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An Analytical Method of Computation of Radial Distribution Functions at Large Distances for Liquids and Amorphous Substances

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Abstract

An analytical method is proposed to obtain quantitatively the radial distribution function (RDF) at large distances for liquids and amorphous materials from the structure factor [$S(q)$] data in the region of its main peak only. The RDF's obtained prove to be unaffected by the random spread of the experimental points at the tail of $S(q)$. The method is illustrated for a number of simple liquids and for liquid and amorphous solid water. The application of the method to the $S(q)$ extrapolation to the low-q region and the problem of the experimental determination of the direct correlation function are discussed.

Introduction

The problem of determination of the radial distribution function (RDF) for a liquid or amorphous material from the structure factor $S(q)$ ($q = 4\pi \sin \theta/\lambda$) consists in the computation of the Fourier transform

$$4\pi\rho r h(r) = \frac{2}{\pi} \int\limits_0^\infty q[S(q) - 1] \sin qr \, \mathrm{d}q, \qquad (1)$$

where ρ is the average density, r the interparticle distance and $g(r) = h(r) + 1$ the pair correlation function. Formula (1) requires experimental determination of $S(q)$ over as large a range of q as possible. However, the experimental $S(q)$ is distorted at large q by a rather large random deviation (noise) which is still more pronounced in the integrand $q[S(q) - 1]$ in (1). It is possible to represent the noise error of the RDF computation in the form (Choudry, Banerjee & Ailawadi, 1976; Konnert & Karle, 1973)

$$\Delta[4\pi\rho r h(r)] = \frac{2\Delta q}{\pi} \sum_i q_i \, \Delta S(q_i) \sin q_i r \qquad (2)$$

with summation over the discrete experimental values of q_i. Here $\Delta S(q_i)$ is the random deviation of $S(q)$ at the point q_i and Δq is a step of the numerical integration in (1). It is seen from (2) that the random errors in $S(q)$ result in undamped sinusoidal terms in the calculated RDF, the maximum contribution being from errors at large q. Such noise, together with termination errors, distorts the picture of the RDF. To eliminate the above errors one must apply to $S(q)$ various smoothing procedures (Narten, Vaslow & Levy, 1973; Yarnell, Katz, Wenzel & Koenig, 1973; Greenfield, Wellendorf & Wieser, 1971), which are often rather refined and have some elements of arbitrariness.

The errors in the RDF, arising from the noise at the tail of $S(q)$, are most pronounced at large r because of the rapid damping of the RDF oscillations in noncrystalline substances. But the tail of $S(q)$ in itself produces a negligible contribution to the tail of the RDF since the latter is largely defined by the location and shape of the main peak of $S(q)$, the most narrow among the others (Verlet, 1968). This fact allows us to suggest a method for the computation of the RDF at large r which operates with the $S(q)$ data in the region of the main peak only, where experiment has the best accuracy. In such a way, the RDF distortion by the random errors at the tail of $S(q)$ is entirely eliminated.

The idea of the method is as follows. It is possible to write an analytical formula for the RDF asymptotic behaviour containing a set of parameters. The Fourier transform of this formula gives the analytical form of $S(q)$ in the region of its main peak. The values of parameters are obtained by a least-squares fit of the $S(q)$ experimental data. Then the RDF at large r is calculated with these parameters. It is found that the RDF is determined quantitatively by this method starting from the second or third peak.

This formalism is described in the next section and applied to some simple liquids. The third section considers its application to the more complicated case of liquid and amorphous solid water. In addition to the determination of the RDF at large r, the proposed formalism allows us to extrapolate the structure factor in the low-q region. In the fourth section we discuss the results obtained by this method and their application to the computation of the direct correlation function $C(r)$.

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Simple liquids

The problem of the RDF asymptotic behaviour was analysed by Verlet (1968), Fisher (1964), Throop & Fisk (1972), Perry & Throop (1972) and Nezbeda (1977), and their results can be summarized as follows. The exact form of the RDF asymptote is unknown for a liquid with arbitrary intermolecular potential. It can only be shown that the RDF has a form of damped oscillations at large r if the pair potential is of a short-range character and the density is sufficiently high. The most general form of the oscillating RDF asymptote was obtained by Fisher (1964)

$$rh_{\rm as}(r) = \sum_i a_{1i} \exp(-a_{2i} r) \sin(a_{3i} r + a_{4i}). \qquad (3)$$

In particular, the same form has the asymptote for a liquid of hard spheres (Perry & Throop, 1972). The term with the smallest a_2 usually dominates in (3) at large r. However, as is shown below, it is necessary to consider the other terms also to obtain the correct formula for $S(q)$.

At present (3) has a sufficiently good empirical basis. It gives a good description of the RDF obtained by the molecular dynamics method for a dense system of particles which interact through a Lennard-Jones potential (Verlet, 1968). In addition, the experimental RDF curves at large r have the same form for dense simple liquids together with those calculated in a quasi-crystalline model (Medvedev & Naberukhin, 1977). The results of this paper also provide an empirical justification of (3).

Separating the term $S_{\rm as}(q)$ in $S(q)$ which corresponds to the RDF asymptote (3), it is possible to write

$$q[S(q) - 1] = qS_{\rm as}(q) + q[S_{\rm res}(q) - 1]$$
$$= 4\pi\rho \int_0^\infty r[h_{\rm as}(r) + h_{\rm res}(r)] \sin qr \, {\rm d}r.$$

$S_{\rm as}(q)$ can be calculated in an analytical form:

$$S_{\rm as}(q) = 4\pi\rho \sum_i S^i_{\rm as}(q),$$

$$S^i_{\rm as}(q) = a_{1i}[2a_{2i}a_{3i} \cos a_{4i} + (a^2_{2i} - a^2_{3i} + q^2) \sin a_{4i}]$$
$$\times \{[a^2_{2i} + (q - a_{3i})^2][a^2_{2i} + (q + a_{3i})^2]\}^{-1}. \qquad (4)$$

Each term in (4) describes some peak in $S(q)$. The parameter a_1 determines its intensity, a_2 the width, a_3 the location and a_4 its asymmetry. The term having the smallest parameters a_2 and a_3 ($i = 1$) corresponds to the first peak in $S(q)$. However, other terms ($i > 1$) also give a significant contribution to the first peak region. The magnitude of the corresponding terms in the RDF tail (3) is much less than the contribution due to the first peak because $a_{2i} \gg a_{21}$, but owing to the same condition the peaks with $i > 1$ in the structure factor (4) are very wide. For the computations we retained the first two terms in (4) in explicit form and the others were represented as a series expansion at low q up to the quadratic term. The final result is

$$S_{\rm as}(q) = 4\pi\rho \sum_{i=1}^{2} S^i_{\rm as}(q) + bq^2 + c. \qquad (5)$$

The parameters of this formula were obtained by least-squares fitting to the first experimental peak of $S(q)$. The parameters of the term with $i = 1$ are determined with reasonable accuracy because it describes the main portion of the first peak. The second term in the sum ($i = 2$) produces only some background under the main peak of $S(q)$. Therefore, we introduced a restriction in the fitting procedure in order that the maximum of this term (a_{32}) should be located under the second peak of $S(q)$. The following fact may serve as some justification of this. It is possible to obtain theoretically the exact values of the parameters of (3) for the Percus–Yevick hard-sphere liquid with the method of Perry & Throop (1972). The peaks of $S^i_{\rm as}(q)$ in (4) were found to be situated exactly under the

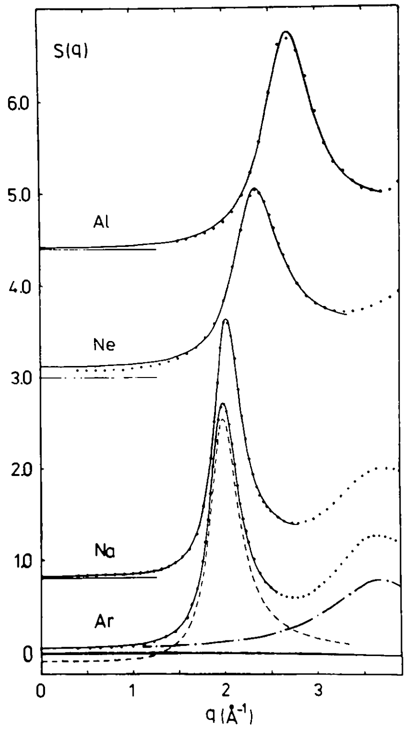

Fig. 1. Structure factors of simple dense liquids in the region of the main peak: the points represent experiment; the solid lines give computation according to (5). The dashed line shows the contribution of the first term of the sum (5) ($i = 1$), the dashed-and-dotted line that of the second one ($i = 2$). Experimental data are obtained for Ar from Yarnell, Katz, Wenzel & Koenig (1973), for Na from Greenfield, Wellendorf & Wieser (1971) ($T = 373$ K), for Ne from de Graaf & Mozer (1971) ($P = 8$ MPa), and for Al from Waseda & Suzuki (1973) ($T = 1023$ K).

Table 1. *Parameters of* (5) *obtained by the fitting to the experimental $S(q)$ in the region of the main peak*

$\Delta = \left\{ \sum_{j=1}^{N} [S_{\rm theor}(q_j) - S_{\rm exp}(q_j)]^2/N \right\}^{1/2}$, N is the number of experimental points.

	Ar	Ne	Na	Al
a_{11}	7·1385	6·1541	6·4084	5·9938
a_{21}	0·1857	0·3032	0·1765	0·3236
a_{31}	1·9677	2·3015	2·0044	2·6677
a_{41}	0·3213	0·4460	0·3320	0·3210
a_{12}	14·9681	13·2173	12·0088	11·9960
a_{22}	0·6743	1·3873	0·7253	0·7041
a_{32}	3·6847	4·4513	3·6808	4·9352
a_{42}	0·1841	0·1153	0·1659	0·1801
b	$0{\cdot}6634 \times 10^{-3}$	$0{\cdot}9401 \times 10^{-3}$	$0{\cdot}4329 \times 10^{-3}$	$0{\cdot}4554 \times 10^{-3}$
c	$0{\cdot}6656 \times 10^{-1}$	$0{\cdot}8477 \times 10^{-1}$	$0{\cdot}4056 \times 10^{-1}$	$0{\cdot}2765 \times 10^{-1}$
$S(0)$	0·0522	0·117	0·024	0·017
Δ	0·0117	0·0170	0·0169	0·0323

maxima of the calculated total structure factor and no peaks were located in intermediate positions. In addition, a_{11} was eliminated from the set of variable parameters in (5) with the known value of $S(0) = \rho k T \kappa_T$ (k is Boltzmann's constant, κ_T is the isothermal compressibility).

The results of computations according to (5) are compared with the experimental $S(q)$ for various simple liquids (Fig. 1). The parameters of (5) for these liquids are listed in Table 1. The close correspondence of the experimental and calculated curves demonstrates that (5) is indeed a rather exact analytical representation for the main peak of the structure factor. This fact provides us with a reliable method for determination of the RDF asymptote (3) parameters.

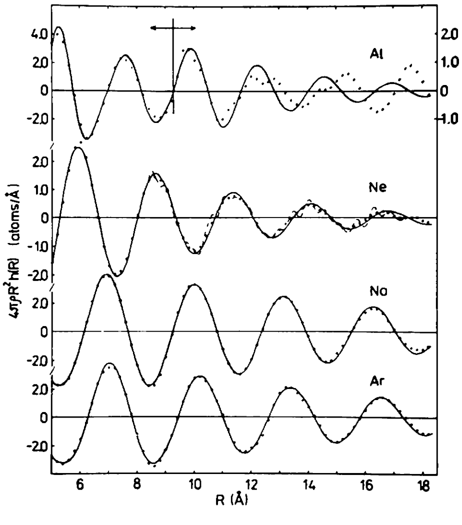

Fig. 2. The RDF's $4\pi\rho r^2 h(r)$ computed from (6) from the total $S(q)$ (dots) and calculated from (3) (solid lines). The upper limit of integration $q_{\rm max}$ in (6) is for Ar 11·0, for Na 6·0, for Ne 8·15, and for Al 8·55 Å^{-1}. Only the tails of the RDF's beginning from the second peak are shown. The solid lines are the sums of two damped sinusoidal curves with the parameters from Table 1. The contribution of the second curve is already negligible in the region of the third peak. The dashed line (Ne graph) represents for comparison the results of direct calculation from (1) using the total table of $S(q)$ from de Graaf & Mozer (1971).

It is interesting to note that the first term in (5) ($i = 1$) produces a negative contribution at low q as seen in Fig. 1. The same is true for the hard-sphere liquid at high density where the parameters of (5) are obtained theoretically (Perry & Throop, 1972). Probably this implies that terms of the sum (5) by themselves, in contrast to the total structure factor, do not have the meaning of diffraction intensity. The physical meaning of this expansion is not clear and one must consider it at present as purely formal.

Fig. 2 allows one to compare the curves $4\pi\rho r^2 h(r)$ for the above liquids computed from the total $S(q)$ with those obtained according to (3) with the parameters taken from Table 1. In the first case, when calculating the Fourier integral (1) with the finite upper limit $q_{\rm max}$, a procedure was employed analogous to that described by Narten, Venkatesh & Rice (1976) to minimize the termination error. It can be written as

$$4\pi\rho r h(r) = F[\tilde{S}(q) - \tilde{S}_1(q)] + F_1(r), \qquad (6)$$

where F denotes the symbol of the Fourier transform, $\tilde{S}(q) = q[S(q) - 1]$,

$$\tilde{S}_1(q) = F^{-1}[F_1(r)] = \sum_{i=1}^{2} a_i \exp(-\alpha_i q^2) \sin q r_{mi},$$

$$F_1(r) = \sum_{i=1}^{2} a_i (4\pi\alpha_i)^{-1/2} \{\exp[-(r - r_{mi})^2/4\alpha_i] - \exp[-(r + r_{mi})^2/4\alpha_i]\}. \qquad (7)$$

$F_1(r)$ is the first, the most narrow, peak of the RDF considered as the sum of two Gaussians to represent its asymmetry. Now the Fourier transform of the difference $\tilde{S}(q) - \tilde{S}_1(q)$ in (6) does not contain this peak, hence removing the most pronounced termination ripples produced by it. The parameters a, α and r_m in (7) were obtained by fitting (7) to the experimental curve $\tilde{S}(q)$ at large q, since $\tilde{S}_1(q)$ is its asymptotic form. The difference $\tilde{S}(q) - \tilde{S}_1(q)$ tends rapidly to zero when q becomes large. But in the real experimental data there are undamped irregular deviations from zero after some value $q_{\rm max}$ caused by the random errors. This $q_{\rm max}$ was chosen as the upper limit in the Fourier integral in (6).

It can be seen from Fig. 2 that there is good agreement between the RDF's calculated from the total $S(q)$ and reconstructed on the basis of data belonging only to the region of its main peak. It is important that the proposed procedure gives sufficiently accurate values of the RDF in the region of the second or third peak though, strictly speaking, (3) is asymptotic. Thus, we have an additional justification of (3) as the analytical form of the RDF asymptote. Fig. 2 shows that this method allows us to obtain the correct RDF up to a very large r while the RDF tails, when calculated from the total $S(q)$, are aggravated by the irregular ripples, *e.g.* for Ne and especially for Al.

Liquid and amorphous solid water

At present there are neither theoretical nor empirical justifications for the RDF asymptotic form of liquids or amorphous materials with directional interactions between their molecules. We have postulated that (3) and (4) are valid also for these systems. Such an approach will be tested by a comparison of the computational results with experiment.

The molecular structure factors of liquid and amorphous solid water, obtained by X-ray diffraction (Narten & Levy, 1971; Narten, Venkatesh & Rice, 1976), differ strongly from the analogous functions of simple liquids. They have a doublet structure of the main peak. To describe this doublet by a formula similar to (5), it is necessary to retain one additional term in (4) in the explicit form. Thus, we have now the sum $\sum_{i=1}^{3}$ in the modified computational formula (5); the other details of obtaining the parameters and of the RDF calculation at large r remain unchanged.

The results of computations for liquid water at 298 K are shown in Figs. 3 and 4. Here, as in simple liquids, the modified formula (5) gives an excellent description of the double maximum of $S(q)$ (Fig. 3). The RDF curve calculated from (3) represents correctly the complicated picture of the water RDF in the region of r just after the first peak of the nearest neighbours. The two components of the doublet in $S(q)$ have approximately equal intensities and widths (parameters a_1 and a_2 in Table 2). Therefore, their contributions to the RDF represent two damped sinusoidal curves having comparable intensities but different frequencies and phases (a_3 and a_4 in Table 2). Interference of these curves shows the behaviour of the RDF at large r which is completely different from that in simple liquids. The second and third peaks turn out to be of the same heights. A deep minimum is observed between them, much deeper than the gap between the first and second peaks. The amplitude of the RDF oscillations diminishes abruptly at $r > 9$ Å because the contributions from the two peaks in $S(q)$ prove to be out of phase. The RDF curve computed from the total $S(q)$ demonstrates at $r > 9$ Å only irregular oscillations caused by the experimental errors in $S(q)$, whereas the proposed method allows one to obtain the RDF up to larger distances.

The analogous interference effect of the contributions of (3) takes place also on the RDF's of water at other temperatures up to 373 K until the main maximum of $S(q)$ remains double-peaked (Fig. 5). All the curves show the same feature: the amplitude of the RDF oscillations diminishes abruptly after the third peak. Moreover, the amplitude of the second peak in the vicinity of 4·5 Å becomes even less than that for the third when the temperature increases. These facts are in contrast to the picture of monotonous damping of the RDF oscillations in simple liquids and are undoubtedly significant for understanding the water structure. The non-trivial facts mentioned can be considered as quite reliable because they are defined exclusively by the

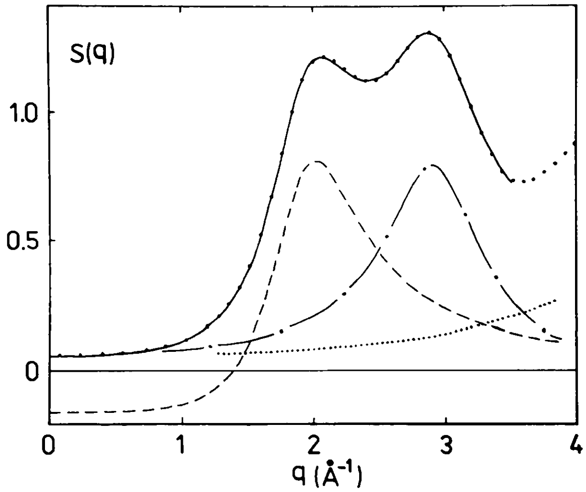

Fig. 3. The structure factor of liquid water at 298 K: the points represent experiment (Narten & Levy, 1971), the solid line gives calculation according to modified formula (5) with the parameters given in Table 2. The dashed line corresponds to the term with $i = 1$, dashed-and-dotted line to $i = 2$, dotted line to $i = 3$.

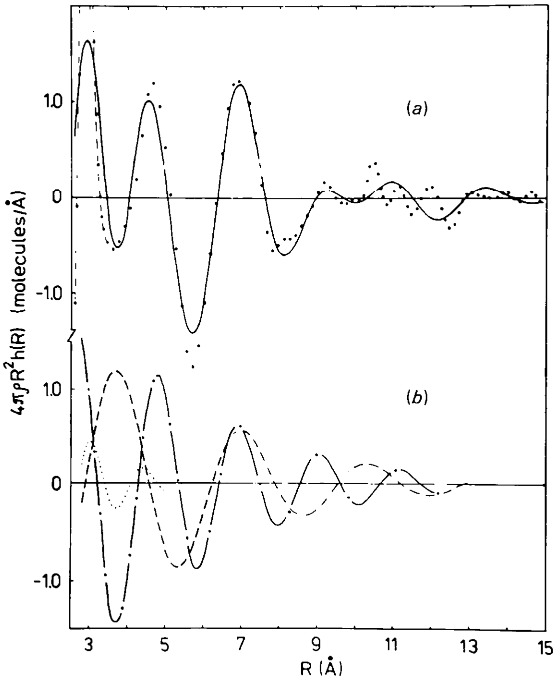

Fig. 4.(a) RDF $4\pi\rho r^2 h(r)$ for liquid water at 298 K: the points give the result computed from the total $S(q)$ according to (6) with $q_{\max} = 10{\cdot}8$ Å^{-1}, the solid line is calculated as the sum of the three terms in (3) with parameters from Table 2. (b) The contributions of the separate terms in (3) corresponding to the peaks in the decomposition of $S(q)$ in Fig. 3. Dashed line: $i = 1$; dashed-and-dotted: $i = 2$; dotted: $i = 3$.

Table 2. *Parameters of the modified formula* (5) *for liquid water at* 298 K

i	a_{1i}	a_{2i}	a_{3i}	a_{4i}
1	3·6722	0·4182	1·8878	0·8000
2	5·1008	0·4534	2·9390	0·02354
3	8·0355	1·0205	4·6107	0·0321

$b = 0{\cdot}00313$; $c = 0{\cdot}0878$; $S(0) = 0{\cdot}0635$; $\Delta = 0{\cdot}0045$.

shape of the main double peak which is the most accurately measured part of the experimental $S(q)$.

The main double peak of $S(q)$ for one of the samples of amorphous solid water according to data of Narten, Venkatesh & Rice (1976) is shown in Fig. 6. It is described accurately by the modified formula (5) as it was in liquid water. But in the solid the components of the doublet are narrower than in the liquid. They produce more slowly damped sinusoidal contributions to the RDF and the interference of these terms gives a rather complicated picture of the observed oscillations up to large r (Fig. 7). Here, as above, the RDF calculated by the proposed procedure accurately repeats the significant features of the RDF computed directly from (1) and smooths the small irregular details caused by errors of experiment and the numerical Fourier transform.

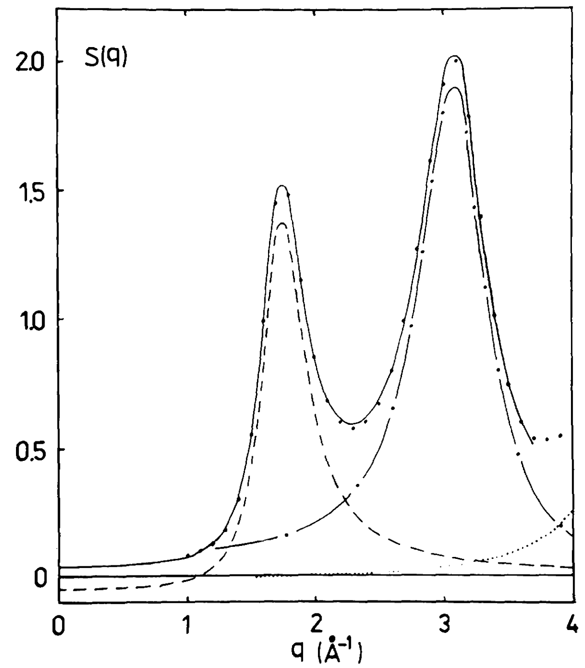

Fig. 6. The data analogous to those in Fig. 3 for amorphous solid water at 77/77 K (Narten, Venkatesh & Rice, 1976).

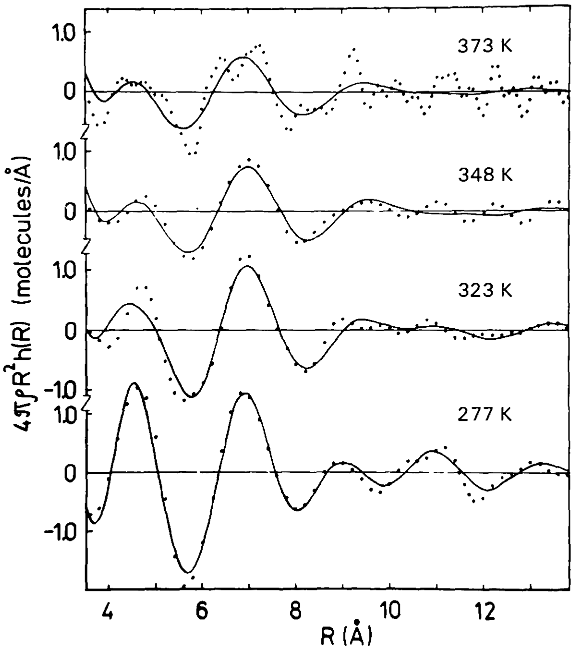

Fig. 5. RDF's of liquid water at various temperatures computed from the $S(q)$ data of Narten & Levy (1971). The dots and lines represent the same as in Fig. 4(a). The RDF at 373 K (dots) is obtained by direct calculation from (1) from the total table of $S(q)$ ($q_{\max} = 16$ Å^{-1}). It demonstrates the influence of errors in $S(q)$ on the RDF at large r.

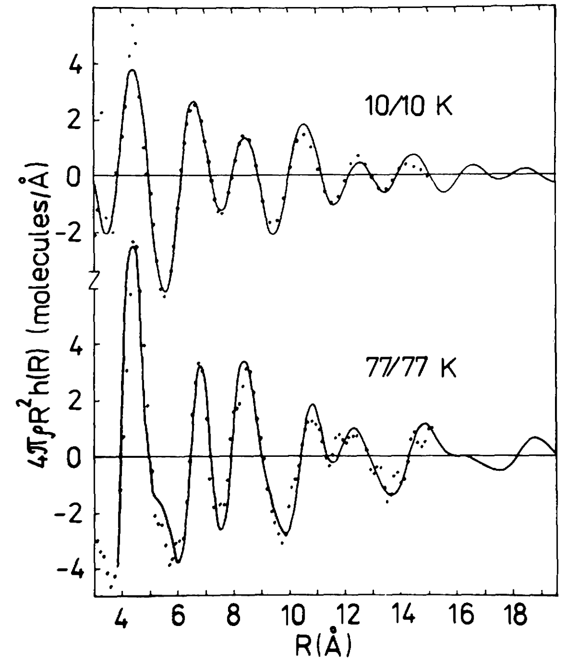

Fig. 7. RDF's $4\pi\rho r^2\,h(r)$ for two samples of amorphous solid water (the notations of samples correspond to those of Narten, Venkatesh & Rice, 1976). The points give the data evaluated from the table for $g_{oo}(r)$ by Narten, Venkatesh & Rice (1976), the solid lines show the computations from (3) analogous to those of liquid water.

Problem of extrapolation of the structure factor to the low-q region and computation of the direct correlation function

Equation (5) allows one to extrapolate $S(q)$ to the experimentally inaccessible region of very small q. This formula has some advantage compared with series expansions of $S(q)$ or $S^{-1}(q)$ usually applied for such a purpose (Mikolaj & Pings, 1967; Albers & Mountain, 1972). Indeed, to determine the parameters of (5) we use the experimental data in the region of the main peak of $S(q)$, whereas in the mentioned methods one has to use only the data at the lowest experimentally accessible q, where the accuracy of their determination is rather low or the series expansion is an inadequate approximation for $S(q)$.

It is well known that the low-q region in $S(q)$ is of decisive influence for the calculation of the direct correlation function $C(r)$ and pair potential in liquids (Enderby, 1968, 1972; March, 1968; Ballentine & Jones, 1973). Therefore, it is interesting to investigate what result gives extrapolation according to (5) for these functions. Such results are displayed for liquid Ar and Na in Figs. 8 and 9. For comparison we show also the results obtained directly from the data for $S(q)$ tabulated in the papers of Yarnell, Katz, Wenzel & Koenig (1973) and Greenfield, Wellendorf & Weiser (1971), where the extrapolation to low q was made by hand by the smooth prolongation of the accessible experimental data. The curve $C(r)$ for Ar computed from $S(q)$ according to the extrapolation procedure (5) has an unusual form: at $r \geq 5{\cdot}5$ Å it becomes negative. As a result, the pair potential computed from $C(r)$ and $g(r)$ in the Percus–Yevick (PY) and hyper-netted chain (HNC) approximations has positive values at the same r (Fig. 8) and is considerably different from the Lennard-Jones potential which is the most convenient form of the effective pair interaction for Ar (Yarnell, Katz, Wenzel & Koenig, 1973; Verlet, 1968). On the contrary, for Na (Fig. 9) the negative values of $C(r)$ at $5{\cdot}5 \leq r < 5{\cdot}9$ Å are too small, though it is conventional to assume that $C(r)$ must oscillate around the r axis in metallic liquids (Enderby, 1968; March, 1968).

It may seem that (5) gives an erroneous extrapolation of $S(q)$ in the low-q region and this settles the question. However, the problem is, in our opinion, more complicated. Here we deal with a calculation of $C(r)$ in fine detail [in comparison with the amplitude $C(0)$]. Such details are so sensitive to the slightest differences in the shape of $S(q)$ on the left of the main peak that the extrapolation may be hardly a satisfactory method to make up a deficiency in the experimental data. The deviations of the dots from the solid lines at $q < 1{\cdot}3$ Å^{-1} in Fig. 1 for Ar and Na are evidently less than the uncertainty of the experimental data. Nevertheless,

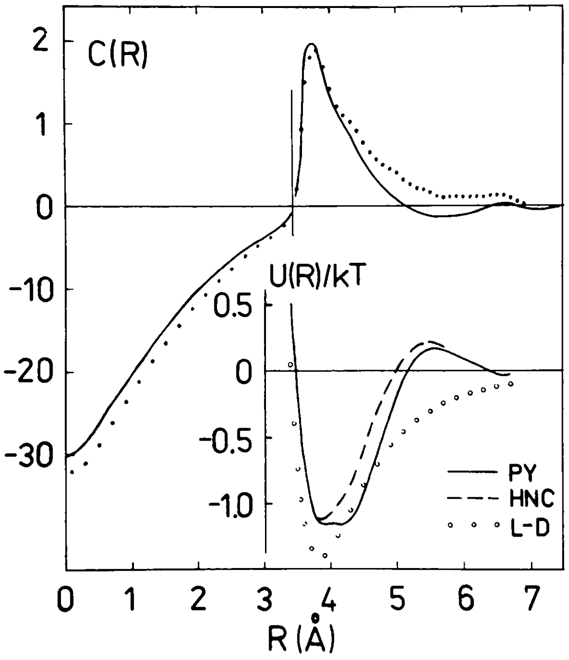

Fig. 8. At the top: $C(r)$ for Ar at 85 K. The points give the results calculated directly from the $S(q)$ data of Yarnell, Katz, Wenzel & Koenig (1973); the solid line gives the computation after extrapolation of $S(q)$ in the region of low q by (5) with parameters from Table 1. Up to $q = 1{\cdot}3$ Å^{-1} the extrapolated values were used and at $q > 1{\cdot}3$ Å^{-1} the experimental ones. The scale in the ordinate axis changes when the curve $C(r)$ intersects the r axis for the first time. At the bottom: the curves of the pair potential obtained from $C(r)$ and $h(r)$ in PY and HNC approximations. The open circles represent the Lennard-Jones potential with parameters $\varepsilon/k = 119{\cdot}8$ K and $\sigma = 3{\cdot}405$ Å (Verlet, 1968).

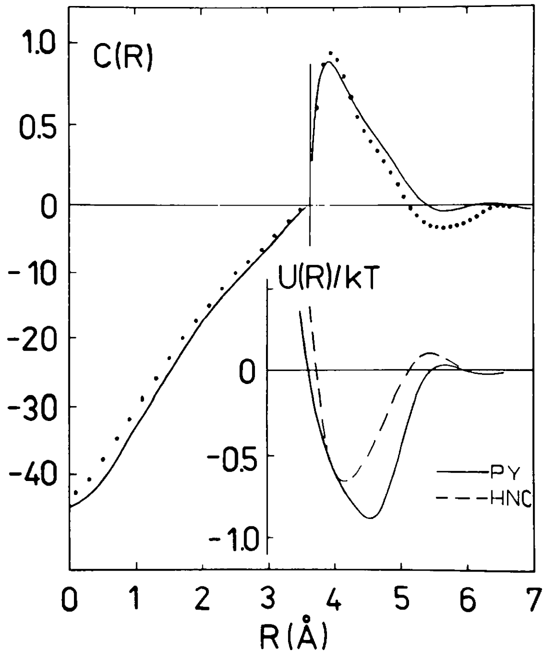

Fig. 9. The same as in Fig. 8 for Na at 373 K (Greenfield, Wellendorf & Wieser, 1971).

these differences produce the fundamental changes in the form of $C(r)$ (Figs. 8 and 9).

The possibility of direct calculation of $C(r)$ from the diffraction experimental data in dense liquids is determined essentially by the accuracy which can be achieved in $S(q)$ at low q. But $S(q)$ is not obtained immediately in the experiment. When extracting $S(q)$ from the measured scattered intensity one has to take into account in an approximate manner various collateral effects (Yarnell, Katz, Wenzel & Koenig, 1973; Pings, 1968). As a result, the near to zero values of $S(q)$ in the low-q region are untrustworthy due to systematic errors which are unavoidable here. Such errors are a much more serious and hardly removable source of the uncertainty in the $S(q)$ data than the random spread of the experimental points. The last can be reduced to a minimum (Greenfield, Wellendorf & Wieser, 1971) and it is also possible to estimate its influence on the results of calculations (Choudry, Banerjee & Ailawadi, 1976; Ballentine & Jones, 1973). In addition, it is necessary to note that the majority of the published structure factors was treated with the procedure which eliminates the low-frequency terms producing the peaks in $h(r)$ near $r = 0$ (Yarnell, Katz, Wenzel & Koenig, 1973; Kaplow, Strong & Averbach, 1965). This procedure considerably distorts $S(q)$ in the low-q region (Enderby, 1972).

Thus, the diffraction experiment is hardly able to provide at present the necessary accuracy in $S(q)$ to solve empirically the question about the detailed form of $C(r)$. Therefore, our knowledge about this function in dense fluids is intuitive rather than experimentally substantiated.

Conclusions

The method proposed in this paper allows one to obtain quantitatively the RDF of liquids and amorphous materials beginning from the second or third peak on the basis of the experimental structure factor in the region of its main peak only. Noted especially will be the non-trivial fact that the same functions [formulae (3) and (4)] are found to be excellent approximations of $S(q)$ and the RDF both for simple dense fluids and for liquid and amorphous substances with complicated open packing of molecules. Thus, the $S(q)$ data beyond the first diffraction peak prove to be redundant information for the purpose of the RDF computation at large r. The random scattering of experimental data which is most pronounced in this region of q values makes the result worse when computing the RDF directly from (1).

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