

## **The effects of inelastic scattering upon small angle diffraction measurements.**

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### **Abstract.**

*The coherent scattering from the large objects studied by small angle scattering (SANS) is predominantly elastic. Experimental measurements show however that the incoherent "background" may have a significant amount of inelastic scattering. For a hydrogenous sample, such as 1 mm of water, roughly half the transmitted neutrons are inelastically scattered, largely to shorter wavelengths. The proportion of the inelastic scatter detected will depend upon relative detector efficiencies at these shorter wavelengths. Experimenters should be aware of this multiple incoherent inelastic scattering when subtracting "incoherent backgrounds" and when comparing such data between different instruments. The use of incoherent scattering for detector calibration also presents some problems. It is profitable for SANS instruments on both pulsed and reactor sources to be able to operate with a pulsed, monochromatic incident beam and time-of-flight analysis in order to be able to examine these effects.*

### **Introduction**

The success of the SANS technique in many and varied fields of science often relies on data being obtained in absolute units prior to model fitting or Fourier inversion procedures [1]. The precision with which an often relatively large background subtraction can be made, notably from hydrogenous solvents, becomes very important. This is particularly so with techniques that emphasise asymptotic limits of the data such as Porod or Kratky plots [1]. Measurements made at long wavelength at a reactor source, D17, ILL [2] and at shorter wavelengths on LOQ at ISIS [3] demonstrate that the incoherent scattering from hydrogenous materials is highly inelastic. Those familiar with inelastic scattering of neutrons will realise that the slow neutrons used by SANS instruments (wavelength  $\sim 1 - 20 \text{ \AA}$ ) are thermalised by these hydrogenous samples, which are typically 1 mm thick. Since the sample is normally at ambient temperature the neutrons are predominantly accelerated to shorter wavelengths, as illustrated below. An uneducated user of a SANS instrument believes that "hydrogen is a strong absorber of neutrons", as verified by sample transmission measurements, so instead expects the neutrons to be slowed down. The purpose of this paper is to illustrate the actual effects and to consider their practical consequences in terms with which the average SANS user will be familiar. For this reason we show inelastic neutron spectra against wavelength rather than energy.

### **Experimental**

The LOQ small angle scattering diffractometer at ISIS is equipped with a variable aperture chopper synchronised to the source neutron pulses. In normal use, at 25 Hz, the chopper transmits a range of wavelengths from 2 to 10  $\text{\AA}$ . For the measurements here a small open duty cycle was selected to provide a nearly monochromatic neutron

beam at 50 Hz. Small angle scattering was observed on the two-dimensional  $^3\text{He}$  multidetector and the energy transfer was determined by the normal time-of-flight electronics. The detector has a useful area of about 64 cm diameter and is at a distance of 4.4 m from the sample, centred on the primary beam. In order to accumulate reasonable statistics, the entire data were summed together to give a single spectrum.

Typical raw data, with time of flight converted to apparent elastic neutron wavelength are shown in Figure 1. Corrections were then made for the background scattering from the empty cell and for the expected wavelength variation of detector efficiency, some results being shown in Figures 2 and 3 against inelastic wavelength. Corrected data for a 1 mm thick sample of  $\text{H}_2\text{O}$  at 25 C using three different incident neutron energies are shown in Figure 3. The spectra show clearly the peak corresponding to the incident beam at wavelengths of 2.5, 4.1 and 8.8 Å as well as a significant signal of neutrons with a lower wavelength (higher energy). At the shorter wavelengths particularly a small fraction of the neutrons are also slowed down.

A simple consideration of sample transmissions shows that not only is roughly half the scattering inelastic but that it must be dominated by multiple scattering events. Simple fitting of Maxwellian profiles of different temperatures indicates however that the SANS samples are not sufficiently thick for the neutrons to be fully moderated. This makes such scattering inherently difficult to model [4], especially as the  $S(Q,\omega)$  cross section for thin samples of materials such as water are not well known.

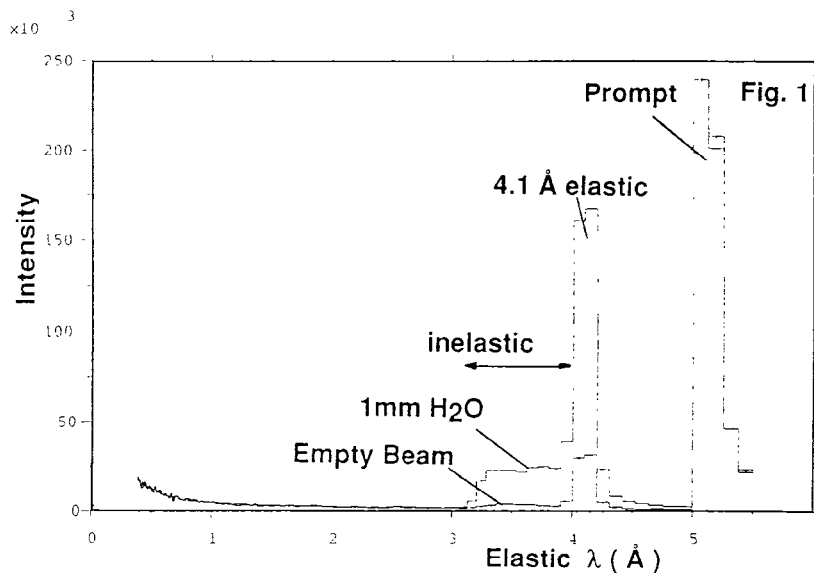


Figure 1. Raw time of flight spectra ( as apparent wavelength from the total flight time) from LOQ at ISIS, summed over whole area detector, for 1 mm  $\text{H}_2\text{O}$  at 298K and an empty beam run (of the same number of incident neutrons), with a monochromatic incident wavelength of 4.1 Å. The "prompt" peak is a background spike from the next ISIS accelerator proton pulse.

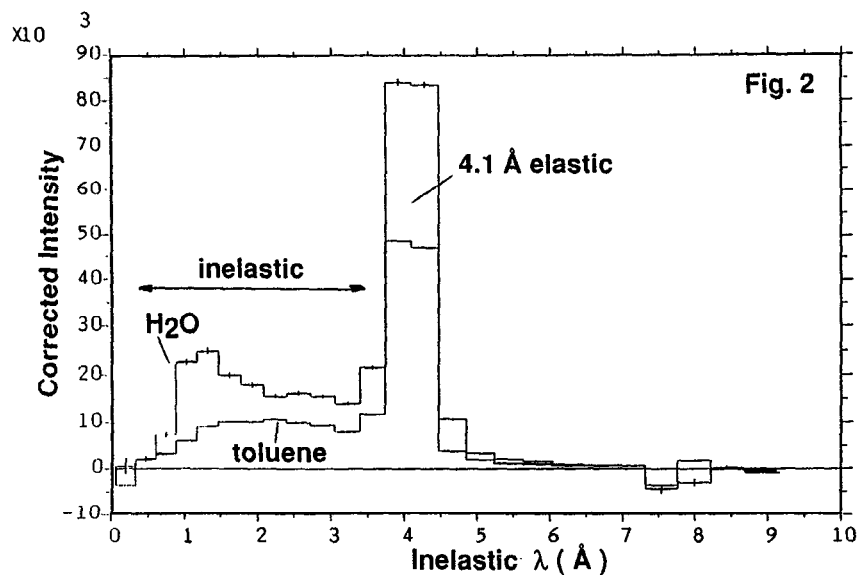


Figure 2.  $H_2O$  data of Figure 1 after conversion to the scattered beam inelastic wavelength and allowing approximately for detector efficiency. Also shown is the inelastic spectrum for 1 mm of toluene  $C_6H_5CH_3$ , also at 298 K, for the same number of incident neutrons.

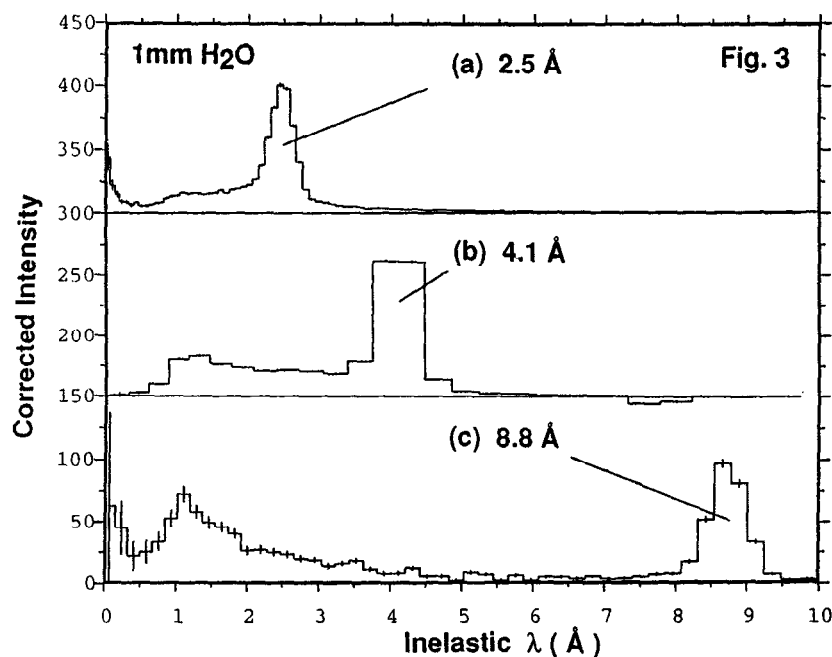


Figure 3. Time-of-flight spectra of a 1 mm water sample at 298 K measured with incident beams of (a) 2.5, (b) 4.1 and (c) 8.8 Å wavelengths, corrected for expected detector efficiency at the inelastic scattered wavelengths shown.

### Incoherent background subtraction

The best choice of "incoherent background" material, to subtract from a sample with a coherent elastic SANS signal should have the same multiple inelastic, incoherent spectrum. Summation of proportions of the scattering from separate measurements of fully deuterated and fully hydrogenated samples will not, in detail, be accurate as

their multiple scattering components will not be the same. A mixed D<sub>2</sub>O plus H<sub>2</sub>O sample will be a reasonable background for a water based sample where the SANS scatterer is at a low volume fraction and itself contains little or no hydrogen [12]. At higher volume fractions, with other types of solvent, or with say a bulk polymer sample, a H<sub>2</sub>O/D<sub>2</sub>O background might not work so well. We note (for example in Figure 2) that the spectrum from H<sub>2</sub>O is quite different from other hydrogenous samples, even when normalised to the same proton density. Perhaps the most ingenious answer, at least for systems such as single polymers where all the coherent scatter is generated by D/H substitution, is to prepare a background sample in which the positions of all H and D atoms have been randomised but are on average in the same chemical sites.

In general it should be noted that an absolute subtraction of a large incoherent signal from beneath a small coherent SANS signal will be difficult to achieve and that the consequences, in terms of systematic errors, of a residual background should always be allowed for in any subsequent model fitting, inversion procedure, or graphical interpretation.

### **Data normalisation and comparisons between instruments**

Water has frequently been used as a secondary standard for SANS experiments [5]. It is used both as an 'isotropic' scattering material to determine cell by cell variation in detector efficiency and to calibrate the absolute intensity. For the second purpose it is normally necessary to use empirical formulae to obtain the effective scattering cross-section as a function of wavelength or temperature [6-8]. To examine these assumptions, the corrected data for the 1 mm water sample with an incident wavelength of 4.1 is shown as a function of radius (from the beam centre) on the detector in Figure 4. The two curves correspond to the elastic peak (3.9 to 4.3 Å) and the neutrons scattered to higher energies (1.5 to 3.9 Å). In this case no allowance has been made for the variation of detector efficiency with wavelength. Over this rather limited angular range, it appears that, within statistical errors, both the elastic and inelastic parts of the spectrum are "flat", in agreement with earlier results at 12 Å [2]. More detailed measurements of the scattering from different thicknesses of H<sub>2</sub>O at the ILL [9] showed that the total scattering scales non-linearly at larger radii on the detector, though the effects are small compared to other geometric effects allowed for by the usual "water normalisation".

It is important to note however that the proportion of the short wavelength inelastic scatter of Figure 4 that will be detected will depend on the nature of the detector used on a particular SANS instrument. For example a high pressure <sup>3</sup>He detector will record considerably more than a low pressure BF<sub>3</sub> based detector. The apparent cross section of H<sub>2</sub>O will thus vary from instrument to instrument, thus it should be regarded as only a secondary standard in relation to intensities from agreed coherent SANS scatterers [10].

On a pulsed neutron source the actual effect of inelastic incoherent scatter depends not only on the detector type but also on the incident spectrum shape and the distance of the detector from the sample. The inelastic incoherent signal (Figure 1) arrives in

different time channels to its elastic part, mostly to shorter wavelength. On following the normal data reduction route [11] into Q space the flat total signal of Figure 4 becomes distorted, dipping at the lowest Q values (longest apparent elastic wavelengths). In fact at the longest wavelength (lowest Q) a nearly pure elastic incoherent signal is seen. Thus in general, and particularly at the lowest Q, the combined data from a range of incident wavelengths from a hydrogenous material need not give a flat cross section. This will be true even though the normalisation procedure for coherent SANS data is correctly allowing for the wavelength dependencies of sample transmission, incident beam spectrum and detector efficiency. LOQ and other pulsed source SANS instruments avoid the use of water as a primary calibrant by making a direct measurement of the efficiency ratio of the main detector to the beam monitor as a function of wavelength. Absolute scaling of cross sections is then checked against coherent SANS scatterers [10]. Vanadium is not used as its cross section is too small to obtain good statistics at all wavelengths in a reasonable time. It is also prone to having small angle scattering from voids or adsorbed hydrogen unless carefully prepared and stored.

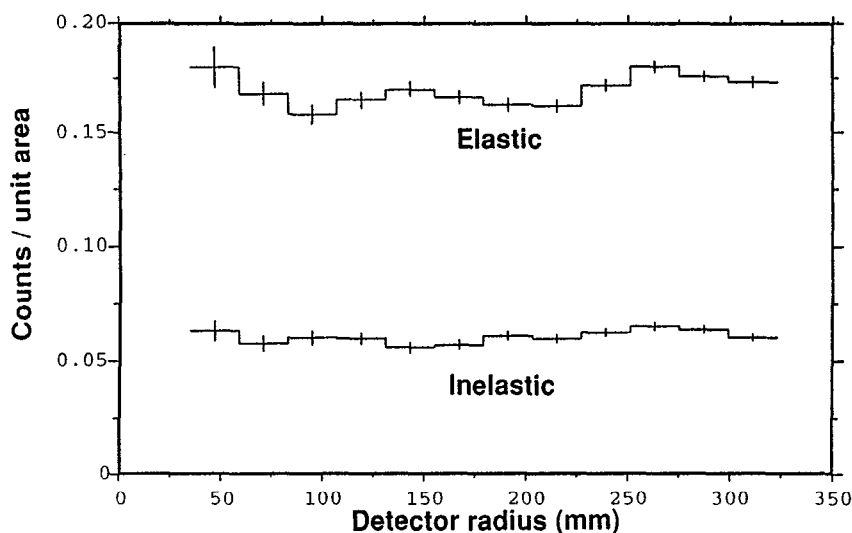


Figure 4. Elastic and inelastic scattering from 1 mm  $H_2O$  with an incident beam of 4.1 Å as a function of the radial position on the detector.

### Transmission measurements

Absolute SANS scattering cross sections are normally obtained by dividing the recorded scattering by the sample transmission. This is particularly important on a pulsed source instrument where coherent SANS signals from different wavelengths are combined since the transmission varies with neutron wavelength [11]. This in itself may pose difficulties as the largest variations of transmission with wavelength are for incoherent scatterers. A detail discussion of all the possible effects is beyond the scope of this paper. One must consider exactly how the "cross-section" is defined, generally SANS results assume it to be proportional to the probability of coherent scattering only from the particles of interest, and assume that the total scattering cross

section for all processes is low. The optimal method for measuring the transmission will depend on the size of the coherent SANS signal compared to any incoherent background, how the data will be processed, and on all the instrumental factors mentioned above, such as detector type ! In the ideal some iteration of the derived cross section back into the transmission measurement may be required. Some compensation for the variation of the recorded inelastic incoherent scatter with detector type may occur in that the apparent transmission, if measured with the same detector, will also be higher with detectors that are more efficient at short wavelengths.

Various semi-empirical methods for either incoherent background subtraction or data normalisation between different detector positions use the assumption that, for a sample such as H<sub>2</sub>O, the total incoherent scatter is proportional to  $(1-T(\lambda))I(\lambda)$  where  $I(\lambda)$  is the incident flux. Again it should be noted that due to the presence of considerable inelastic scattering the counts detected will vary from instrument to instrument, thus the scaling parameters used will not be universal constants. The same warnings made above about changes of inelastic spectra between a sample and the chosen "background" material will also apply to  $(1-T(\lambda))$  methods of compensating for background subtraction of different D/H ratios of water [12-14], polymer solutions [15] or solid polymers [16].

## Conclusions

As outlined above the effects of inelastic incoherent scattering on a SANS instrument can be subtle, and vary from one instrument to another and even with different detector types on the same instrument. The results described here and in earlier work [2] both required an ability to operate SANS instruments in an unfamiliar mode, namely with time of flight data collection and a pulsed, monochromatic neutron beam. It would be useful for those designing or upgrading SANS equipment to include such a facility to empirically quantify inelastic effects on their particular instrument.

Care needs to be taken when subtracting a large incoherent background from a small coherent SANS signal, though only general guidelines rather than quantitative formulae can at present be offered to help to do this in an absolute sense.

For most SANS experiments the effects of inelastic scattering will be minimal compared to other effects such as detector inhomogeneities or resolution smearing. As far as normalisation of data is concerned the "incoherent" scattering from 1 mm of H<sub>2</sub>O at a given temperature, or any other hydrogenous material, though so far appearing to be "flat", should not be regarded as universally constant as the proportion of the considerable inelastic component detected will vary from one detector type to another.

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