Calculation of Double Scattering of X-rays in Two Scattering Geometries for a Compressible Fluid (Argon)

By G. D. Wignall and J. A. J. Jarvis

Imperial Chemical Industries Limited, Corporate Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire, WA7 4QE, England

AND W. E. Munsil and C. J. Pings

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91109, U.S.A.

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Numerical estimates of double scattering of X-rays have been made in cylindrical and parallel-plate geometries for fluid argon in two states. For the cylindrical geometry the ratio of double scattering to single scattering is ~0.01 and independent of scatter angle to a first approximation, and thus does not seriously affect estimates of the radial distribution function. For the parallel-plate geometry the ratio is to a first approximation linear with angle and increases to ~0.15 at high angles; it thus seriously effects estimates of the radial distribution function and direct correlation function. The ratio can reach very high levels at low scatter angles if primary scattering is low.

Introduction

The conventional theory of the diffraction of X-rays by liquids or 'amorphous solids' relates the intensity of singly scattered radiation to the radial distribution function by means of a Fourier transform equation (Paalman & Pings, 1963). The experimentally measured intensities of diffracted X-rays include a proportion of photons which originate from multiple scattering. This effect is often ignored and it is only recently that numerical estimates of the magnitude of multiple scattering have been made (Warren & Mozzi, 1966; Strong & Kaplow, 1967; Malet, Cabos, Escande & Delord, 1973), the calculations being limited to the doubly scattered component, which represents the major part of the multiple scattering. We have worked where \( I_0 \) is the incident intensity, \( n \) is the number of out the magnitude of the effect of double scattering for fluid argon, which has been the subject of many structural investigations, and have performed the calculation for two commonly used scattering geometries, i.e. cylindrical and parallel-plate sample containers.

Method

We wish to calculate the ratio of double scattering to single scattering in a beam diffracted through an angle of \( 2\theta_0 \) to the incident beam. The basic equations are found in Warren & Mozzi (1966). Using the notation of Figs. 1 and 2, consider an incident beam \( AF \) which enters the sample at \( F \) and is scattered by a volume element \( dV \) centred at \( B \) through an angle of \( 2\theta_0 \) along \( BC \), leaving the sample at \( H \). If \( dI_1(2\theta_0) \) is the intensity of radiation scattered by \( dV_1 \) at the point of observation a distance \( R \) away from the sample we have

\[
dI_1(2\theta_0) = \frac{I_0 e^{4 \sin^2 \theta_0} J(2\theta_0) (1 + \cos^2 2\theta_0)}{m^2 e^4 R^2} \times \exp \left[ -\mu (FB + BH) \right] dV_1
\]

units of composition per unit volume, \( J(2\theta_0) \) is the first-order scattering intensity in electron units per unit of composition for scattering at an angle \( 2\theta_0 \), and
$(1 + \cos^2 \theta_0)/2$ is the single-scattering polarization factor. The total first-scattered intensity is then given by summing (1) over all volume elements which are irradiated by the incident beam. To calculate the double-scattering component consider the intensity of radiation $dI^2(\theta_0)$ scattered through an angle of $\theta_0$ by the volume element $dV_1$ centred at $B$ which travels a distance $BD$ before being rescattered through $\theta_0$ by the volume element $dV_2$ centred at $D$, and travels along $DG$ at an angle of $\theta_0$ to the incident beam, leaving the sample at $E$. We then have

$$dI^2(\theta_0) = I_0 \left[ \frac{e^4 \gamma^4}{m^4 c^4} \right] \frac{J(2\theta_0) J(2\theta_0) n^2}{R^2(BD)^2} \times \exp \left[ -\mu(FB + BD + DE)PF2dV_1dV_2 \right],$$

(2)

where $PF2$ is the double-scattering polarization factor which is given by

$$PF2 = \frac{1}{2} [\cos^2 \theta_0 + \cos^2 2\theta_0]
+ (\cos \theta_0 \cos 2\theta_0 - \cos \theta_0)^2].$$

(3)

The total double-scattered intensity is given by summing (2) over all potential second-scattering elements for every potential first-scattering element irradiated by the incident beam. Various methods have been used to evaluate this summation which in the limit becomes an integral. Warren & Mozzi (1966) used an approximate analytical expression for $J(\theta)$, Strong & Kaplow (1971) used Monte Carlo methods, and Malet, Cabos, Escande & Delord (1973) used numerical integration methods. The method chosen in this work was to subdivide the scattering volume into convenient volume elements and carry out the summation by means of a computer. The size of the volume elements is then progressively decreased to give a good approximation for the integral. This method has the advantage that it is applicable to any scattering geometry and any shape scattering function, $J(\theta)$. The disadvantage is that one is limited by computing costs in the choice of the size of volume elements.

The scattering geometry for the parallel-plate specimen is shown in Fig. 1. The sample is held in the $\theta$-$2\theta$ geometry, i.e. the sample rotates at half the angular rate of the counter and thus bisects the incident and scattered beams. The calculation is performed for an incident beam with a square cross-sectional area $a^2$ and the ‘diffracted’ beam which defines the potential secondary scattering elements also has a square cross section, with area $b^2$. The irradiated volume is divided into volume elements by a series of parallel planes: $N_1$ planes parallel to the specimen surface, of spacing $T/N_1$ where $T$ is the specimen thickness; $N_2$ planes containing the incident and scattered beam axes of spacing $a/N_2$ and $N_3$ planes (perpendicular to the latter set of planes) with spacing $a/N_3$. $N_3$ is adjusted for each $2\theta_0$ to maintain the volume elements roughly independent of $2\theta_0$.

Similarly the diffracted beam is divided into potential secondary scattering elements with the diffracted-beam cross section divided by $M_1$ and $M_2$ planes respectively, the secondary scattering elements will overlap the primary scattering elements in the irradiated beam volume. The overlap is omitted in Fig. 1 to avoid confusion.

The positions of the volume-element centres are represented by points at their centres, expressed in terms of an orthogonal axis system centred at $O$. All the necessary distances in Figs. 1 and 2 are calculated via Pythagoras’ theorem.

For the cylindrical geometry (Fig. 2) the sample is divided into $N_z$ concentric equiradial rings each of which is subdivided into $2M - 1$ equiangular sections. The volume of any section in the $i$th ring is given by

![Fig. 1. Parallel-plate geometry.](image1)

![Fig. 2. Cylindrical scattering geometry.](image2)
where \( R \) is the radius of the cylinder and \( h \) is the height (perpendicular to the plane of Fig. 2) of the irradiated beam area. Each section is further subdivided into \( N_s \) congruent semisections each of height \( h/N_s \). Subdivision of the scattering volume in this manner means that each semi-sectional element has the same volume, \( \pi R^2 h / N_s^2 N_s \), and the \( N_s \) semi-sections are used as volume increments in the integrations of (1) and (2). The position of each element is again represented by a point at its centre and expressed in terms of an orthogonal system of axes centred at the centre of the cylinder. The necessary distances in the integrations of (1) and (2) are worked out as before.

**Results and discussion**

Figs. 3 and 4 show the ratio of \( I^1(2\theta_0)/I^1(2\theta_0) \) for two different states of argon in Table 1. The scattering data (coherent and incoherent) were taken from Smelser (1970) measured in the cylindrical geometry of Fig. 2 from which the double-scattering component has already been removed. This geometry is almost identical to that of Mikolaj & Pings (1965, 1966, 1967). Smelser (1970) obtained the value of \( I^1(2\theta_0) \) at \( 2\theta_0 = 0 \) by an extrapolation technique and this value was used in the calculation of \( I^1(2\theta_0)/I^2(2\theta_0) \) for the points at \( 2\theta_0 = 0 \) shown in Figs. 3, 4, 5 and 6.

**Table 1. Thermodynamic parameters for states 2 and 6**

<table>
<thead>
<tr>
<th>State</th>
<th>Temperature (°K)</th>
<th>Density (g cm(^{-3}))</th>
<th>Pressure (Atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>143.15</td>
<td>0.91</td>
<td>39.92</td>
</tr>
<tr>
<td>6</td>
<td>108.18</td>
<td>1.26</td>
<td>20.69</td>
</tr>
</tbody>
</table>

The shape of \( I^1(2\theta_0) \) is shown in Figs. 5 and 6 for Runs 2 and 6 for an incident wavelength of 0.7107 Å. This data was chosen because Run 2 exhibited appreciable low-angle scattering whereas State 6 showed the more usual low-angle behaviour for scattering from liquids. For the cylindrical geometry the experimental parameters were \( R = 0.145 \) cm, incident beam height \( 0.033 \) cm, incident beam centre line \( 0.070 \) cm above cylindrical axis \( h = 0.2 \) cm, \( N_s = 5, N_s = 10 \) and \( \mu = 13.5 \) c.g.s. For argon the unit of composition in Figs. 1 and 2 is the argon atom. For both states the ratio \( I^1(2\theta_0)/I^2(2\theta_0) \) calculated from the integrations of equations (1) and (2) is \( \sim 0.01 \) and to a first approximation independent of angle. The double-scattering component to a first approximation will merely change the normalization constant by \( \sim 1\% \) and will not distort the resultant \( g(r) \). The data of Mikolaj & Pings (1965, 1966, 1967) in this geometry were not corrected for multiple scattering, though the effect on \( g(r) \) is \(< 1\% \). Second-order calculations to remove the weak angular dependence of the double scattering will effectively eliminate any effect on \( g(r) \) in this geometry.

For the parallel-plate geometry the 'diffracted' beam is usually set wide enough to collect all first scattering from the irradiated volume at every angle \( 2\theta_0 \), and this implies that \( b - a > 2\theta \). For a plate thickness \( \sim 1 \) mm and incident-beam cross section of \( 1 \times 1 \) mm this means \( b \) should be \( > 3 \) mm. The results of Figs. 3 and 4 in the parallel-plate geometry were taken with \( a = 1 \) mm, \( b = 4 \) mm and a volume element size of \( \sim 0.3 \) mm. The proportional double-scattering component is much greater than in the cylindrical geometry and is greater than 0.10 at high scatter angles where the ratio is roughly linear in \( 2\theta_0 \). This is due to the much greater secondary scattering volume in the case of the parallel-plate geometry which is necessary to ensure that all the primary scattering from the irradiated volume enters the detector. The ratio can be reduced by relaxing this condition and using a much smaller diffracted beam, but this requires extremely accurate knowledge of the collimation geometry, the incident-beam intensity profile and divergence to calculate the fraction of the incident-beam intensity.
radiated volume which is contributing to the single scattering. In the case of the cylindrical geometry the secondary scattering volume is limited by the cell volume and this keeps the double scattering down to an acceptable level.

For both geometries it is difficult to choose a sufficiently small mesh to reach the limit where \( I^2(2\theta_0)/I^1(2\theta_0) \) is independent of the volume element size, because halving the volume element increases the number of computing operations by \( \sim 2^6 \). From a study of the variation of the ratio with element size it was estimated that the ratios shown in Figs. 3 and 4 were of an acceptable accuracy, i.e. within 0.005 of the limiting value. This is not the case however for a parallel-plate geometry where a halving of the element size from that used in the calculations changed the ratio from 0.118 to 0.161 when performed for one scatter angle, \( 2\theta_0 = 80^\circ \) (Run 2). It is therefore necessary to be much more careful in calculating the ratio when double scattering approaches this magnitude. In some cases the ratio might be sufficiently linear with \( 2\theta_0 \) to use a linear correction term; alternatively to avoid computer costs becoming prohibitively expensive one might, following Warren & Mozi (1966) approximate the double scattering in terms of an analytically integrable function and evaluate the integral in terms of the parameters of this function. This method was applied by Warren & Mozi (1966) for the reflexion geometry and would have to be simulated for the particular experimental geometry in question.

It is interesting to note that double scattering is only weakly angle dependent whereas at low angles the primary scattering varies rapidly with angle (Fig. 6). Thus the ratio \( I^2(2\theta_0)/I^1(2\theta_0) \) reflects the rapid angular variation of \( I^1(2\theta_0) \) in this region. At low angles, \( 2\theta_0 < 8^\circ \), the magnitude of this ratio depends mainly on whether \( I^1(2\theta_0) \) exhibits pronounced low-angle scattering, and can be very high where this is not the case (see Fig. 4). Thus low-angle scattering, to which the direct correlation function, \( C(r) \), is particularly sensitive, can be seriously affected by double scattering if the primary scattering is low and the relevant corrections are not made. \( C(r) \) data derived from scattering patterns which are not corrected for multiple scattering are therefore suspect.

The above results are worked out for the case of homogeneous samples. In the instance where fluids are confined within thin walls there are possible contributions from cell-cell, cell-sample, and sample-cell double scattering. Calculation of these contributions would require exact knowledge of the scattering curve of both sample and cell and would therefore be much more involved than the above calculations. Preliminary estimates indicate that these three terms might be of comparable magnitude to the sample-sample scattering (Karnicky, 1973).

### References