SECTION 2

STEPS IN DATA ANALYSIS OF TOF DIFFRACTION DATA

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2.1 INTRODUCTION

The initial goal of the experimenter is to obtain the TDCS of his or her sample. The success of subsequent analysis to g(r) or partial structure factors depends critically on obtaining the TDCS accurately. A number of corrections are required to the measured data: these are straightforward to apply but nonetheless easy to get wrong. Four main sources of error can be identified:

- (i) the experimenter doesn't have complete information about his or her sample, e.g. dimensions, densities, cross sections, etc.;
- (ii) incorrect data analysis procedures are used;
- (iii) the detectors are not sufficiently stable;
- (iv) sample environment equipment introduces unexpected backgrounds and sample positioning errors.

The last two causes require action by the instrument scientists, but there is little or nothing that can correct for poorly characterised samples or incorrect data analysis procedures.

Occasionally on LAD we have achieved absolute accuracies of 1%, accuracy being measured by the difference between the measured high Q limit of the TDCS and the expected high Q limit. With care this accuracy could be achieved routinely. However at present we typically obtain accuracies on the order of 5%, and in the majority of cases the reason for this is either because the sample is poorly characterised or because the data analysis is inadequate.

With the exceptions of sections 2.9 and 2.11, which concern the estimation of inelasticity corrections and transforming the final result to g(r), we believe the methods of analysis of diffraction data from liquids and amorphous samples are well understood and routine. In the sections which follow we have attempted to describe the correct sequence of steps.

As seen in section 1.1, the scattered intensity is measured as a function of time-of-flight which in turn is proportional to wavelength. The data can also be presented as a function of wave vector, k, wave vector transfer, Q, or energy, E, by using the relationships (1.1.5) to apply the appropriate rescaling. The choice is subject to the preference of the experimenter, although the Q representation is the most common as it relates to the reciprocal space in which the structure factor is defined, equation (1.2.1). Therefore we shall use the Q representation here. Thus if the sample is very small so that the effects of attenuation and multiple scattering are negligible, the detected count rate would be proportional to the incident flux, $\Phi(k_e)$ the TDCS of the sample, $\Sigma(Q_e)$, the detector solid angle, $\Delta\Omega$, and the detector efficiency, $E_d(k_e)$:

$$I(k_{a}) = \Phi(k_{a}) N \Sigma(Q_{a}) E_{d}(k_{a}) \Delta \Omega \qquad (2.1.1)$$

where N is the number of scattering units in the neutron beam, and $Q_e = 2k_e \sin\theta$. The incident flux and detector efficiency are represented here as a function of k_e to emphasize that they are not a function of the scattering angle of the detector.

Equation (2.1.1) is an idealized count rate: the first correction that must be applied is for detector deadtime.

2.2 DEADTIME CORRECTIONS

No matter how well made a detector is always "dead" for a short while after a neutron event has occurred. For a ³He tube this DEADTIME might be 3µs, whilst for a glass scintillator it is perhaps 250ns, before another event can be recorded. The zinc sulphide detectors will have a deadtime of betweeen 2 and 10 µs, depending on how they are set up. Normally the correction for deadtime is a few percent and so can be made by a simple formula. Suppose τ is the deadtime in µs for a detector. First consider the case where the time channel is broad compared to the deadtime. If R_m is the measured count rate in the time channel (in $cts/\mu S$), then the detector is dead for a time

$$D = \Delta R_{m} \tau \qquad (2.2.1)$$

where Δ is the width of the time channel in μ S. Hence the count rate, R, which would have been measured if the detector had zero deadtime, is greater than R_m in proportion to the time that the detector is dead:

$$R = \frac{\Delta}{(\Delta - D)} R_{m} = \frac{R_{m}}{(1 - R_{m}\tau)}$$
(2.2.2)

At the other extreme if the time channels are narrower than the deadtime, then some of the previous time channels may contribute to the deadtime in a particular channel. For example if channels n to m contribute to the deadtime in channel m, then the length of time channel m is dead is given by

$$D_{m} = \tau \sum_{j=n,m} \Delta_{j} R_{j} \qquad (2.2.3)$$

where Δ_j and R_j are the channel width and count rate in channel j respectively. The limits of j are determined by inspection. This correction is used in the same way as before, with D_m in place of D in (2.2.2).

A subtlety occurs in practice that renders the correction more complicated. When many detectors exist it is not practical to have a separate input for each detector into the DAE. Instead an ENCODER is used to create a binary address which describes which detector fired. If the deadtime of the encoder is longer than that of the detector, then it is the encoder's deadtime which determines the detector deadtime. Moreover since the encoder can process only one event at a time, <u>all</u> the detectors that feed into that encoder are effectively dead when any one detector fires. Therefore in this situation the sum in (2.2.3) should include a sum over all channels which feed into a decoder. In that case if $R_{j,k}$ is the count rate in time channel j and encoder channel k, then the detector deadtime is given by

$$D_{m} = \tau \sum_{j=n,m} \sum_{k} \Delta_{j} R_{j,k} \qquad (2.2.4)$$

and the sum over k is over all detector channels that feed into the encoder. In the situation when (2.2.4) applies Δ_j is the encoder's deadtime, NOT the detector's. Hence even though the deadtime for an individual detector may be small, the grouping of say 50 detectors into an encoder results in a 50-fold enhancement in the count rate as far as deadtime is concerned. So the deadtime correction could be much larger than might be apparent from the count rate in an individual detector.

2.3 NORMALIZING TO THE INCIDENT BEAM MONITOR

Having corrected $I(Q_e)$ for deadtime, the next stage is to divide out the incident spectrum, which is measured by means of a MONITOR detector placed in the incident beam before the sample. The spectrum is divided out at this stage because small variations in moderator temperature and proton beam steering can modify the energy dependence of the spectrum from time to time at the 1-2% level. Since the calibration run must be performed before or after the sample run, it will only give a reliable result if the dependence on the incident spectrum is removed at the end of each run. The count rate in the monitor detector, which of course must also be corrected for deadtime, is proportional only to the incident spectrum and the monitor efficiency:

$$I_{m}(k_{e}) = \Phi(k_{e}) E_{m}(k_{e})$$
 (2.3.1).

Thus when used to normalize the scattered neutron count rate, a NORMALIZED count rate is obtained:

NRM(Q_e) = I(k_e)/I_m(k_e) = N
$$\Sigma(Q_e) \frac{E_d(k_e)}{E_m(k_e)} \Delta\Omega$$
 (2.3.2).

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A second measurement which is made at the same time as the scattered count rate from the sample is the fraction of neutrons transmitted by the sample. This number is monitored by a TRANSMISSION MONITOR, with efficiency $E_t(k_e)$, placed after the sample. Again this fraction cannot be measured directly, but must be determined by ratioing different runs, e.g. with and without sample. If $I_t(k_e)$ is the count rate in the transmission monitor, then this count rate is proportional to the incident flux, the transmission monitor efficiency and the TRANSMISSION of the sample, $T(k_e)$, which will be defined in the next section and is dependent on the total neutron cross section of the sample. Hence when normalized to the incident monitor, the transmitted intensity is given by

$$MON(k_e) = I_t(k_e)/I_m(k_e) = T(k_e) \frac{E_t(k_e)}{E_m(k_e)}$$
(2.3.3).

The transmission monitor is used to provide information on the neutron cross section and density of the sample: it can often confirm that the sample is what it is supposed to be.

There will then be a set of NRM files for every detector or detector group, and a MON file, for every run, whether it be sample, container, vanadium (calibration) or background. The stages covered by sections 2.2 and 2.3 are obtained by running the NORM program of section 3.6

2.4 MEASURING THE NEUTRON CROSS SECTION

a) The Total Neutron Cross Section

Neutron cross sections arise from two primary processes: scattering and capture. Provided there are no nuclear resonances in the energy region of interest, the probability for capture is inversely proportional to neutron velocity, i.e. proportional to neutron wavelength, and the constant of proportionality, usually defined for 2200m/s neutrons ($\lambda = 1.8$ Å), is called the CAPTURE CROSS SECTION, σ_a . There is a value of σ_a for every nucleus, although in many cases it is quite small or zero.

The SCATTERING CROSS SECTION, $\sigma_{s}(\lambda)$, on the other hand has no such simple dependence on energy or wavelength, because it represents the integral of the DIFFERENTIAL SCATTERING CROSS SECTION, $d\sigma/d\Omega$ at a particular wavelength over all scattering angles:

$$\sigma_{\rm s}(\lambda) = \int \frac{d\sigma}{d\Omega}(\lambda) \ d\Omega = 4\pi \int \frac{d\sigma}{d\Omega}(\lambda) \ \sin 2\theta \ d\theta \qquad (2.4.1)$$

As an example of the application of this result we will assume the static approximation applies and that the liquid under inverstigation is a hard sphere fluid of reduced density $\rho\sigma^3 = 0.5$, where σ , the hard core diameter, is 3.142Å. In that case S(Q) is known exactly in the Percus-Yevick approximation, and so (2.4.1) can be integrated numerically for all wavelengths, using

$$\frac{d\sigma}{d\Omega}(\lambda) = b^2 S(Q) = b^2 S(\frac{4\pi \sin\theta}{\lambda}) \qquad (2.4.2)$$

where b is the bound scattering length of the fictitious nucleus. The result is shown in figure 2.1: it will be seen that the scattering cross section for a material with structure will certainly deviate from the bound value. In particular the scattering cross section will display a similar structure to that seen in the differential scattering cross section.

For light atoms such as hydrogen and deuterium the consequences are quite drastic: the differential cross section falls dramatically with scattering angle at all but the longest neutron wavelengths, and the shape of the fall, which depends on the details of $S(Q,\omega)$, also varies with energy. Thus at low energies the neutron can excite only diffusional type motions, while at high energies the neutron can excite all possible modes, including dissociation of molecules if present. Thus the scattering cross section must vary between its so-called "BOUND" and "FREE" values as we go from low energy to high. The "bound" values are those quoted in tables of neutron scattering lengths such as the compilation by Koester et. al. [14] or Sears [15] and correspond to the case of an immovable nucleus: they are essentially nuclear parameters. The corresponding "free" values at high energies can be computed by multiplying the "bound" cross sections by the ratio

$$\left(\frac{A}{A+1}\right)^2$$

where A is the mass of the nucleus in question. This has the value 0.25 for hydrogen and 0.44 for deuterium, which tells us to expect a large fall in the scattering cross section of these materials with increasing energy. Such a fall is readily visible in the transmission data from hydrogen containing samples. For heavy atoms on the other hand this factor is close to unity and so within the likely accuracy of the transmission measurement is not significant.

In practice it is not possible to ever obtain the true bound cross section for a liquid containing light atoms since the low energy cross section is intimately related to the details of $S(Q,\omega)$ at small Q and ω . However the free cross section should appear as the asymptotic limit as $\lambda \Rightarrow 0$, since then all neutron capture processes have gone to zero.

Figure 2.1 also shows a second quantity, the TOTAL NEUTRON CROSS SECTION, $\sigma_{_{+}}(\lambda),$ where

$$\sigma_{t}(\lambda) = \sigma_{s}(\lambda) + \sigma_{a}(\lambda) \qquad (2.4.3)$$

In this case it has been assumed that the fictitious material has a capture cross section $\sigma_a = 0.4$ at $\lambda = 1.8$ Å. It can be seen that the approximation of treating the total cross section as a sum of a constant plus linear term in λ will be inadequate for accurate work at long wavelengths.

If nuclear resonances are present in the total cross section then the above treatment must be modified. A nuclear resonance occurs when the neutron excites the nucleus to an excited state, and so is (slightly) analogous to an absorption edge in X-ray scattering. However the possible nuclear states are quite complicated in general and can be accompanied by several processes, including the emission of a γ photon. Usually both scattering and capture are not simple at a resonance, and full treatment of the effects of this on the data analysis are beyond the present purpose, and certainly are not included in any of the correction routines. At present the only recourse is to ignore the energy regions where resonances occur and hope that there is sufficient angular coverage that all Q values can be obtained away from a resonance. Figure 2.2 shows the measured total cross section for a solution of ¹⁴⁸Sm-perchlorate in D₂0. Note the strong resonance at $\lambda \approx$ 1Å, corresponding to a nuclear resonance in a ¹⁴⁹Sm impurity. This resonance was so broad that analysis of these data to TDCS was impossible. Appendix E lists the more commonly occurring resonances.

b) Measuring the Neutron Cross Section

We have seen above that the total cross section depends on the STRUCTURE and DYNAMICS of the sample, which in turn relates to the thermodynamic state of the sample. Therefore it strictly has to be measured for each and every sample, and this is why a transmission monitor is placed after the sample. In practice it is difficult to measure the total cross section on an ABSOLUTE scale with the necessary precision, so the transmission monitor is used to obtain the ENERGY DEPENDENCE of the total cross section, with absolute values obtained by reference to the known free and bound values at short and long wavelengths. Note that using a separate experiment to measure transmissions is very time consuming and not necessarily useful since it is not always possible to reproduce the exact conditions of the experiment at a later time.

If the sample is a flat plate which uniformly covers the beam then the TRANSMISSION of the sample is given simply by

$$T(k_{\rho}) = \exp\{-\rho\sigma_{+}(\lambda)L\}$$
(2.4.4)

where ρ is the number density and L is the neutron flight path within the sample. Hence if T(k_e) can be obtained from monitor ratios as described in section 2.3 then it is a trivial inversion to obtain σ_t .

For any other shape of sample however the flight path through the sample is a function of position within the beam. Figure 2.3 shows the geometry of the problem in this case. If x measures the perpendicular distance from one edge of the beam then L becomes a function of x and the transmission in this case can be written as

$$T(k_e) = \int_0^{W} \exp\{-\rho\sigma_t(\lambda)L(x)\} dx / W \qquad (2.4.5)$$

where W is the width of the beam. In this case there is no simple inversion to σ_t , which has to be obtained by trial and error. However if a Newton-Raphson technique is used to do this convergence to a solution is quite rapid. Further efficiency can be gained by noting that only a finite number of terms in the exponential are needed. Writing $\mu = \rho \sigma_t$, we see that

$$T(k_{e}) = 1 - \mu M_{1} + (\mu M_{2})^{2} - (\mu M_{3})^{3} + \dots \qquad (2.4.6)$$

where

$$M_{n} = \frac{1}{n!} \int_{0}^{W} L^{n}(x) dx / W$$
 (2.4.7)

The latter integrals are dependent only on the shape of the sample and not on neutron energy and so need only be evaluated once.

If the sample is contained in a holder then the monitor ratio that is used is the ratio of sample plus can to can alone. In that case the measured transmission is given by

$$T(k_{e}) = \frac{\int_{0}^{W} \exp\{-[\mu_{S}L_{S}(x) + \mu_{C}L_{C}(x)]\} dx}{\int_{0}^{W} \exp\{-\mu_{C}L_{C}(x)\} dx}$$
(2.4.8)

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where the capital suffix S applies to the sample and C applies to the container. Similar expansions of the top exponential term can be used as before. However the values of μ_{C} must be supplied separately or obtained in a separate transmission experiment on the container alone. Finally note that if the beam profile is not uniform a simple modification of the above formulae is needed: because the profile function can be included in the moments (2.4.7) it does not lead to any increase in computing time.

2.5 ATTENUATION AND MULTIPLE SCATTERING CORRECTIONS

Much of the underlying methodology for calculating ATTENUATION and MULTIPLE SCATTERING corrections has been covered in numerous previous publications and so will not be repeated here. Although there are a number of approaches to the calculation, the formalism of Soper and Egelstaff [16], which uses numerical integrations to estimate corrections for the cylindrical geometry, is used here, because it is written in a sufficiently general form to allow corrections for furnaces and radiation shields if they are sufficiently absorbing or scattering to require a separate correction. These latter corrections will be the subject of the next section.

The most common case is that of a sample contained in a holder. In that case two measurements are needed: one for the sample plus can, $I_{SC}(k_e)$, and one for the can alone, $I_C(k_e)$. These two quantities are each affected by attenuation and multiple scattering so our simple definition (2.1.1) has to be modified for the general case:

$$I_{SC}(k_e) = \Phi(k_e) [N_S \Sigma_S(Q_e) A_{S,SC} + N_C \Sigma_C(Q_e) A_{C,SC} + M_{SC}(k_e)]$$

$$\times E_d(k_e) \Delta \Omega \qquad (2.5.1)$$

$$I_{C}(k_{e}) = \Phi(k_{e})[N_{C}\Sigma_{C}(Q_{e})A_{C,C} + M_{C}(k_{e})]E_{d}(k_{e}) \Delta\Omega \qquad (2.5.2)$$

Here N_S and N_C are the number of atoms in the sample and container respectively, while $A_{S,SC}$, $A_{C,SC}$ and $A_{C,C}$ are the usual Paalman and Pings [17] attenuation factors. For example $A_{S,SC}$ is the attenuation factor for scattering in the sample and attenuation in the sample plus container. The quantities M_{SC} and M_C are the total multiple scattering differential scattering cross sections for sample plus can and can alone respectively. Note that the multiple scattering terms cannot in general be included in first scattering terms because they are not linear in N_S and N_C . Both attenuation and multiple scattering terms are functions of neutron energy by virtue of the energy dependence of the scattering and capture cross sections.

The attenuation factors depend only on the sample geometry and the total neutron cross section and so can be evaluated exactly in the static approximation, within the limits of numerical precision.

On the other hand the multiple scattering terms can never be evaluated very accurately since in principle they require detailed knowledge of the sample's structure (and dynamics if the inelastic scattering is significant). The method of calculation normally employed makes use of the measured total transmission cross section to give the scattering cross section at each neutron energy, but then assumes the scattering at this energy to be isotropic with scattering angle. This is called the ISOTROPIC approximation. (This is NOT the same as assuming that the multiple scattering is isotropic, an approximation introduced by Blech and Averbach [18] which is not needed in practice.) Sears [19] has described how the isotropic approximation can be improved although direct calculation with a Monte Carlo algorithm which includes the measured TDCS is probably the best way to cope with multiple scattering from thick samples. Given the speed of modern computers this is not an unreasonable approach. Howells has a program, ELMS, (Elastic Multiple Scattering) which does this and it can be made available if there is sufficient demand.

There is a general consensus that the isotropic approximation is expected to be acceptable if the sample scatters less than ~20% of the incident beam, although there has never been a quantitative study of the size of sample at which this approximation starts to introduce a serious systematic error in the measured structure factor. Clearly it greatly assists the multiple scattering problem if the container can be made of an incoherent scatterer, such as vanadium or zirconium-titanium, or of an amorphous material, such as silica, since Bragg peaks introduce a severe difficulty to any quantitiative multiple scattering calculation.

In summary, to be confident that multiple scattering will not introduce too large a systematic error it is a useful rule of thumb to ensure that the sample scatters between 10% and 20% of the incident neutron beam.

2.6 FURNACE CORRECTIONS

If the sample and container are in a furnace and the furnace element contributes significantly to the attenuation and scattering processes then three measurements are needed: sample plus can plus furnace, $I_{SCF}(k_e)$, empty can plus furnace, $I_{CF}k_e$), and furnace alone, $I_C(ke)$. These three quantities are related to the corresponding differential cross sections by:

$$I_{SCF}(k_e) = \Phi(k_e) [N_S \Sigma_S(Q_e) A_{S,SCF} + N_C \Sigma_C(Q_e) A_{C,SCF} + N_F \Sigma_F(Q_e) A_{F,SCF} + M_{SCF}(k_e)] E_d(k_e) \Delta \Omega$$
(2.6.1)

$$I_{CF}(k_e) = \Phi(k_e) [N_C \Sigma_C(Q_e) A_{C,CF} + N_F \Sigma_F(Q_e) A_{F,CF} + M_{CF}(k_e)]$$

$$\times E_d(k_e) \Delta \Omega \qquad (2.6.2)$$

$$I_{F}(k_{e}) = \Phi(k_{e})[N_{F}\Sigma_{F}(Q_{e})A_{F,F} + M_{F}(k_{e})] E_{d}(k_{e}) \Delta\Omega \qquad (2.6.3)$$

The attenuation factors have the same definition as before, e.g. $A_{S,SCF}$ is the attenuation factor for scattering in the sample and attenuation in the sample, can and furnace. Similarly the multiple scattering cross sections have an equivalent definition as before. N_F is the number of furnace atoms in the incident beam.

2.7 VANADIUM OR STANDARD SAMPLE CALIBRATION

A unique characteristic of neutron scattering is the ability to perform an independent estimate of the instrumental calibration. This calibration consists of the unknown quantities, either

$$F_1(ke) = \Phi(k_0) E_d(k_0) \Delta \Omega \qquad (2.7.1)$$

in sections 2.1, 2.5 and 2.6 above, or

$$F_2(k_e) = \frac{E_d(k_e)}{E_m(k_e)} \Delta\Omega$$
(2.7.2)

in section 2.3. With these definitions we can for example rewrite equations (2.5.1) and (2.5.2) which become, after normalizing to the monitor:

$$NRM_{SC}(Q_{e}) = F_{2}(k_{e})[N_{S}\Sigma_{S}(Q_{e})A_{S,SC} + N_{C}\Sigma_{C}(Q_{e})A_{C,SC} + M_{SC}(k_{e})]$$
(2.7.3)

$$NRM_{C}(Q_{e}) = F_{2}(k_{e})[N_{C}\Sigma_{C}(Q_{e})A_{C,C} + M_{C}(k_{e})]$$
(2.7.4)

Estimation of these calibration constants is usually achieved with a standard vanadium sample because vanadium has a largely incoherent cross section and so it is believed that the differential cross section for vanadium can be estimated reasonably accurately, an assumption which of course is difficult to check! As described in section 2.9 the inelasticity correction has two principal terms, one relating to scattering angle, the other proportional to temperature and inversely proportional to neutron energy, and since energy is being varied in a TOF experiment it is crucial to estimate this latter term correctly. Figure 2.4 shows the estimated single atom differential cross section at 20° scattering angle for a free vanadium nucleus at two temperatures. At the time of writing experiments are planned on LAD to determine if the estimated temperature dependence is indeed observed.

The normalized spectrum from vanadium is defined by

$$NRM_{V}(Q_{e}) = F_{2}(k_{e})[N_{V}\Sigma_{V}(Q_{e})A_{V,V} + M_{V}(k_{e})]$$
(2.7.5)

The quantity in square ([...]) brackets is the vanadium differential cross section which is estimated using exactly the same methods as in the previous section. This leads to a VANADIUM CALIBRATION, $CAL_V(Q_e)$, where

$$CAL_V(Q_e) = NRM_V(Q_e) / [N_V \Sigma_V(Q_e) A_{V,V} + M_V(k_e)] = F_2(k_e).$$
 (2.7.6)

In fact scattering from vanadium exhibits the usual statistical noise plus weak Bragg reflections due to the small coherent scattering amplitude. Since the data from the sample must be divided by CAL_V it is obviously undesirable to transfer either effect to the sample data, so an expansion in terms of Chebyshev polynomials is fitted to NRM_V with zero weighting of points in the region of Bragg peaks. This has the effect of smoothing out the Bragg peaks and noise without introducing any appreciable artifacts. However it is clearly important to check that this smoothing has in fact removed only the noise from NRM_V and none of the underlying structure. In any case whether to smooth or not is an option which can be overridden if needed. The computer programs associated with this section are described in section 3.9.

2.8 BASIC ALGORITHM TO DETERMINE DIFFERENTIAL CROSS SECTION

All of the main quantities needed to calculate the differential cross section (DCS) from the TOF diffraction data of the sample have now been described, and the algorithm ANALYSE (see section 3.10) is used to perform this operation. The stages are described in sequence for the case of a sample held in a can. Note that the arrow \Rightarrow is used to indicate that the result of an operation on the left hand side is placed in the quantity on the right. The symbol TOTAL applies to the total scattering, SINGLE applies to single scattering, and the suffixes S, C and B refer to sample, can and background.

1) Subtract background

$$TOTAL_{SC}(Q_e) = NRM_{SC}(Q_e) - NRM_B(Q_e)$$
$$TOTAL_C(Q_e) = NRM_C(Q_e) - NRM_B(Q_e)$$

2) Normalize to calibration

$$TOTAL_{SC}(Q_e) \Rightarrow TOTAL_{SC}(Q_e)/CAL_V(Q_e)$$
$$TOTAL_C(Q_e) \Rightarrow TOTAL_C(Q_e)/CAL_V(Q_e)$$

3) <u>Subtract multiple scattering</u>

$$SINGLE_{SC}(Q_e) = TOTAL_{SC}(Q_e) - M_{SC}(k_e)$$

 $SINGLE_C(Q_e) = TOTAL_C(Q_e) - M_C(k_e)$

4) Apply absorption corrections

$$SINGLE_{S}(Q_{e}) = \frac{\left(SINGLE_{SC}(Q_{e}) - SINGLE_{C}(Q_{e}) \frac{A_{C,SC}}{A_{C,C}}\right)}{A_{S,SC}}$$

5) Divide by number of atoms in sample

$$DCS(Q_e) = \frac{SINGLE_S(Q_e)}{N_S}$$

If the furnace correction is being applied then the following modified sequence is used:-

1) Subtract_background

$$TOTAL_{SCF}(Q_e) = NRM_{SCF}(Q_e) - NRM_B(Q_e)$$
$$TOTAL_{CF}(Q_e) = NRM_{CF}(Q_e) - NRM_B(Q_e)$$
$$TOTAL_F(Q_e) = NRM_F(Q_e) - NRM_B(Q_e)$$

2) Normalize to calibration

$$TOTAL_{SCF}(Q_e) \Rightarrow TOTAL_{SCF}(Q_e)/CAL_V(Q_e)$$
$$TOTAL_{CF}(Q_e) \Rightarrow TOTAL_{CF}(Q_e)/CAL_V(Q_e)$$
$$TOTAL_F(Q_e) \Rightarrow TOTAL_F(Q_e)/CAL_V(Q_e)$$

3) Subtract multiple scattering

$$SINGLE_{SCF}(Q_e) = TOTAL_{SC}F_F(Q_e) - M_{SCF}(k_e)$$

$$SINGLE_{CF}(Q_e) = TOTAL_{CF}(Q_e) - M_{SC}(k_e)$$

$$SINGLE_F(Q_e) = TOTAL_F(Q_e) - M_F(k_e)$$

4) Subtract furnace from sample and can

$$\text{SINGLE}_{\text{SC}}(\text{Q}_{e}) = \left(\text{SINGLE}_{\text{SCF}}(\text{Q}_{e}) - \text{SINGLE}_{\text{F}}(\text{Q}_{e}) \frac{\text{A}_{\text{F},\text{SCF}}}{\text{A}_{\text{F},\text{F}}} \right)$$

$$SINGLE_{C}(Qe) = \left(SINGLE_{CF}(Qe) - SINGLE_{F}(Qe) \frac{A_{F,CF}}{A_{F,F}}\right)$$

5) Apply absorption corrections

$$SINGLE_{S}(Q_{e}) = \frac{\left(SINGLE_{SC}(Q_{e}) - SINGLE_{C}(Q_{e}) \frac{A_{C,SCF}}{A_{C,CF}}\right)}{A_{S,SCF}}$$

5) <u>Divide by number of atoms in sample</u> $DCS(Q_e) = \frac{SINGLE_S(Q_e)}{N_S}$

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2.9 INELASTICITY (PLACZEK) CORRECTIONS

Equations 1.2.9, 1.2.11 and 1.2.12 serve to define the inelasticity correction, $P(Q_e, \theta)$ in a TOF diffraction experiment: $P(Q_e, \theta)$ represents the difference between the static approximation F(Q) and the TDCS, $\Sigma(Q_e)$. Strictly speaking to obtain $P(Q_e, \theta)$ one needs to know $F(Q, \omega)$ which preempts the need for a diffraction experiment since then the static structure factors (1.3.4) would be obtainable by direct integration of $F(Q, \omega)$. Obviously this is an impractical proposition, mostly because of the time that would be required in measuring the complete dynamic structure factor.

However in 1952 Placzek [5] showed that for nuclei much more massive than the neutron the correction adopts a form which is essentially independent of the detailed dynamics, and is related only to the nuclear mass, the sample temperature, the incident neutron energy, and the geometry and efficiency of the neutron detection process. Moreover at neutron energies well above those of any bound states that occur in the sample he showed that the correction to the interference term $S_{\alpha\beta}(Q)$ is zero to first order. These conclusions arose from the fact that the first two moments of $S(Q,\omega)$ can be estimated more or less exactly:

$${}^{1}S_{\alpha}(Q) = \int_{-\infty}^{\infty} \omega S_{\alpha}(Q,\omega) \, d\omega = \frac{\hbar Q^{2}}{2M_{\alpha}}$$
(2.9.1)

$${}^{2}S_{\alpha}(Q) = \int_{-\infty}^{\infty} {}^{\infty}\omega^{2}S_{\alpha}(Q,\omega) d\omega = \frac{k_{B}ThQ^{2}}{M_{\alpha}} + \frac{h^{2}Q^{4}}{4M_{\alpha}^{2}} \qquad (2.9.2)$$

and

$${}^{1}S_{\alpha\beta}(Q) = \int_{-\infty}^{\infty} S_{\alpha\beta}(Q,\omega) \, d\omega = 0 \qquad (2.9.3)$$

Here (2.9.1) and (2.9.3) are exact results, but (2.9.2) strictly only applies to a classical fluid.

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Unfortunately Placzek's results cannot always be applied directly to thermal neutron diffraction because the conditions under which they apply are often not obtained. In particular the sampling factor (equation 1.2.10) rapidly drops to zero as k' becomes less than k. Hence as in the fixed wavelength reactor experiment the scope for exciting high vibrational levels in a molecule depends on the incident energy. There is an extensive literature on the attempts to modify the original Placzek approach to include the cases where the system is only partly excited by the neutron. See for example the papers by Powles [6-11] and Egelstaff [4,12,13] and references therein. All of these involve lengthy algebra, and while there seems to be general agreement in the case of the self scattering for an atomic fluid the correct form of the terms for molecules, which involve a 0-depedent effective mass is still disputed. The advantage of the Placzek type of expansion is that in enables one to understand by inspection the effect of various instrument parameters on the inelasticity correction, in particular the path ratio, sample temperature, detector efficiency, and flight incident spectrum shape,.

As an example below is quoted the Egelstaff [4] formula for the self scattering inelasticity correction for an atomc fluid of nuclear mass M at temperature T, for a 1/E incident spectrum, at incident enrgy E_0 :

$$P(Q_e, \theta) = -\frac{2ym}{M}X + \frac{m}{M}\frac{k_BT}{2E_0}Y$$
 (2.9.4)

where

$$X = \left[\frac{aA + a + 2}{a + 1}\right],$$

$$Y = \left[1 - 2y + \frac{4y(Aa+3)}{a+1} - \frac{2y\{a^{2}B - 6a(A+1) - 3(5a-1)\}}{(a+1)^{2}}\right]$$

and $y = \sin^2 \theta$, m = mass of neutron, a = 1/R = L/L', and A and B are detector constants:

$$A = 1 - \frac{\varepsilon}{k_e} \left[\frac{1}{E_d(k_e)} - 1 \right]$$
$$B = A + \left(\frac{\varepsilon}{k_e} \right)^2 \left[\frac{1}{E_d(k_e)} - 1 \right]$$

with

 $E_d(k_e) = 1 - \exp(-\varepsilon/k_e)$

and ϵ a detector constant which determines the efficiency. Further terms are needed in the Maxwellian region.

This formula gives the quantitative behaviour of the Placzek correction at large neutron energies, but also indicates qualitatively what will happen at all energies. In particular we see that the correction gets notably larger at low neutron energies, high temperatures, and small nuclear masses. Hence the often quoted maxim that the ideal diffraction experiment is performed at high energies and small scattering angles. The routine PLATOM described in Section 3.11 uses a modification of the Powles [10] formula derived by Howe, McGreevy and Howells [20]. Detailed comparison of this formula with the numerical methods described below shows some quantitative discrepencies which are not understood at the present time.

An alternative to the Placzek expansion is to define a model neutron scattering law $S(Q,\omega)$ which incorporates the properties defined in (2.9.1) and (2.9.2), or any alternative scattering laws which are know to represent $S(Q,\omega)$ correctly in the region of (Q,ω) space explored by experiment, and then perform the integral (1.2.9) numerically. This method is most useful when a particular scattering law is known to apply, such as that for a diffusing particle or for a rigid molecular rotor, or when the nuclear mass is small: in all these cases the Placzek expansion is not helpful. Figure 2.5 shows a comparison between the numerical integration of the free particle $S(Q,\omega)$ (ideal gas formula) and equation (2.9.4) for a nucleus of mass 51 (vanadium) and scattering angle of 20°. Note that at this small angle the expansion formula gives good agreement with the numerical calculation: at larger angles such as 90° and 150° the agreement is much worse, although in every case the high Q limit is the same. Figure 2.6 shows the numerical calculation for a mass 2 particle at two tempertures. A pronounced temperature effect is seen. Moreover the correction now has a clear hump at $-2Å^{-1}$ corresponding to the derivative of the incident spectrum. Results such as this can only be obtained by numerical integration.

Two computer programs exist to perform these numerical integrations: PLACID calculates the Placzek correction for an ideal gas, i.e. treating the particle as free. The other program is called PLATOF and it allows the user to input a table of $S(Q,\omega)$ values from a separate calculation. Both programs can be made available for general use if there is sufficient demand.

2.10 MERGING THE DATA TO FORM THE STRUCTURE FACTOR

Typically one will record the TDCS at several scattering angles in a TOF diffraction experiment. On LAD there are currently 14 groups of detectors, 7 on each side of the instrument. Which of these groups are to be combined requires a decision by the experimentalist. A typical approach might be as follows:

a) Correct each angle for inelasticity effects, particularly in the self scattering.

b) Plot all the spectra on top of each other

c) For each group choose a range of Q values over which this spectrum overlaps with at least one spectrum from a neighbouring group at higher or lower scattering angle, and ignore those spectra which clearly disagree with the others. Obviously this is a highly subjective point in the analysis, but if all has gone well with the experiment it should be fairly obvious where the overlaps occur. The object is to avoid combining different detector banks where there are clearly differences due to say not being able to perform the Placzek correction accurately, such as occurs with light atoms such as deuterium.

d) Merge the selected spectra over the selected Q range, using the MERGE command, see section 3.12 and below.

e) Finally perform any remaining normalizations as needed such as removing the incoherent scattering and dividing out the scattering cross section. The result should either be in the units of differential cross section (barns per steradian per $atom/4\pi$) or have dimensionless units as a structure factor, S(Q).

The merging of spectra is achieved by weighting each spectrum with the intensity with which it was measured. The weighting function is obtained from the corrected intensity data of the vanadium sample contained in the quantity

$$W_{j}(Q_{e}) = CAL_{V}(Q_{e}) * I_{m}(k_{e})$$
 (2.10.1)

where the suffix j is used to label the j'th group of detectors. Hence if $\Sigma_j(Q_e)$ is the measured differential cross section for the j'th group, the merged differential cross section is obtained by forming the sum

$$\Sigma_{M}(Q_{e}) = \frac{\sum \Sigma_{j}(Q_{e}) * W_{j}(Q_{e})}{\sum W_{j}(Q_{e})}$$
(2.11.1)

This is achieved with the MERGE command, section 3.12

2.11 ANALYSIS TO PAIR CORRELATION FUNCTION

The inversion of the S(Q) data to pair correlation function, g(r), i.e. inversion of equation 1.3.2, can be done by trivial Fourier transform. Routines GTOS and STOG (see section 3.13) are available to do this, and will allow the inclusion of a window or modification function if needed.

However such direct Fourier transforms will inevitably lead to spurious structure in the calculated distribution due to the finite extent and statistical noise present in the data. This has been the subject of a number of reports, including a preliminary one from the Rutherford Appleton Laboratory by Soper [21], which was presented at the ICANS-X meeting in October 1988. In this new method it is proposed to limit the fluctuations in r(g(r)-1) with increasing r to those that are compatible with the observed width of the peaks in S(Q). In this way the noise and truncation of the data are not reproduced in the simulated pair correlation functions, at the same time that excellent fits to the measured data are obtained. At the time of writing a full account of this technique has still to be prepared for publication, and the program, called MCGOFR, is not in a particularly user friendly form, so at present it must be run under careful supervision. Even so it is fully intended to make this program generally available to anyone interested in using it. The basic philosophy of the approach is described in Appendix C, which is a reproduction of the ICANS paper in full.



TITLE : Total hard sphere cross section

Figure 2.1 Calculated scattering and total cross section for a hard sphere fluid of density $\rho\sigma^3 = 0.5$, with $\sigma=3.142$. The fluid is assumed to have unit scattering cross section per atom, and the capture cross section is 0.4 at 1.8Å. The crosses correspond to a structureless fluid



TITLE : Sm148 perchlorate in D20

Figure 2.2 Measured transmission cross section for a solution of 148 Sm-perchlorate in D₂O. Note the pronounced neutron resonance near λ =1Å which arises from a 149 Sm impurity. Higher energy resonances are visible at shorter wavelengths.



Figure 2.3 Geometry of transmission problem for an arbitrary shaped sample



TITLE : Placzek correction for vanadium at 20 deg.

Figure 2.4 Calculated TOF recoil correction (1+P) for a free vanadium nucleus at two temperatures: 20K and 300K, and at a scattering angle of 20°. Note the large temperature effect at small Q values.



TITLE : Vanadium Placzek correction at 20 deg.

Figure 2.5 Comparison of numerical calculation of recoil correction for a vanadium nucleus at T=300K and scattering angle 20°, with Egelstaff's approximate formula, equation (2.9.4), which does not have the correct spectral dependence at small Q. Even so it gives good agreement at all Q values



TITLE : Placzek correction for deuterium at 20 deg.

Figure 2.6 Recoil correction for a free deuterium atom at 20K and 300K. The scattering angle is 20°. Note again the large temperature effect at small Q, and that a pronounced structure appears due to the substantial energy transfers that take place in the scattering process,