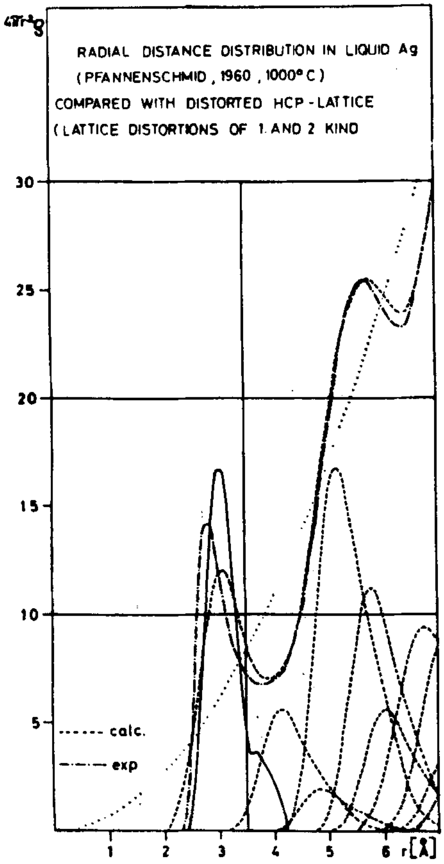

4πr²ρ
RADIAL DISTANCE DISTRIBUTION IN LIQUID Ag
(PFANNENSCHMID, 1960, 1000° C)
COMPARED WITH DISTORTED HCP-LATTICE
(LATTICE DISTORTIONS OF 1. AND 2 KIND
30
25
20
15
10
5
------ calc.
—·—·— exp
1
2
3
4
5
6
r[Å]

Figure 4b

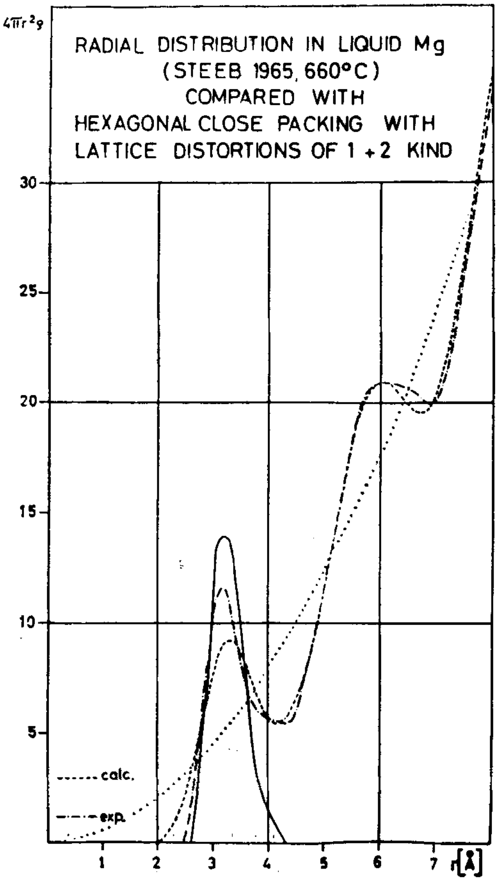

RADIAL DISTRIBUTION IN LIQUID Mg
(STEEB 1965, 660°C)
COMPARED WITH
HEXAGONAL CLOSE PACKING WITH
LATTICE DISTORTIONS OF 1 + 2 KIND
4πr²ϱ
30
25
20
15
10
5
calc.
exp.
1
2
3
4
5
6
7
r[Å]

Figure 5a

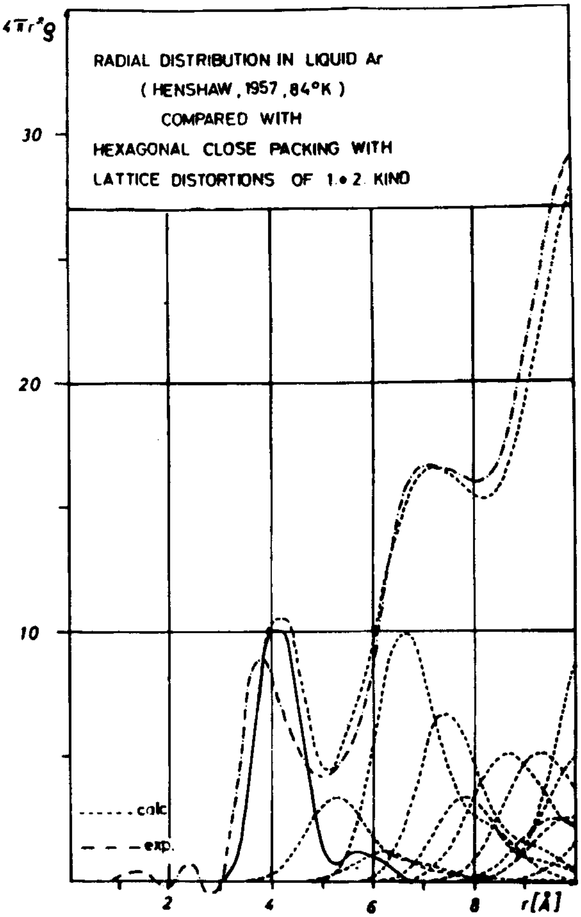


Figure 5b

same experimental RDF compared with a synthetic one of hcp type, which fits the experimental curve very well. Because the corrolations between next neighbor atoms were not considered in this calculation it was impossible to fit the synthetic curve to the first maximum in all details. The drawn line is the first distance statistic which is only disturbed according to the distortions of the second kind, the – – – line shows the whole synthetic RDF with distortions of the 1st and 2nd kind and the – · – gives the experimental curve.

Further the single distance statistics, which by summing up give the synthetic RDF, are noted in Fig. 4b. Further examples are demonstrated in Figs. 5a, b and c. Here are the hcp-fits to the fcc-crystallizing inert gas Ar,[4] to the hcp-crystallizing Mg[12] and to the bcc-crystallizing K.[2]

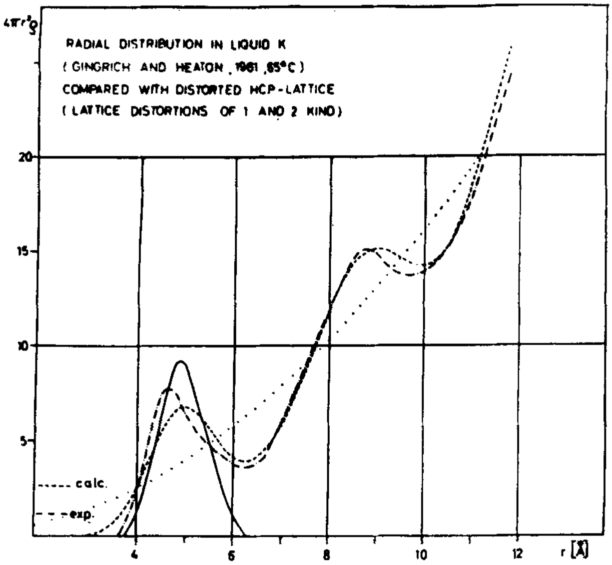


Figure 5c

In the same way we got similar results with all elements of that group which is considered here. The other elements which can be liquefied seem to have more complicated structures in the liquid state. The very difficult calculations on the computer are still running. After removing some difficulties it is planned to extend this method to molecular liquids.‡

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