

## The X-ray Forward Scattering Coefficient of Water

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The X-ray (1.54 Å) scattering coefficient per unit solid angle, per unit thickness of sample has been measured for water in the forward direction. It is about eight per cent greater than the value given by density fluctuation theory. Double scattering is calculated and shown to contribute a six per cent excess flux in the forward direction in our geometry. In addition, short wavelength continuum X-rays slightly increase the measured scattering coefficient. After these corrections theory and experiment are in good agreement. The double scattered flux is sensitive to certain parameters of the diffractometer geometry. It is argued that water is not a desirable reference standard for absolute intensity calibrations.

### Introduction

The X-ray scattering coefficient per unit solid angle has been measured at small scattering angles by Weinberg (1963) for water and by Shaffer (1964) for water and other liquids and solutions. Both investigators found that the measured coefficients for water, extrapolated to zero angle, gave results 9 or 10% in excess of the predictions of density fluctuation theory (Ornstein & Zernicke, 1918). The measurements of Weinberg and Shaffer were made in the course of developing techniques for the determination of absolute X-ray scattering coefficients at small angles. The failure in the case of water to agree with well established theory has remained puzzling and has cast doubt on procedures which are important in many applications of small angle X-ray scattering and which have been assumed reliable to one or two per cent.

We have repeated, with great care, measurements of the absolute X-ray scattering coefficient of water which, uncorrected, are still about 8% above the theoretical value. In this contribution we discuss certain systematic errors which appear to be the source of the discrepancy.

Lack of monochromaticity of the incident X-ray beam can lead to a small excess scattering in the forward direction but double scattering involving two successive single scatterings at large angles can be a major source of error. Double scattering can contribute a forward flux as high as 8% of the actual single scattered flux. When the proper corrections are made experiment and theory are in satisfactory agreement.

Double scattering is a more acute problem in slow neutron experiments where absorption can be very low, and numerous discussions are available. Double X-ray scattering from polycrystalline metal foils has been treated by Webb & Beeman (1959). Warren & Mozzi (1966) treat double X-ray scattering, in a reflection geometry, by amorphous samples. None of the discussions is directly applicable to our problem of high

resolution small angle X-ray scattering by liquid samples used in transmission. We describe the necessary calculations.

### Experimental

Measurements of scattered flux were made in a symmetrical four-slit diffractometer first described by Ritland, Kaesberg & Beeman (1950). The geometry of the slit system is illustrated schematically in Fig. 1. In the apparatus employed the separation of successive slits,  $a$ , is 10 cm, the slit height,  $h$ , is 0.6 cm and the slit width,  $d$ , usually 0.04 cm in our experiments with water. The entire slit assembly is in a chamber which can be evacuated or filled with helium.

The X-ray source is a rotating copper anode tube run at 35 kV and 120 mA. The voltage is smoothed and both current and voltage are electronically regulated. A nickel filter is used to reduce Cu  $K\alpha$  radiation. Detection is with a xenon-filled proportional counter and single channel pulse-height discrimination.

The focal line, on the outside vertical surface of the rotating anode, is about 1.0 cm high and 0.1 cm wide. As viewed by the slits the focal line appears about 0.02 cm wide. The counter is just outside the scattering chamber and linked to move with the third and fourth slits which rotate about a vertical axis through the center of the scatterer. Measurements of the scattered flux can be made to a scattering angle of  $15^\circ$  on one side of the central beam and  $105^\circ$  on the other.

An absolute scattering coefficient is determined by a substitution method. With the same tube power and diffractometer settings we compare the flux scattered by water with that scattered by a gas. Several gases have been used as primary standards but octafluorocyclobutane ( $C_4F_8$ ) seems the most convenient. It is a good scatterer ( $Z=96$ ), it can be obtained in high purity and the deviations from perfect gas behavior at room temperature and pressure are small. The substitution method eliminates nearly all geometrical and solid angle considerations. In addition to the scattered fluxes one need only measure and subtract the small parasitic scattering of sample holder windows and

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helium, correct for the difference in transmission between the gas and water, and determine the mass per unit area of each scatterer. The scatterers are contained in identical sample holders 0.1 cm thick between crystalline quartz windows each about 0.0025 cm thick.

Data were usually taken at scattering angles from  $1^\circ$  to  $5^\circ$ . Both water and  $C_4F_8$  give excellent straight lines in this angular range when the logarithm of the scattered flux is plotted against the square of the scattering angle. Such a plot for some of our water data is shown in Fig. 2. The extrapolation to zero angle in this plot gives the required forward scattered fluxes. It is assumed that the gas is scattering with the classical Thomson cross section. Anomalous dispersion corrections are negligible. The equation of state of  $C_4F_8$  is accurately known and corrections of one or two per cent are made for deviations of density and compressibility from perfect gas behavior. All of our measurements were made at ambient pressure and temperatures near  $20^\circ C$ .

More detailed discussions of such measurements are available in the theses of Shaffer (1964) and Chonacky (1967) and a short review has been given by Beeman (1967). The latter reference also discusses slit height corrections. These usually must be done with care if accurate absolute intensity measurements are desired. In the present work they are not important since the scattering from neither the reference gas nor water varies rapidly with angle in the angular range integrated by the slits.

### Double scattering

In our geometry (Fig. 1) the contribution from double scattering is a sensitive function of certain instrumental

parameters, particularly the slit width,  $d$ . We first calculate a ratio of double scattered to single scattered forward flux which is correct for slit widths large compared with the thickness of the sample. We then discuss the necessary corrections when this ratio is near unity, or less.

Fig. 3 represents a horizontal section through the scattering sample.  $I_0$  is the incident flux. We may write the total first scattered flux in the forward direction, which reaches the detector, as follows:

$$P_1 = I_0 \sigma(0) t \Omega \exp(-\mu t). \quad (1)$$

The thickness of the sample is  $t$ ;  $\Omega$  is the solid angle admitted by the detector,  $\sigma(0)$  is the scattering coefficient in the forward direction per unit solid angle per unit thickness of sample and  $\mu$  is the linear absorption coefficient of the sample.

A ray scattered at the angle  $\theta$  may also leave the sample in the forward direction as illustrated in Fig. 3. A short calculation leads to the following result or the ratio of the twice scattered flux to the actual single scattered forward flux. Unpolarized incident radiation is assumed:

$$\frac{P_2}{P_1} = 2\pi\sigma(0)t \int_0^\pi d\theta \left[ \frac{\sigma(\theta)}{\sigma(0)} \right]^2 \left[ \frac{1}{2}(1 + \cos^4 \theta) \right] |\tan \theta| \times \left\{ \frac{1}{|\alpha t|} + \frac{1}{\alpha^2 t^2} [\exp(-|\alpha t|) - 1] \right\}. \quad (2)$$

The factor  $I_0 \Omega \exp(-\mu t)$  appears in both  $P_1$  and  $P_2$  and cancels in the ratio. The solid angle cancellation is not exact and necessitates the much more complex

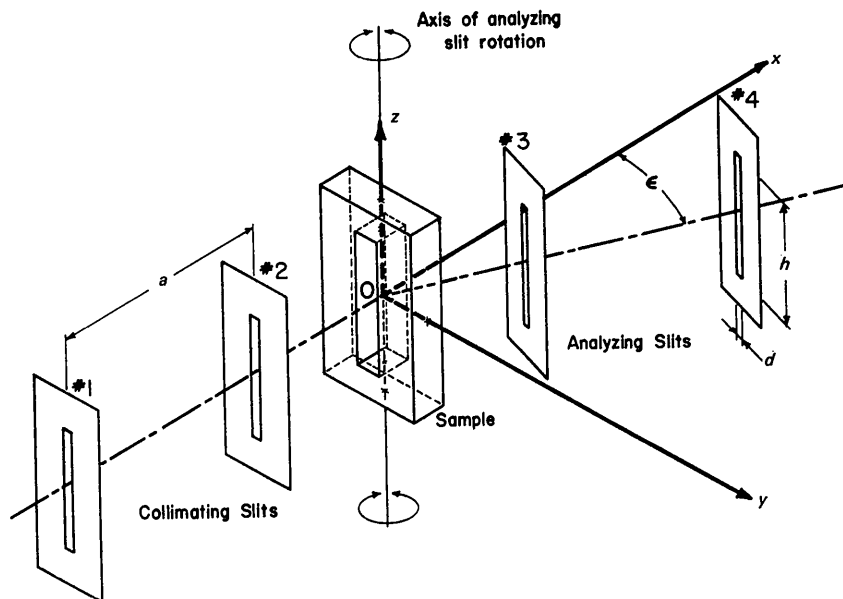


Fig. 1. Schematic diagram of symmetrical four slit diffractometer for small angle scattering studies. The incident beam is collimated by slits 1 and 2. The scattered beam is defined by slits 3 and 4 which rotate about the vertical axis  $z$  through the center of the sample. The scale is greatly compressed in the  $x$  direction.

calculations we mention later. The path of a twice scattered ray in the sample is greater than  $t$  by the distance  $(x_2 - x_1)(\sec \theta - 1)$ . This leads to additional absorption which is represented in the integrand by the last factor in square brackets. The integration over  $x_1$  and  $x_2$  has been carried out and  $\alpha = \mu(\sec \theta - 1)$ .

We have evaluated the integral graphically. For our sample thickness  $t = 0.1$  cm and  $\mu t = 1$ . The scattering coefficients as a function of angle,  $\sigma(\theta)$ , are from Morgan & Warren (1938). Since we know the double scattering correction to be small we take  $\sigma(0)$  to be the theoretical value. We must, of course, know  $\sigma(\theta)$  on an absolute scale. Morgan & Warren determined this by measurements at large angles and the assumption of independent atom scattering. We have independently calibrated their scattering curve by extending our small angle measurements to angles overlapping their data. The two calibrations agree to within 3 or 4%.

We obtain  $P_2/P_1 = 0.08$ . This result is sensitive to the scattering coefficient which enters the expression as a squared term. Our value for  $P_2/P_1$  could be in error by as much as 8 or 10%. More than half the contribution to the integral is from the broad peak in the water scattering curve between  $20^\circ$  and  $50^\circ$  (with Cu  $K\alpha$ ). Only about 13% comes from single scattering at more than  $90^\circ$ .

One notes that double scattering is important only when the forward scattering coefficient is small compared with scattering coefficients at larger angles. Thus the gases we use as primary standards will have quite negligible double scattering corrections.

We now consider the corrections which depend upon slit width. In Fig. 3 the scattering volume is divided by vertical planes at  $y = \pm d/2$  and  $y = \pm d$  where  $d$  is the slit width. A volume element of the scatterer in the region  $-d/2 < y < d/2$  sees the maximum solid angle of X-ray target and of detector. The solid angles are limited by the first or fourth slits only and the magnitude of the solid angle is  $hd/(1.5a)^2$  steradians in each case. These results are easily verified by reference to Fig. 1.

For  $|y| > d/2$  the solid angle is limited also by the second or third slits. The solid angle decreases linearly from its maximum value becoming zero at  $|y| = d$ . The fact that a volume element makes a contribution to the scattered flux which depends upon its position is no problem when only single scattering is involved. The geometrical considerations are identical for the primary standard and the scatterer of interest. However in double scattering there is a sidewise motion of the ray between the first and second scattering whose maximum value, when the scattering is in the  $xy$  plane, is  $(x_2 - x_1) \tan \theta$ . Thus the effective source of second scattering is broader than that of first scattering and is seen less efficiently by the detector. The effective sidewise motion is limited by the absorption of the sample. It may be characterized by the length  $1/\mu$  where  $\mu$  is the linear absorption coefficient.

For a sample of fixed thickness two extreme cases are easily discussed. If  $d \gg 1/\mu$  then sidewise motion may be neglected and the contribution of double scattering is correctly given by equation (2). If  $d \ll 1/\mu$  a very small sidewise motion removes the ray from the region seen by the detector and the double scattering approaches zero.

In our experiments  $1/\mu$  and the sample thickness are both 0.1 cm. The slit width,  $d$ , is 0.04 cm. We are between the extreme cases and a detailed consideration of geometric effects is necessary. The somewhat laborious but straightforward calculations are given in the thesis of Chonacky (1967). A double scattered ray is traced through the sample, weighted by the scattering efficiencies appropriate to the positions of first and second scattering, and the necessary angular and volume integrations carried out. We find that in our geometry  $P_2/P_1$  is reduced from its maximum value of 8% to about 6%.

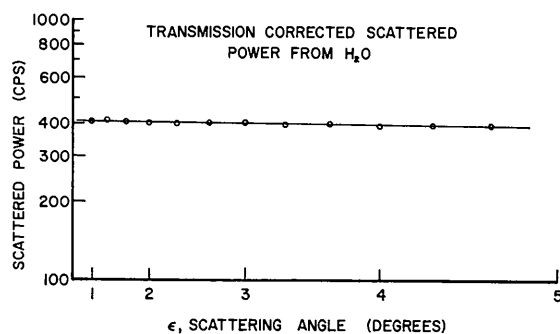


Fig. 2. Plot of the logarithm of the scattered power (counts  $\text{sec}^{-1}$ ) versus the square of the scattering angle for water. The data have been corrected to an unsupported non-absorbing water sample. Actual counting rates were about 100 counts  $\text{sec}^{-1}$ .

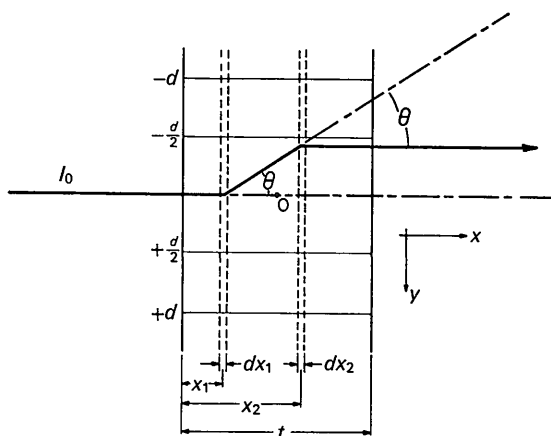


Fig. 3. The geometry of double scattering in a horizontal plane through the center of the scatterer. The incident beam,  $I_0$ , fully illuminates the sample between  $-d/2$  and  $+d/2$  where  $d$  is the slit width. Beyond  $\pm d/2$  the illumination decreases, becoming zero at  $\pm d$ .

A few additional points are worth mentioning. The translation of a ray between the first and second scattering has, in general, a component in the  $z$  direction, parallel to the slit height, as well as in the  $y$  direction. In addition the intensity of illumination of the sample and the solid angle seen by the detector are the same functions of  $z$  as of  $y$ . However, the characteristic length in the  $z$  direction is the slit height,  $h=0.6$  cm. This is large compared with  $1/\mu$  and only the  $y$  component of the translation is effective in removing the twice scattered ray from the volume seen by the detector. It will also be noted that our X-ray focal line of width 0.02 cm does not fill the area of the target seen by the first two slits. The distribution of incident intensity on the sample is not quite that illustrated in Fig. 3. The actual distribution was used in the calculations.

If one wishes to measure a forward scattering coefficient and use the simplest possible double scattering correction, namely that of equation (2), it can be accomplished by making slits 3 and 4 somewhat wider than 1 and 2. The volume of scatterer seen by the detector is then greater than the volume illuminated and the effects of sidewise motion can be eliminated. This was not done in the experiments of Weinberg and Shaffer, nor in most of ours, since the importance of double scattering had not been foreseen. It is not usually a desirable arrangement of slit widths because it increases the smallest angle at which data can be taken.

Finally we remark that in extrapolating to zero angle a scattering curve measured between  $1^\circ$  and  $5^\circ$  we are assuming that the observed smooth linear behaviour of the total scattering continues below  $1^\circ$ . We can think of no reason to doubt this. Also the assumption of equation (2) that the first and second scattering must be at the same angle is incorrect. The finite slit height and width pass a range of angles about the nominal angle. Most of the scattering is within two degrees of the nominal angle. This will reduce  $P_2/P_1$  but by an amount well within our stated uncertainty of 8 or 10%.

Levelut & Guinier (1967) have recently measured the scattering between  $2^\circ$  and  $5^\circ$  (Cu  $K\alpha$ ) of a number of liquids. The results are extrapolated to zero angle and put on an absolute basis by measuring the incident beam after attenuation by calibrated absorbers. The diffractometer is based upon a point focusing a doubly curved lithium fluoride crystal. They detect the entire scattered flux through an annular ring of variable radius about the focus. They report that the scattering from water and from ethyl acetate agrees with density fluctuation theory. Benzene scatters about six per cent and ethanol about nine per cent more than theory predicts. The precision of their measurements is between one and three per cent. To this should be added a possible  $\pm 5\%$  systematic error in the absolute intensity calibration. The results quoted are without a double scattering correction.

The errors in our separate experiments will accommodate our separate results. However, Levelut & Guinier claim that double scattering made no important contribution to their scattered flux. This is based not upon calculation but upon measurements on a series of samples of different thicknesses. The scattered flux was found to be proportional to sample thickness (after correction for absorption).

Dimensional details of their diffractometer are not given but the scatterer is placed in the converging beam between the crystal and the point focus and we assume the illuminated spot on the sample must have had a diameter of at least 0.2 or 0.3 cm. Our calculations would then imply a double scattering contribution of close to 8% for  $\mu t = 1$ .

In this connection we point out that the ratio of double scattered to single scattered flux in the forward direction is not, in general, a simple function of sample thickness. The first approximation that gives  $P_2/P_1$  proportional to sample thickness ignores the additional absorption of the twice scattered flux which arises from its longer path in the sample. It is because of this effect that  $\mu t$  occurs in the integrand of equation (2). We have computed  $P_2/P_1$  from equation (2) for several values of  $\mu t$ . The results are given in Table 1.

Table 1.  $P_2/P_1$  computed from equation (2)

$\mu t$	$\frac{1}{2}$	1	2	3
$P_2/P_1$	4.8%	8%	13.1%	17.2%

It is seen that  $P_2/P_1$  is not directly proportional to  $t$ : the variation is appreciably less rapid. To distinguish this dependence on sample thickness from that of pure single scattering requires that a scattering deficit of 3.2% at  $\mu t = \frac{1}{2}$  or an excess of 5.1% at  $\mu t = 2$  be detected (compared with  $\mu t = 1$ ). We feel that such differences might easily have been missed.

### Monochromatization

We gave careful attention to the spectral composition of our X-ray beam and its possible effects on the measurement of  $\sigma(0)$ . A Ni foil  $\beta$  filter  $7.6 \times 10^{-4}$  cm thick reduces Cu  $K\beta$  to about 2.6% of Cu  $K\alpha$  in the beam leaving the X-ray tube. This is reduced to 2% or a little less in terms of pulses counted by the proportional counter and passed by the pulse height discriminator. The discriminator was operated with a band width to base line ratio of 0.18, a little less than we usually use. The contribution from harder continuum X-rays is between 1 and 2% of the pulses counted. This was estimated by crystal diffraction analysis of the beam and by transmission measurements through pure aluminum.

There are two ways in which spectral inhomogeneity affects the determination of  $\sigma(0)$ . Hard X-rays which have been scattered by small equivalent Bragg spacings will appear in the small angle scattered flux. Because

of the difference in the shapes of their scattering curves this contamination is greater with water than with the calibration gas. The effect is to increase the measured  $\sigma(0)$ .

In addition the measurement of sample transmission is sensitive to spectral composition. Ideally one should measure a transmission with the same incident beam used in the scattering experiments. In practice the intensity of the incident beam is many orders of magnitude too high for a transmission measurement. We attenuate it by scattering from carbon black. The sample transmissions are measured in this scattered beam, which is, however, somewhat softer than the incident beam. Thus, sample transmissions are underestimated and the transmission corrected sample scattering is overestimated. Again the effect is greater for water than for the calibration gas, whose transmission is close to unity.

Together these increase our measured  $\sigma(0)$  by about one per cent. The transmission measurement is the major contributor. Our uncorrected scattering coefficient for water is somewhat lower than those of Weinberg and Shaffer perhaps because of a more monochromatic beam.

### Conclusions

From density fluctuation theory one obtains:

$$\sigma(0) = \sigma_e(0)nZ^2(nkT\beta) = 1.64 \times 10^{-2} \text{ cm}^{-1} \\ (\text{H}_2\text{O at } 20^\circ\text{C}),$$

where  $\sigma_e(0)$  is the scattering cross section per unit solid angle in the forward direction of an electron,  $n$  is the number density of molecules,  $Z$  is the number of electrons per molecule, and  $\beta$  is the isothermal compressibility of the fluid.

Our experimental value is  $1.66 \times 10^{-2} \text{ cm}^{-1}$ . This is after a 6% correction for double scattering and a 1%

correction for the effects of spectral impurity of the incident beam. Both corrections reduce the observed scattering coefficient. Our experimental value should be reliable to about  $\pm 2\%$ . Half of the uncertainty is in the measurement of the uncorrected scattering coefficient and the other half in the calculation of the corrections.

These results support our procedures for the measurement of absolute scattered intensities but imply the necessity of a gas as a reference standard. In particular the strong dependence of the double scattering correction on the slit and sample geometry make water, and probably most other liquids, quite unsuitable as standards.

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