RADIAL DENSITY FUNCTION OF LIQUIDS OBTAINED FROM THE TERMINATED NEUTRON DIFFRACTION DATA SCALING BY THE KROGH MOE-NORMAN-VAINSHTEIN METHOD

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(Received July 2, 1971)

A numerical analysis is performed of the influence of neutron data termination on the normalization constants, radial distribution functions, and on interatomic distances and coordination numbers determined from these functions. Computations are carried out for liquid copper at 1423, 1573 and 1723°K and for liquid zinc at 743°K. Neutron data of Breuil and Tourand (copper) and Caglioti *et al.* (zinc) are normalized using the Krogh Moe-Norman-Vainshtein method. For large neutron scattering angles the normalization constant is found to depend only weakly on the termination angle. The influence of wrong normalization of experimental data on the radial distribution function is discussed. The interatomic distances determined from the radial distribution function $g(r)$ are shown to be practically independent of the termination angle and insensitive to wrong normalization. The strong dependence of coordination number on the termination angle, observed by other authors, is confirmed. An approximately linear dependence of coordination numbers on $\lambda/4\pi \sin\theta$ is found. The possibility of comparing coordination numbers obtained in different laboratories for the same liquids is discussed.

1. Introduction

The conventional neutron diffraction is, besides the X-ray and electron diffraction, a widely used technique for the investigation of the atomic structure of liquids (Vineyard 1958, Furukawa 1962, Caglioti 1968, Enderby 1968, Steeb 1968). Atomic arrangement in liquids is usually described in terms of the radial density function (RDF) which is the Fourier transform of a suitably normalized intensity of coherently scattered neutrons. Physically, the RDF determines the probability of finding an atom in a volume element dV at a distance r from a given atom. Once the RDF is known, the interatomic distances and coordination numbers, which are essential for the study of the atomic structure of liquids, can be obtained immediately. (By "coordination number" we mean here the

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"first coordination number", *i. e.* the number of neighbours in the first coordination shell.) The interatomic distances, as measured by different authors, agree rather well. On the other hand, there are serious discrepancies between the values of coordination numbers obtained in different laboratories. (The differences amount in some cases several tens per cent.) The reason for these discrepancies seems to lie in the diversity of methods used for the determination of the coordination numbers (Mikolaj *et al.* 1968, Pings 1968), as well as in various errors made in the diffraction measurements.

The accuracy of determining the RDF from diffraction measurements, both using *X*-rays and neutrons, has been studied by many authors. Reviews of some of these studies can be found in the papers of Furukawa (1962) and Pings (1968). From among the papers not quoted there or published more recently we would like to mention the following: Hosemann *et al.* 1964, Schlup 1965, Wagner *et al.* 1965, Henninger *et al.* 1966, Ocken *et al.* 1966, Caglioti, *et al.* 1967, Henninger *et al.* 1967, Dasannacharya *et al.* 1968, North *et al.* 1968, Schlup 1968, Caglioti *et al.* 1969, Lorch 1969. However, the errors in neutron diffraction measurements which influence the value of coordination number are discussed in a relatively small number of papers only; the majority of them being devoted to the effect of data termination at various scattering angles. Clayton *et al.* (1961) presented a numerical analysis of the influence of the data termination on the coordination number and the position of the main maximum of the RDF for liquid krypton. Similar analyses were performed by Gingrich *et al.* (1962) for liquid argon and Caglioti *et al.* (1967) for liquid zinc. In all these three cases the coordination numbers and interatomic distances, as determined from RDF, increased with decreasing maximum neutron scattering angle. A more theoretical approach to the problem of the influence of data termination on the coordination number was presented by Hosemann *et al.* (1964). They proposed a method for determining a "true" value of coordination number from experimental data (called HLK method in the following text).

In the present paper we study the data termination effect in a more systematic way using a numerical method. The influence of the data termination on the RDF and, in particular, on interatomic distances and coordination numbers is investigated for different methods used for the determination of the coordination numbers. The computations were performed for liquid copper at 1423, 1573 and 1723°K, and for liquid zinc at 743°K using neutron diffraction data of Breuil and Tourand (1970) (Cu), and Caglioti *et al.* (1967) (Zn).

2. *Theory*

The intensity of neutrons scattered coherently from a monoatomic liquid at an angle 2θ can be expressed in the static approximation (Enderby 1968) by the well-known formula

$$I_{\mathrm{coh}}(Q) \propto \langle b \rangle^2 \left[1 + \int_0^\infty 4\pi r^2 [\varrho(r) - \varrho_0] \frac{\sin Qr}{Qr} \right] dr, \tag{1}$$

where $Q = 4\pi \sin \theta/\lambda$, λ is the neutron wave-length, $\varrho(r)$ is the radial atomic density, ϱ_0 the mean atomic density of the liquid, and $\langle b \rangle$ represents the averaged neutron scattering

amplitude. Self-absorption and absorption in the container are neglected in deriving Eq. (1).

For large $Q(Q \to \infty)$, $I_{\text{coh}}(Q) \propto \langle b \rangle^2$. This permits the definition of a structure factor

$$S(Q) \equiv \frac{I_{\text{coh}}(Q)}{I_{\text{coh}}(Q \to \infty)}. \tag{2}$$

Using (2) we can write Eq. (1) in the form

$$S(Q) - 1 = \int_0^\infty 4\pi r^2 [\varrho(r) - \varrho_0] \frac{\sin Qr}{Qr} dr. \tag{3}$$

Taking the Fourier transform we obtain the following equation for the RDF.

$$4\pi r[\varrho(r) - \varrho_0] = \frac{2}{\pi} \int_0^\infty [S(Q) - 1] Q \sin Qr dQ. \tag{4}$$

Since it is impossible to measure the neutron intensity in the whole Q range $(0, \infty)$, the RDF is, in practice, determined from the equation

$$4\pi r[\varrho(r) - \varrho_0] = \frac{2}{\pi} \int_0^{Q_{\max}} [S(Q) - 1] Q \sin Qr dQ. \tag{5}$$

Here, $Q_{\max}$ is the maximum parameter Q for which the intensity of neutrons is measured.

The structure factor defined by Eq. (2) approaches the following limits

$$S(Q) \to \begin{cases} 1, & Q \to \infty \quad \text{(6a)} \\ K_B \varrho_0 T \kappa_T, & Q \to 0, \quad \text{(6b)} \end{cases}$$

where K_B is the Boltzmann constant, κ_T is the isothermal compressibility, and T is the absolute temperature. Eqs (6a) and (6b) permit the normalization of experimental data.

The neutron intensity $I(Q)$ can be expressed as

$$I(Q) = I_{\text{coh}}(Q) + I_A. \tag{7}$$

I_A stands here for the total intensity of neutrons which have undergone incoherent or multiple scattering. In diffraction studies it is usually assumed that I_A is independent of the scattering angle 2θ.

There are four methods usually applied to the determination of $S(Q)$ from the neutron intensity $I(Q)$ (normalization of experimental data):

a) Method of high angles (HA). The basic assumption of the HA method is that at large neutron scattering angles ($Q \to \infty$) the interference effects are negligible. The method requires the measurements to be extended to relatively large angles θ (Steeb 1968).

b) North *et al.* (1968) have proposed a method in which a vanadium sample is used for the normalization of experimental data. Advantage is there taken of the property of vanadium whose neutron coherent scattering amplitude is nearly zero.

c) The method proposed independently by Krogh Moe (1956), Norman (1957), and Vainshtein (1957) (called KMNV in the following text) will be given more attention here with regard to its use in our calculations.

The fundamental equation of the KMNV method

$$\int_0^{Q_{max}} [S(Q)-1]Q^2 dQ = -2\pi^2 \varrho_0 \tag{8}$$

can be obtained from Eq. (5) assuming that two atoms never occur in the same site, *i. e.* that the radial atomic density $\varrho(r)$ vanishes at small r, and replacing sin Qr by Qr.

Let us assume now that $I(Q)$ is known for $0 \leqslant Q \leqslant Q_{max}$. Since measurements down to $Q = 0$ are not feasible, $I(0)$ is usually obtained by extrapolation. From Eqs (2) and (7) we get for the structure factor

$$S(Q) = \frac{I(Q)-I_A}{I(\infty)-I_A}. \tag{9}$$

Substitution of $Q = 0$ into Eq. (9) leads to the expression for the contribution of multiple and incoherent scattering I_A to the neutron intensity $I(Q)$

$$I_A = \frac{S(0)I(\infty)-I(0)}{S(0)-1}, \tag{10}$$

where $S(0)$ is calculated from Eq. (6b). By substitution of Eqs (9) and (10) into Eq. (8) and evaluation of the integral we get the expression for $I(Q)$ at the limit $Q \to \infty$

$$I(\infty)_{KMNV} = \frac{\int_0^{Q_{max}} I(Q)Q^2 dQ + \dfrac{2\pi^2 \varrho_0 I(0)}{S(0)-1}}{\dfrac{Q_{max}^3}{3} + \dfrac{2\pi^2 \varrho_0}{S(0)-1}}. \tag{11}$$

$I(\infty)$ determined from the above equation can now be inserted into Eq. (10) and the value of I_A can be evaluated. Eq. (9) can be used, then, to determine the structure factor $S(Q)$ which, in turn, gives the radial density function (Eq. (5)).

d) Rahman (1965) has proposed another method based on assumptions similar to those of KMNV. In deriving his normalization equation he assumed that $\varrho(r)$ vanishes at moderate temperatures for any $r < r_c$, where r_c is a rather well-defined minimum distance at which atoms may approach each other. The assumptions of the Rahman method were discussed by Dasannacharya *et al.* (1968) who indicated a possibility of formulating a series of necessary (and not sufficient) normalization criteria similar to those of KMNV. Their conclusion is that out of the normalization criteria derived the best point of start to calculate the structure factor ($S(Q)$ from experimental data is the KMNV equation.

Below we briefly describe the methods for determining the coordination number from the RDF. We follow the classification of the methods due to Pings (1968). (Method C according to this classification is ommitted owing to its rather arbitrary nature.)

Method A — symmetrization of $r\varrho(r)$

In this method the first peak of $r\varrho(r)$ is symmetrized with respect to the position of its maximum, $R^A_{\max}$ (the interatomic distance). Coordination number N_A is then given by the integral

$$N_A = 2 \int_{R^A_{\min}}^{R^A_{\max}} 4\pi r[r\varrho(r)]_{\text{sym}} dr. \tag{12}$$

Here, $R^A_{\min}$ is the position of the nearest minimum of $r\varrho(r)$ for $r < R^A_{\max}$ or, in the case when $r\varrho(r)$ is negative at this minimum, $R^A_{\min}$ is the value of r at which the first peak of the function $r\varrho(r)$ becomes positive.

Method B — symmetrization of $r^2\varrho(r)$

Here, the first peak of $r^2\varrho(r)$ is symmetrized with respect to the position of the maximum $R^B_{\max}$ (the interatomic distance) and the coordination number N_B is given by the integral

$$N_B = 2 \int_{R^B_{\min 1}}^{R^B_{\max}} 4\pi[r^2\varrho(r)]_{\text{sym}} dr, \tag{13}$$

where $R^B_{\min 1}$ is defined analogously to $R^A_{\min}$ with $r\varrho(r)$ replaced by $r^2\varrho(r)$. It should be noted that the interatomic distances determined by the two methods are slightly different ($R^B_{\max} > R^A_{\max}$).

Method D — integration up to the first minimum of $4\pi r^2\varrho(r)$

Here, the coordination number N_D is calculated from the integral

$$N_D = \int_{R^B_{\min 1}}^{R^B_{\min 2}} 4\pi r^2\varrho(r) dr. \tag{14}$$

where $R^B_{\min 2}$ is the position of the minimum of $r^2\varrho(r)$ which follows the first maximum.

It should be noted in connection with this discussion of the methods for determining coordination number from the RDF that many authors use $r = 0$ instead of $R^A_{\min}$ or $R^B_{\min}$ (see *e. g.* Pings (1968)). However, in view of a rather frequent appearing of spurious fluctuations in the RDF on the left from the main peak, the integral over these fluctuations may give a contribution to the coordination number.

We shall now briefly describe the HLK method for determining the "true" value of the coordination number from experimental data (Hosemann *et al.* 1964). The method is aimed to give such a value of coordination number (the "true" value) which is free of

errors due to data termination. The authors propose a formula from which the "true" value N_B^* may be calculated once the value of coordination number determined by method B is given and the shape of the function $\varrho(r)$ is known. The formula can be written as

$$N_B^* = \frac{N_B}{1+0.18\exp\left[-18\left(\frac{LQ_{\max}}{4\pi}\right)^2\right]}, \tag{15}$$

where

$$L = \left[\frac{N_B}{4\pi[R_{\max}^B]^2\varrho(R_{\max}^B)}\right]^2 - \left[\frac{\pi}{Q_{\max}}\right]^2. \tag{16}$$

Other symbols are defined earlier in this paper.

To end the discussion we would like to mention a critical analysis by Bagchi (1970) of the principles of determination of the coordination numbers and interatomic distances directly from the RDF.

3. Results and discussion

The computations were carried out using ODRA 1204 computer with a program in ODRA-ALGOL specially written for this purpose. Table I presents the values of ϱ_0 and $S(0)$ used in the calculations. For liquid copper the experimental value of $S(0)$ given by Egelstaff (1967) was used at all three temperatures, and for liquid zinc the value calculated from Eq. (6b) by Caglioti *et al.* (1967) was adopted.

TABLE I

Values of atomic density ϱ_0 and structure factor $S(0)$ for liquid copper and zinc

Metal	T(°K)	$\varrho_0 \frac{\text{atoms}}{\text{Å}^3}$	Ref.	$S(0)$	Ref.
Cu	1423	0.0752	a	0.016	b
	1573	0.0741			
	1723	0.0730			
Zn	743	0.0603	c	0.019	d

a — Cahill and Kirshenbaum (1962), b — Egelstaff (1967), c — Hogness (1921), d — Caglioti, Corchia and Rizzi (1967).

3.1. Normalization constants

First, for liquid copper, we calculated the intensity $I(\infty)_{\text{KMNV}}$ for various $Q_{\max}$, using Eq. (11) and compared it to the intensity $I(\infty)_{\text{HA}}$ obtained by the HA method. The integral in Eq. (11) was evaluated numerically using the trapezoidal rule. In evaluating the integral the values of $S(Q)$ given by Breuil *et al.* (1970) were substituted for $I(Q)$. (It should be pointed out that $S(Q)$ was obtained there by normalization of neutron intensity using

the HA method.) In such a procedure the constancy of the neutron intensity I_A, to which both incoherent and multiple scattering contribute, is not taken into account which increases relative variations of $I(\infty)_{\mathrm{KMNV}}$ with $Q_{\max}$.

For $Q_{\max} = 9.40$ Å^{-1}, which is the largest termination value used so far, the values of the ratio $I(\infty)_{\mathrm{KMNV}}/I(\infty)_{\mathrm{HA}}$ obtained in this way are 1.017, 0.992 and 0.994 for 1423, 1573, and 1723°K, respectively. In deriving these values, the value of $I(Q)$ for $Q > 8.70$ Å^{-1}, which is constant, is substituted for $I(\infty)_{\mathrm{HA}}$. (According to Breuil *et al.* (1970), $S(Q) = 1$ for $Q > 8.70$ Å^{-1} at all three temperatures considered here.)

In order to determine the dependence of $I(\infty)_{\mathrm{KMNV}}/I(\infty)_{\mathrm{HA}}$ on $Q_{\max}$ this ratio was calculated for all values of $Q_{\max}$ for which $S(Q)$ had been given by Breuil and Tourand

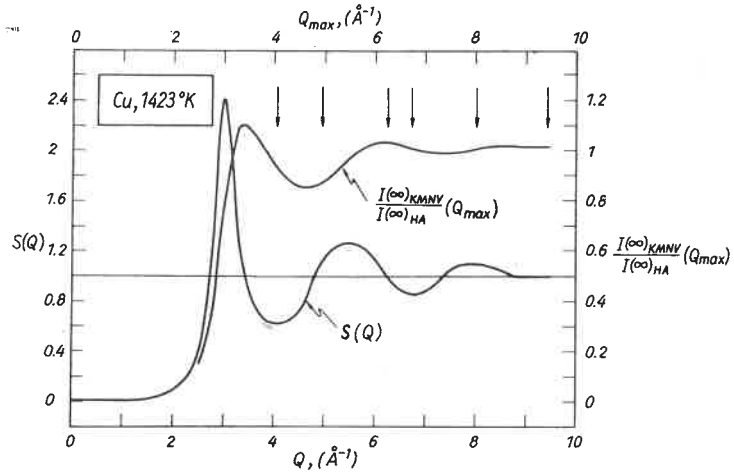

Fig. 1. Ratio $I(\infty)_{\mathrm{KMNV}}/I(\infty)_{\mathrm{NH}}$ *versus* $Q_{\max}$ and structure factor $S(Q)$ for liquid copper at 1423°K. Arrows indicate the values of $Q_{\max}$ at which the values of RDF are determined

(1970). Fig. 1 represents this dependence for liquid copper at 1423°K. For comparison the structure factor $S(Q)$ is also plotted in the figure. Similar behaviour is observed for other two temperatures.

Similar analysis of the dependence of $I(\infty)_{\mathrm{KMNV}}$ on $Q_{\max}$ was performed for liquid zinc using the data of Caglioti *et al.* (1967). The absence of large angle data in that reference, however (normalization was performed there by the KMNV method) made it impossible to compare $I(\infty)_{\mathrm{KMNV}}$ to $I(\infty)_{\mathrm{HA}}$.

The results of our computations show only slight differences between the values of $I(\infty)_{\mathrm{KMNV}}$ and $I(\infty)_{\mathrm{HA}}$ in the region of large angles (large values of Q). For liquid copper the differences do not exceed 2%. It is also found (see Fig. 1) that, for a rather wide range of $Q_{\max}$, the values of $I(\infty)_{\mathrm{KMNV}}$ determined from Eq. (11) depend only weakly on $Q_{\max}$: for liquid copper in the interval 6 Å$^{-1} \leqslant Q_{\max} \leqslant 9.4$ Å^{-1} and liquid zinc in the interval 6 Å$^{-1} \leqslant Q_{\max} \leqslant 8.6$ Å^{-1} the differences between the extreme values of $I(\infty)_{\mathrm{KMNV}}$ do not exceed 5%.

The influence of assuming a wrong value for the atomic density ϱ_0 on the calculated value of $I(\infty)_{\mathrm{KMNV}}$ was also studied. Computations performed for liquid copper show

that a 5% change in ϱ_0 implies merely an 0.03% variation of $I(\infty)_{\mathrm{KMNV}}$. The influence of variations of $S(0)$ on $I(\infty)_{\mathrm{KMNV}}$ appears to be meaningless. Even changes of several tens per cent in $S(0)$ leave the value of $I(\infty)_{\mathrm{KMNV}}$ practically unchanged.

3.2. Radial density functions

In the next point characteristics of variation of RDF with $Q_{\max}$ were examined. The values of the RDF were computed for liquid copper at 1423°K for several arbitrarily chosen values of $Q_{\max}$ 9.40, 8.01, 6.72, 6.25, 4.93, and 4.05 Å^{-1}. These values are indicated by arrows in Fig. 1. The computations were carried out according to the procedure described in Section 2 (henceforth referred to as procedure I). $I(\infty)_{\mathrm{KMNV}}$ for respective $Q_{\max}$ was determined, as before, from Eq. (11). It can be easily shown in this case that the substitution of $S(Q)$ for $I(Q)$ in Eq. (11), which is equivalent to neglecting the contribution of multiple and incoherent scattering to the neutron intensity, does not change the values of the structure factor $S(Q)$ calculated from Eq. (9) which are separately normalized at the respective $Q_{\max}$. Integration of Eq. (5) was carried out using a method proposed by Goldstein and Reekie (1955). The values of RDF were calculated every $\Delta r = 0.05$ Å.

In order to obtain a better estimate of the influence of wrong normalization on the RDF, additional calculations were performed for the same values of $Q_{\max}$, with $I(\infty)_{\mathrm{KMNV}}$ kept constant. In contrast to the previous procedure, $I(\infty)_{\mathrm{KMNV}}$ was determined from Eq. (11) only once, for $Q_{\max} = 9.40$ Å^{-1}, and the value of $I(\infty)_{\mathrm{KMNV}}$ determined in this way was then used to normalize the experimental data at the remaining values of $Q_{\max}$. (This will be called procedure II.)

Our results for RDF are represented in Figs 2–8. Fig. 2 shows the radial distribution function $g(r) = \varrho(r)/\varrho_0$ plotted *versus* r for different $Q_{\max}$. In Fig. 3 the function $4\pi r[\varrho(r) - \varrho_0]$ is plotted *versus* r for the same values of $Q_{\max}$ as in Fig. 2. Fig. 4 display the differences between $4\pi r\varrho(r)$ obtained for $Q_{\max} = 9.4$ Å^{-1} and the same function determined for the remaining values of $Q_{\max}$. Fig. 5 represents the dependence of $4\pi r^2\varrho(r)$ on r for different $Q_{\max}$. The functions represented in Figs 2–5 are calculated according to procedure I. Figs 6–8 show the same functions as Figs 2–4, respectively, calculated now according to procedure II.

Figs 2–5 clearly demonstrate that the termination effect which, in this case, is also the reason for wrong normalization of the experimental data (Fig. 1) distorts most significantly the main peak of the RDF. The peak gets wider and lower with decreasing $Q_{\max}$ (see Figs 2, 3 and 5). This behaviour is consistent with the results obtained by other authors (Clayton *et al.* 1961, Gingrich *et al.* 1962, Kaplow *et al.* 1965, Caglioti *et al.* 1967). The effect is best seen in Fig. 4.

Figs 6–8, where $I(\infty)_{\mathrm{KMNV}}$ is assumed constant for all $Q_{\max}$, show that the termination effect again distorts predominantly the main peak of the RDF. The characteristics of the distortion are the same as those observed in Figs 2–5. Comparison with Figs 2–5 shows, however, significant differences for the values of r close to zero. The functions $g(r)$ calculated using the two different procedures behave differently as $r \to 0$. Procedure I

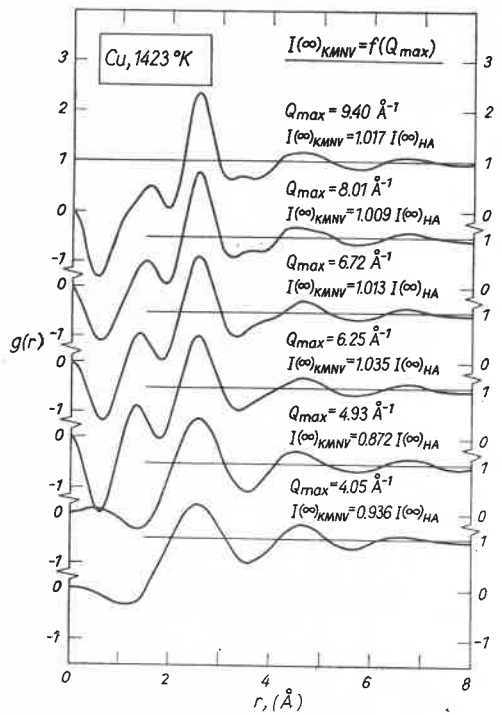

Fig. 2

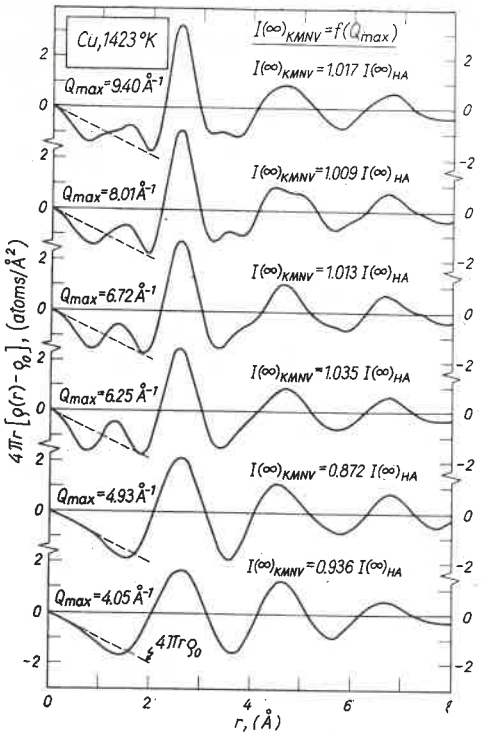

Fig. 3

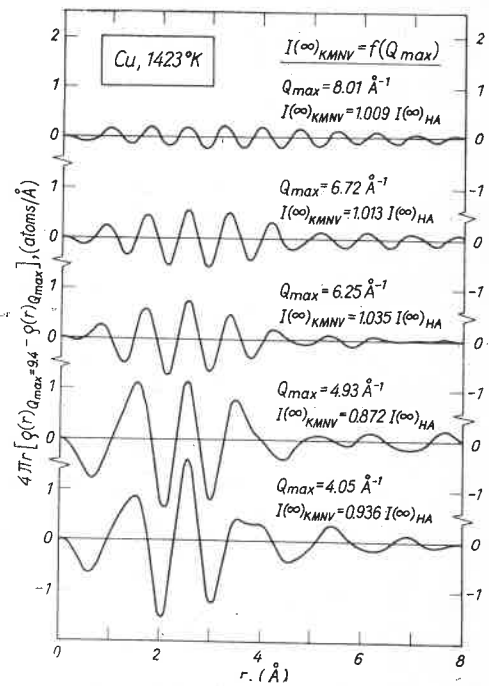

Fig. 4

Fig. 2. $g(r)$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K according to procedure I

Fig. 3. $4\pi r[\varrho(r) - \varrho_0]$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K according to procedure I

Fig. 4. $4\pi r[\varrho(r)_{Q_{max}=9.4} - \varrho(r)_{Q_{max}}]$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K using procedure I

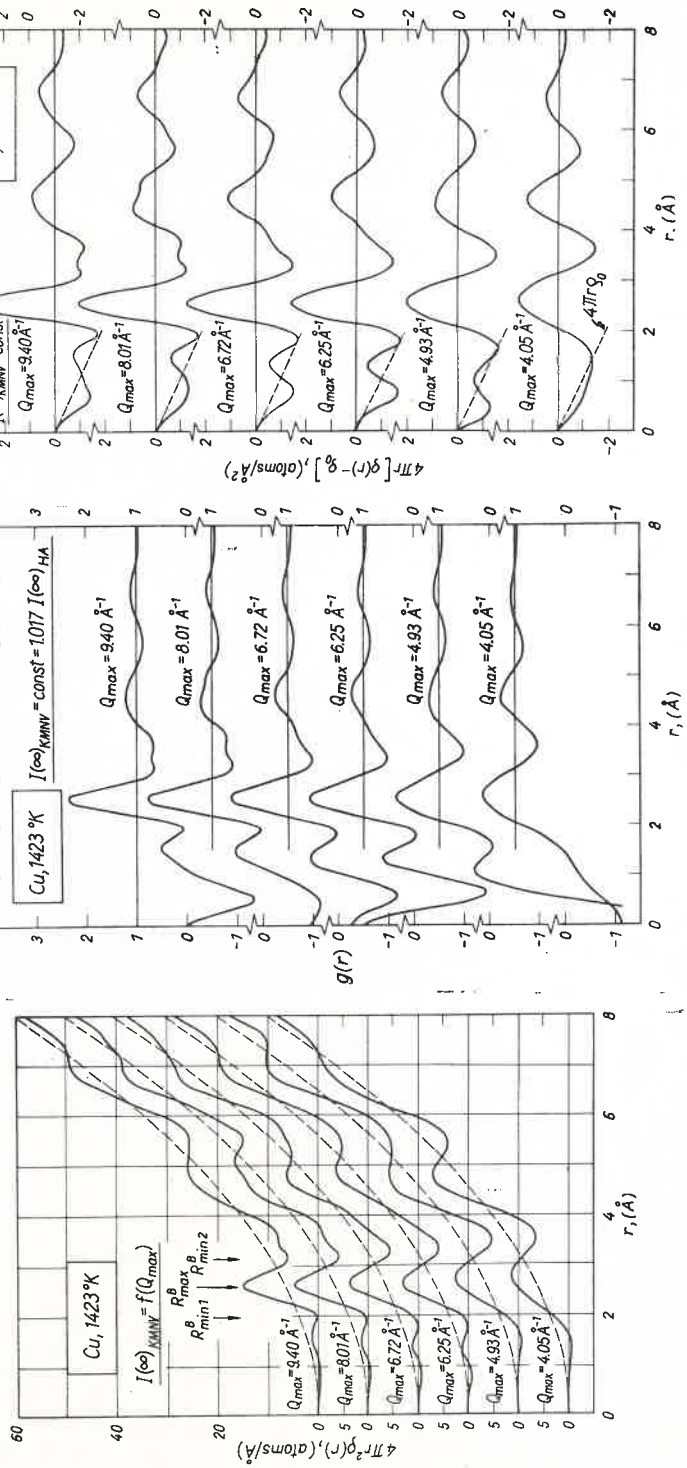

Fig. 5

Fig. 6

Fig. 7

Fig. 5. $4\pi r^2 g(r)$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K using procedure I

Fig. 6. $g(r)$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K using procedure II

Fig. 7. $4\pi r[\varrho(r) - \varrho_0]$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K using procedure II

gives $\lim_{r\to 0} g(r) = 0$, whereas procedure II gives, in general, a value of this limit different from zero.

This difference is obviously reflected in the shape of the function $4\pi r[\varrho(r)-\varrho_0]$ in the same range of r (0–0.3 Å) (Figs 3 and 7). In the first case (procedure I) the function $4\pi r[\varrho(r)-\varrho_0]$ coincides at r near zero with $-4\pi r\varrho_0$ (Fig. 3), whereas in the latter one

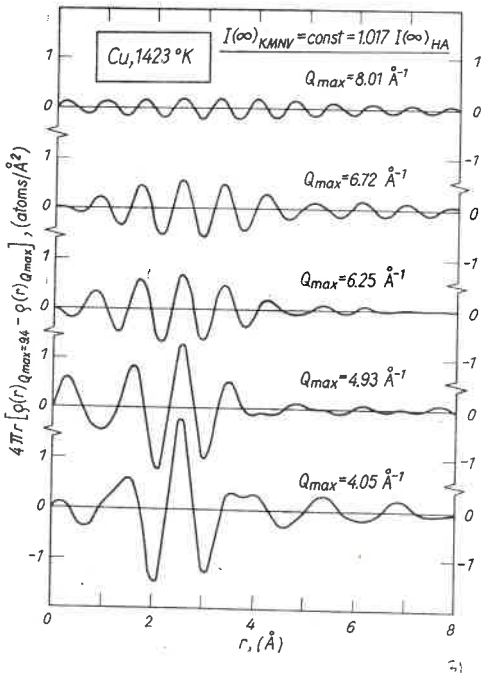

Fig. 8. $4\pi r[\varrho(r)_{Q_{max}=9.4}-\varrho(r)_{Q_{max}}]$ *versus* r for different Q_{max}. The curves are obtained for liquid copper at 1423°K using procedure II

(procedure II), the shapes of $4\pi r([\varrho(r)-\varrho_0]$ and $-4\pi r\varrho_0$ are different in small r. We would like to remind here that this coincidence of $4\pi r[\varrho(r)-\varrho_0]$ with $-4\pi r\varrho_0$ at the values of r close to zero was accepted by Henninger *et al.* (1967) as a criterion for correct normalization of neutron data. The authors, basing on a method proposed by Kaplow *et al.* (1965) for *X*-ray diffraction, tried, by means of numerical calculations, to find such a value of the normalization constant $I(\infty)$ which would give the coincidence of these two functions at r near zero. However, our numerical calculations, as well as theoretical inspection of Eq. (5), show that the two functions will coincide at small r (or equivalently $g(r)\to 0$ as $r\to 0$) always when the criterion (8) is satisfied. In other words, using Eq. (11) to determine the normalization constant $I(\infty)_{KMNV}$ constitutes a sufficient condition for the coincidence of $4\pi r[\varrho(r)-\varrho_0]$ with $-4\pi r\varrho_0$ at r close to zero. The above observation shows that the "correct" value of the normalization constant determined by the method used by Henninger *et al.* (1967) is a function of Q_{max} and should be equal to the value of $I(\infty)_{KMNV}$ evaluated

from Eq. (11). Obviously, the "correct" value determined in this way is, in general, different from the value of the normalization constant $I(\infty)_{HA}$ calculated using the HA method (see Section 3.1).

3.3. Coordination numbers and interatomic distances

Our results, as well as the quoted data from other publications, exhibit a significant dependence of the value of coordination number, determined from the area under the main peak of the RDF, on the termination value Q_{max}. In order to obtain numerical estimates calculations were performed for liquid copper at 1423, 1573, and 1723°K, and for liquid zinc at 743°K. The RDF was determined in the same ways as before at every $\Delta r = 0.01$ Å. The coordination numbers were calculated using each of the methods

TABLE II

Interatomic distances and coordination numbers for different Q_{max} obtained from RDF using procedure I. R_{max} is the possition of the maximum of the main peak of $g(r)$. Δr is the step used in the integration of the RDF. The remaining symbols are defined in Section 2

Metal	Q_{max} 1/Å	R_{max} Å	R^A_{max} Å	R^B_{max} Å	N_A	N_B	N_D	Δr Å
	9.40	2.54	2.57	2.595	8.26	9.00	9.84	
	8.01	2.55	2.585	2.615	8.73	9.60	10.24	
Cu	6.72	2.56	2.60	2.645	9.21	10.43	11.08	0.01
1423 °K	6.25	2.55	2.60	2.65	9.28	10.58	11.39	
	4.93	2.57	2.65	2.73	11.19	13.17	13.35	
	4.05	2.56	2.675	2.78	11.53	13.92	13.83	
	9.40	2.54	2.57	2.605	8.33	9.32	10.20	
	8.01	2.56	2.59	2.63	9.00	10.13	10.48	
Cu	6.72	2.56	2.60	2.65	9.35	10.68	11.19	
1573 °K	6.25	2.55	2.60	2.655	9.40	10.81	11.42	0.01
	4.93	2.55	2.63	2.71	10.71	12.66	13.11	
	4.05	2.57	2.68	2.79	11.41	13.86	13.67	
	9.40	2.55	2.58	2.615	8.30	9.22	9.86	
	8.01	2.56	2.60	2.63	8.93	9.75	10.05	
Cu	6.72	2.56	2.605	2.655	9.16	10.42	10.77	
1723 °K	6.25	2.55	2.60	2.655	9.09	10.44	11.00	0.01
	4.93	2.55	2.635	2.725	10.54	12.61	12.82	
	4.05	2.55	2.67	2.785	11.07	13.52	13.28	
	8.572	2.69	2.72	2.75	7.75	8.55	9.58	
	7.652	2.71	2.74	2.775	8.24	9.18	9.80	
Zn	7.029	2.70	2.74	2.78	8.43	9.46	10.43	
743 °K	6.474	2.72	2.76	2.80	8.80	9.83	10.57	0.01
	5.113	2.74	2.81	2.87	9.93	11.35	11.84	
	4.607	2.72	2.795	2.875	10.00	11.81	12.53	
	3.780	2.77	2.885	2.995	11.19	13.44	13.15	

described in Section 2. The integrals in Eqs (12), (13) and (14) were evaluated numerically using the trapezoidal rule. The results of the calculations are summarized in Tables II and III.

Before we come to the discussion of our results, we would like to point out a considerable discrepancy between our results and those obtained originally by Caglioti *et al.* (1967) whose values of $S(Q)$ are used in this work. The discrepancy is observed for the shape of the main peak, in particular for the value of the function $4\pi r^2\varrho(r)$ at the minimum

TABLE III

Interatomic distances and coordination numbers for different Q_{max} obtained from RDF using procedure II. The symbols are defined as in Table II

Metal	Q_{max} Å	R_{max} Å	R^A_{max} Å	R^B_{max} Å	N_A	N_B	N_D	Δr Å
	9.40	2.55	2.55	2.60	7.68	9.14	9.72	
	8.01	2.55	2.60	2.60	9.15	9.15	10.12	
Cu	6.72	2.55	2.60	2.65	9.21	10.56	10.97	
1423 °K	6.25	2.55	2.60	2.65	9.30	10.61	11.35	0.05
	4.93	2.55	2.65	2.70	10.76	11.95	12.72	
	4.05	2.60	2.70	2.80	11.83	14.04	13.87	
	9.40	2.54	2.57	2.595	8.26	9.00	9.84	
	8.01	2.55	2.58	2.615	8.58	9.58	10.19	
Cu	6.72	2.56	2.60	2.645	9.20	10.42	11.02	
1423 °K	6.25	2.55	2.60	2.645	9.31	10.49	11.35	0.01
	4.93	2.55	2.63	2.705	10.29	12.08	12.60	
	4.05	2.59	2.705	2.81	11.94	14.27	13.80	
	9.40	2.54	2.57	2.605	8.33	9.32	10.20	
	8.01	2.55	2.59	2.625	8.95	9.93	10.42	
Cu	6.72	2.56	2.61	2.655	9.56	10.75	11.15	
1573 °K	6.25	2.55	2.61	2.655	9.64	10.79	11.44	0.01
	4.93	2.53	2.615	2.695	9.97	11.85	12.44	
	4.05	2.58	2.695	2.805	11.59	14.02	13.65	
	9.40	2.55	2.58	2.615	8.30	9.22	9.86	
	8.01	2.56	2.595	2.63	8.75	9.70	10.01	
Cu	6.72	2.56	2.61	2.66	9.25	10.51	10.75	
1723 °K	6.25	2.55	2.60	2.655	9.09	10.43	11.00	0.01
	4.93	2.54	2.62	2.70	9.83	11.60	12.06	
	4.05	2.58	2.70	2.82	11.47	13.99	13.32	
	8.572	2.69	2.72	2.75	7.75	8.55	9.58	
	7.652	2.70	2.74	2.77	8.23	9.02	9.80	
Zn	7.029	2.70	2.735	2.775	8.19	9.21	10.21	
743 °K	6.474	2.72	2.765	2.805	8.83	9.85	10.49	0.01
	5.113	2.73	2.80	2.865	9.68	11.19	11.74	
	4.607	2.71	2.80	2.87	9.85	11.41	12.10	
	3.780	2.76	2.87	2.975	11.01	13.17	13.16	

following the first peak, for coordination numbers (N_D), and for the values of R^B_{max} (*e.g.* for $Q_{max} = 8.572$ Å^{-1} the result of Caglioti *et al.* (1967) is $R^B_{max} = 2.60$ Å while our result is $R^B_{max} = 2.75$ Å). More recently, however, Caglioti *et al.* (1969) repeated the calculations and their new results agree rather well with ours (*e.g.* now for $Q_{max} = 8.572$ Å^{-1} the maximum of the main peak of $g(r)$ is situated, according to Caglioti *et al.* (1969), at $r = 2.65$ Å while the corresponding value of r found in this work is 2.69 Å).

Tables II and III permit the following remarks:

1. The value obtained for interatomic distances depend on which function is used for their determination ($g(r)$, $4\pi r\varrho(r)$ or $4\pi r^2\varrho(r)$). This is in agreement with the results obtained by other authors (Ocken *et al.* 1966, Pings 1968).

An interesting observation is made that the interatomic distances determined using the function $g(r)$ are practically independent of the termination value Q_{max}. Similarly, the interatomic distances determined using the function $4\pi r\varrho(r)$ or $4\pi r^2\varrho(r)$ appear to be only weakly sensitive to the variations of Q_{max}. For instance, at large Q_{max}, a decrease of about 30% results in only a 1–2% increase of R^A_{max} or R^B_{max}. The magnitude of these variations is in good agreement with the results obtained by Clayton *et al.* (1961) for liquid krypton and by Gingrich *et al.* (1962) for liquid argon.

Comparison at equal Q_{max} of the values of interatomic distances from Tables II and III also indicates a weak dependence of the position of the RDF maxima on the normalization constant $I(\infty)$. The difference between the extreme values of interatomic distances does not exceed 1%.

2. The values of coordination numbers and interatomic distances depend on which method is used for their determination from the radial density function. The dependence is here much stronger than in the previous case. At the same time, the values of coordination numbers significantly depend on the values of Q_{max}, which agrees with observations made by other authors (*e.g.*, for liquid copper an about 30% decrease of Q_{max}, from 9.40 Å^{-1} to 6.25 Å^{-1}, results in a 10–15% increase of the value of coordination number).

Comparison of the corresponding value of coordination numbers from Tables II and III shows that uncertainties of the values of coordination numbers due to eventual errors in neutron data normalization are much smaller than the differences between the values of coordination numbers calculated using different methods.

Finally, we investigated the possibility of obtaining the "true" value of coordination number from experimental data using the HLK method. The "true" values were calculated with the help of Eqs (15) and (16) for different values of Q_{max}. The calculations were performed for liquid copper and liquid zinc at the temperatures quoted earlier in this paper. Fig. 9 shows the results obtained for liquid copper at 1423°K. In the same figure the values of coordination numbers calculated using procedure I by the three methods of Section 2 are also presented.

As seen in Fig. 9 the coordination number as a function of Q^{-1}_{max} can be rather well represented by a linear equation. This approximation is particularly good for large Q_{max}. Similar behaviour is observed for liquid copper at 1573 and 1723 °K and liquid zinc at 743 °K, as well as for liquid krypton according to the data of Clayton *et al.* (1961).

Moreover, it is seen from Fig. 9 that the "true" values obtained by the HLK method

also depend strongly on Q_{max}. It should be noted in addition that Eq. (15) used for calculating N_B^* in the HLK method, theoretically does not admit deviations from the "true" value greater than 18%. This is in contradiction with our results since, both for copper and zinc, the differences between the values of N_B for the extreme Q_{max} amount to 30%.

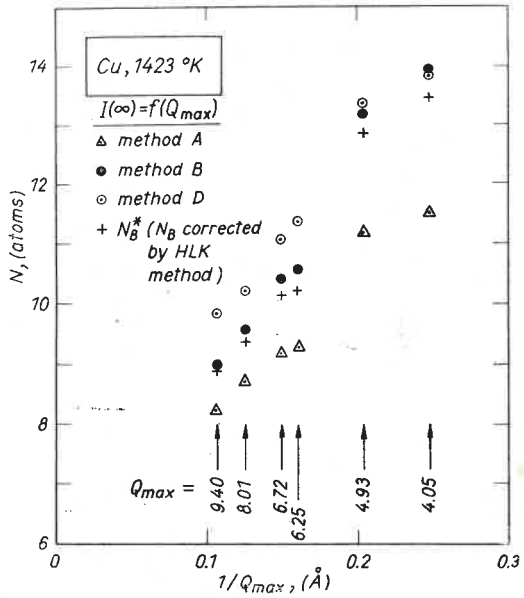

Fig. 9. Coordination numbers *versus* Q_{max}^{-1}. The points are calculated for liquid copper at 1423°K using procedure I. The points correspond to different methods described in Section 2

4. Conclusions

The influence of neutron data termination on the normalization constant $I(\infty)_{KMNV}$ and on the values of interatomic distances and coordination numbers for liquid copper and zinc calculated using these data is analyzed by means of numerical computations.

It is found that for large Q the normalization constant $I(\infty)_{KMNV}$ depends rather weakly on the termination value Q_{max}. It is also shown that even quite large shifts in the atomic density ϱ_0 and structure factor $S(0)$ cause negligible changes in the value of $I(\infty)_{KMNV}$.

The method for normalization of neutron data in which one is looking for such a value of $I(\infty)$ for which the functions $4\pi r[\varrho(r)-\varrho_0]$ and $-4\pi r\varrho_0$ coincide at $r \to 0$ (Henninger *et al.* 1967) is discussed. It is found that Eq. (8) constitutes a sufficient condition for the coincidence of the two functions at small r. In other words, the "correct" value of normalization constant determined by the Henninger method (Henninger *et al.* 1967) is a function of Q_{max} given by Eq. (11).

It is found that interatomic distances in liquid metals determined from $g(r)$ (or $\varrho(r)$) are practically independent of the termination value Q_{max}. On the other hand, interatomic distances determined from the functions $4\pi r\varrho(r)$ and $4\pi r^2\varrho(r)$ increase slightly with decreasing Q_{max}. The latter observation is in agreement with the results obtained by other authors

(Clayton *et al.* 1961, Gingrich *et al.* 1962). It is also observed that oscillations of the normalization constant $I(\infty)$ do not shift significantly the position of the first peak of the radial functions and, in what follows, have no significant influence on the values of interatomic distances.

In contrast to interatomic distances, the values of coordination numbers determined from RDF show a significant dependence on the termination value $Q_{\max}$. The results obtained in this work indicate that reliable, quantitative comparison of coordination numbers for liquid metals obtained in different laboratories requires, in addition to adopting the same method for calculating them from RDF, also the equality of $Q_{\max}$. When the values of $Q_{\max}$ are different, there still exists a possibility for normalizing the coordination numbers to a common value of $Q_{\max}$ which is possible due to the approximately linear dependence of N on $Q_{\max}^{-1}$. Such procedure, however, would require the determination of $N(Q_{\max}^{-1})$ for the diffraction data compared. Nevertheless, it seems to be more appropriate to use this procedure instead of comparing the "true" values of coordination numbers N_B^* calculated by the HLK method.

The author is grateful to Mr P. Malecki and Mr C. Jędrzejek for help in programming and performing the computations and to Docent Dr A. Fuliński for reading the manuscript.

REFERENCES

Bagchi, S. N., *Advances in Phys.*, **77**, 119 (1970).
Breuil, M., Tourand, G., *J. Phys. Chem. Solids*, **31**, 549 (1970).
Caglioti, G., Corchia, M., Rizzi, G., *Nuovo Cimento*, **49B**, 222 (1967).
Caglioti, G., *Theory of Condensed Matter*, Ed. International Atomic Energy Agency, Vienna, p. 539.
Caglioti, G., Corchia, M., Rizzi, G., *Nuovo Cimento*, **60B**, 48 (1969).
Cahill, J. A., Kirshenbaum, A. D., *J. Phys. Chem.*, **66**, 1080 (1962).
Clayton, G. T., Heaton, L., *Phys. Rev.*, **121**, 649 (1961).
Dasannacharya, B. A., Navarro, Q. O., Ibarra, H., Chatraphorn, S., Lee, G. B., *Phys. Rev*, **173**, 241 (1968).
Egelstaff, P. A., *Advances in Phys.*, **16**, 147 (1967).
Enderby, J. E., *Physics of Simple Liquids*, Ed. H. N. V. Temperley, J. S. Rowlinson, G. S. Rushbrooke, Amsterdam 1968, North-Holland Publ. Co., p. 611.
Furukawa, K., *Rep. Progr. Phys.*, **25**, 395 (1962).
Gingrich, N. S., Tompson, C. W., *J. Chem. Phys.*, **36**, 2398 (1962).
Goldstein, L. Reekie, *J., Phys. Rev.*, **98**, 857 (1955).
Henninger, E. H., Buschert, R. C., Heaton, L., *J. Chem. Phys.*, **44**, 1758 (1966).
Henninger, E. H., Buschert, R. C., Heaton, L., *J. Chem. Phys.*, **46**, 586 (1967).
Hogness, T. R., *J. Amer. Chem. Soc.*, **43**, 1621 (1921).
Hosemann, R., Lemm, K., Krebs, H., *Z. Phys. Chem.*, **41**, 121 (1964).
Kaplow, R., Strong, S. L., Averbach, B. L., *Phys. Rev.*, **138**, A1336 (1965).
Krogh Moe, J., *Acta Cryst.*, **9**, 951 (1956).
Lorch, E., *J. Phys. C* (*Solid State Phys.*), **2**, Ser. 2, 229 (1969).
Mikolaj, P. G., Pings, C. J., *Phys. Chem. Liquids*, **1**, 93 (1968).
Norman, N., *Acta Cryst.*, **10**, 370 (1967).
North, D. M., Enderby, J. E., Egelstaff, P. A., *J. Phys. C* (*Proc. Phys. Soc.*), **1**, Ser. 2, 784, 1075 (1968)
Ocken, H., Wagner, C. N. J., *Phys. Rev.*, **149**, 122 (1966).

Pings, C. J., *Physics of Simple Liquid*, Ed. H. N. V. Temperley, J. S. Rowlinson, G. S. Rushbrooke, Amsterdam 1968, North-Holland Publ., Co., p. 387.

Rahman, A., *J. Chem. Phys.*, **42**, 3540 (1965).

Schlup, W. A., *Symposium on Inelastic Scattering of Neutrons by Condensed Systems*, Ed. Brookhaven National Laboratory, Upton, New York: BNL 940 (C-45) 1965, p. 183.

Schlup, W. A., *Phys. Chem. Liquids*, **1**, 75 (1968).

Steeb, S., *Springer Tracts in Modern Physics*, Vol. 47, Ed. G. Höhler, Berlin—Heidelberg—New York 1968, Springer-Verlag, p. 1.

Vainshtein, B. K., *Soviet Phys. Cryst.*, **2**, 24 (1957).

Vineyard, G. H., *Liquid Metals and Solidification*, Ed. American Society for Metals, Cleveland, Ohio, 1958, p. 1.

Wagner, C. N. J., Ocken, H., Joshi, M. D., *Z. Naturforsch.*, **20a**, 325 (1965).