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Multiple Scattering Correction to Neutron Diffraction Data of Isotropic Systems Using Optimized Monte Carlo Techniques*

BY D. F. R. MILDNER,† C. A. PELIZZARI‡ AND J. M. CARPENTER‡

Nuclear Engineering Department, University of Michigan, Ann Arbor, Michigan 48105, *USA*

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A Monte Carlo computer simulation of a neutron diffraction experiment is presented which is of particular use for systems where the structure factor modulates considerably. The program has been optimized by forcing successive scattering events to occur within the specimen under study, and by calculating the score into the detector at each scattering point to allow each simulated path to contribute to the detected scattered intensity. A method of determining the multiple scattering correction for time-of-flight diffraction is shown, and the results of such an analysis are presented for a specimen with intense forward angle scattering and strongly varying $S(Q)$.

1. Introduction

The diffraction of radiation is used for the study of the structure of isotropic systems (randomly oriented polycrystals, liquids, glasses and non-crystalline materials), and the intensity of the scattered radiation as a function of scattering angle gives a measure of the relative ordering of the atoms within the system (Wright, 1974). Various review papers (Enderby, 1968; Leadbetter, 1973; Page, 1973) have described methods used for the analysis of neutron diffraction data of such systems. Coherent scattering by the sample causes the multiple scattering also to be dependent on the scattering angle, so that accurate techniques must be available for correcting the measured data for neutrons scattering more than once within the sample, in order to obtain reliable data from which the static structure factor may be extracted.

A simple method used for correcting for multiple scattering is one in which the loss of neutrons which are first scattered into the detector direction but are later scattered from that path are compensated by the gain of neutrons which are not primarily scattered into the detector direction but are scattered later into that direction. Effectively this correction is similar to the attenuation correction of the primary beam, so that it is not angularly dependent, and it has limited application in diffraction experiments.

An analytic method which has some degree of angular dependence is based on the quasi-isotropic approximation, an extension of a technique suggested by Vineyard (1954). In cases where the angular distribution of primary scattered neutrons is nearly isotropic, it is reasonable to assume that the ratio of successive scattering probabilities is a constant, *i.e.* successive probabilities form a geometric progression. Provided that the probabilities of single and double scatter may be calculated, then the probability of multiple (more than one) scattering may be estimated. The formulation for multiple scattered intensity in terms of orders of scattering may be extended, since the distribution of higher order scattered neutrons tends to become isotropic, and has been evaluated for anisotropic, elastic scattering in plane samples (Cocking & Heard, 1965). It is found that even for systems where the scattering has some angular dependence, the twice scattered component has a roughly isotropic distribution. Additionally the approximation has been shown to give reasonable agreement with the observed multiple scattering for simple systems (Wignall, 1967). However the second scattering component is expressed in terms of an integral which in general may be complicated to perform except for simple geometries. This method has also been extended to inelastic scattering (Cocking, 1968; Demichelis, Raia & Tartaglia, 1975).

Generally neutron diffraction data is taken relative to the scattering from a reference material whose cross sections are well understood, and vanadium is a usual choice. Since the scattering from vanadium is predominantly incoherent and isotropic, Vineyard's method works well for multiple scattering from vanadium. A numerical integration computer program is used to obtain the second scattering probability for an infinite vanadium slab (Agrawal, Das & Mueller, 1971; Copley, Price & Rowe, 1973).

The analytical methods break down completely when the multiple scattering becomes strongly angular dependent, and the question whether *any* corrections can be applied becomes important; that is, whether corrections actually improve the data. While the analytic approximations may be easy to handle, these must at the same time be useful approximations which actually work. The Monte Carlo technique allows a check on the analytic approximations which have been used, and in addition is useful for situations where the scattering law is an awkward function or cannot be expressed analytically. In these situations it is often the

* This work was supported in part by NSF grant GK 35901.

† Present address: Research Reactor Facility, University of Missouri, Columbia, Missouri 65201, USA.

‡ Present address: Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA.

case that the only useful multiple scattering corrections that may be applied are those derived from a Monte Carlo simulation. In addition such a technique allows the real experiment to be analyzed for optimum sample size and geometry, and also allows experimental conditions such as collimation to be investigated. In the present work we discuss an optimized Monte Carlo simulation of neutron diffraction measurements in which the scattering is assumed to be entirely elastic.

2. The Monte Carlo technique

In any computer diffraction simulation, the angles of scatter are determined through the static structure factor $S(Q)$ which is given as input to the program. However, the determination of the position of the scattering events is worthy of more than a cursory glance, for the path length l_n in the direction $\mathbf{\Omega}_n$ between the $(n-1)$th scattering event and the nth scattering event should be selected efficiently. Fig. 1 schematically illustrates multiple scattering events. Nakai (1974) divided the distance t_n from the position $\mathbf{r}_{n-1}$ of the previous scattering point to the sample surface in the direction $\mathbf{\Omega}_n$ into thin slices of thickness Δt_n. The fate of the neutron after entering a slice is determined by the choice of a random number R_l, in the interval (0,1). For $R_l < \Sigma_T \Delta t_n$, an interaction occurs within the slice; the type of interaction is determined by the relative strengths of the coherent and incoherent scattering and the absorption cross sections. For $R_l > \Sigma_T \Delta t_n$, the neutron enters the next slice, and the process is repeated. The number of slices must be determined by considering the thickness and total cross section of the specimen.

This process is somewhat inefficient and the interaction rate along a path length t_n may alternatively be determined from the path length distribution function $F(l)$ given by

$$F(l) = \int_0^l \exp(-\Sigma_T x)\Sigma_T \mathrm{d}x, \qquad (1)$$

which is equivalent to summing over the slices as in Nakai's approach.

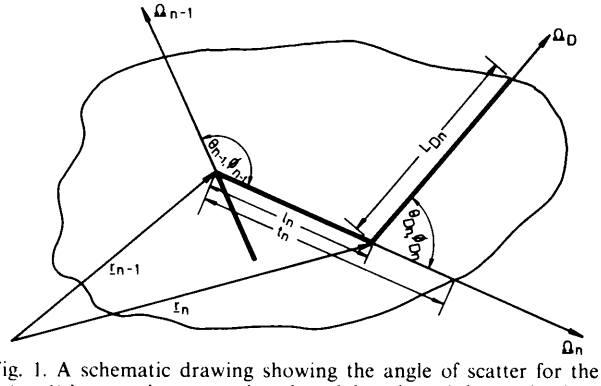

Fig. 1. A schematic drawing showing the angle of scatter for the $(n-1)$th scattering event, the nth path length, and the scoring into the detector for the nth scattering event.

The path length to the next interaction point is determined by the random number R_l in the interval (0,1), *viz.*

$$R_l = F(l) = 1 - \exp(-\Sigma_T l) \qquad (2)$$

so that the path length is given by

$$l = -\frac{1}{\Sigma_T} \log(1 - R_l). \qquad (3)$$

A direct simulation such as Neutron Elastic Scattering Simulation (NESS) (Meardon, 1973) uses this distribution, and since the random number is selected from a uniform distribution in the interval (0,1), then the equation (3) may be replaced by

$$l = -\frac{1}{\Sigma_T} \log R_l. \qquad (4)$$

There are various disadvantages to this method of pursuing the calculation;

(1) Only a fraction Σ_s/Σ_T of the interactions are scattering events, and it is scattering which is exclusively of interest in a diffraction experiment, since absorbed neutrons are not detected;

(2) The path length distribution (equation 1) is such that its cumulative value is unity only at an infinite path length; that is, some interaction points would be outside the sample, and therefore no such interaction occurs and the neutron escapes from the sample.

(3) Most importantly, the majority of scattered neutrons escape from the sample and miss the detector altogether; the histories contribute nothing to the calculation except to evaluate the proportion of neutrons that strike the detector.

Consequently even for a 10% scattering sample with no absorption, of the order of 10% of the neutrons leave the sample after one scatter, about 1% after two scatters, *etc.* Not only are a great number of neutron histories required to be followed for the statistics of the multiply scattered neutrons to be adequate, but also only a small proportion of these are scattered into detector directions. Hence more refined Monte Carlo techniques must be used so that each simulated path contributes to the scattered intensity into the detector.

Our procedure follows the work of Bischoff (1970) and Bischoff, Yeater & Moore (1972) in which the contribution of each simulated path is evaluated by the computation of a score in the detector at each scattering point. The Bischoff program has been extended by Copley (1974) to give the general program *MSCAT* which is useful for correcting inelastic scattering data. A similar program *DISCUS* has been written by Johnson (1974). These programs are wasteful when only diffraction experiments are considered and we have pared Copley's program of all references to inelastic events to make it most efficient for assumedly elastic scattering. This elastic version of *MSCAT* will be most useful for the evaluation of corrections to diffraction data of isotropic systems whose structure

factor is a continuous function over the entire distribution of scattering angles. Though much of the scattering at larger angles will in fact be inelastic, the static approximation allows total diffraction data to be treated as entirely elastic scattering with suitable corrections (for a review, see Wright, 1974).

Consequently the algorithm used is still that of Bischoff; that is, each collision of the neutron is forced both to occur within the sample and to be a scattering event, and the probability of each neutron being scattered into each detector after every collision is determined. This technique allows every neutron at every collision to contribute to the angular scattered intensity or score at every detector, and improves the convergence of the calculation. These forced events are compensated by an adjustment to the statistical weight of the neutron at each scattering event. While the relative numbers of multiply and singly scattered neutrons remain the same, the statistics of the multiply scattered neutrons are built up more efficiently.

The various methods available for reducing the variances in Monte Carlo simulations of neutron scattering experiments have been reviewed by Bischoff (1970) and Kalli (1972, 1973). In our program successive scatterings are forced to occur and the neutron statistical weight is decreased rapidly until it falls below a certain cut-off weight at which point the history is terminated by a game of 'Russian roulette'; that is, there is a half chance that the neutron is 'lost' and a new history started, and a half chance that the neutron weight is incremented by a factor of two and the history is continued. This procedure has the attraction of concentrating the low-weighted events in a relatively small number of neutrons, and need not introduce any biasing of the result.

3. The optimized Monte Carlo simulation

The simulation traces many histories for neutrons of the same incident neutron energy, and the probability that a neutron is scattered into a detector direction is obtained from the summation of the probabilities of neutrons being scattered into that detector direction for all orders of scatter. The algorithms for following a neutron's history between successive scattering events and for scoring into each detector are given, and the various steps are analyzed for optimization.

A. Path length distribution

After the $(n-1)$th scattering event at $\mathbf{r}_{n-1}$ into the direction $\mathbf{\Omega}_n$, the distance t_n to the exit surface in the direction $\mathbf{\Omega}_n$ is computed (see Fig. 1). The escape probability of the neutron is simple $\exp(-\Sigma_T t_n)$, and the collision probability $1-\exp(-\Sigma_T t_n)$. Hence the scattering probability is $(\Sigma_s/\Sigma_T)[1-\exp(-\Sigma_T t_n)]$. The scattering event is forced to occur within the sample by selecting the nth collision point from the cumulative distribution function for path lengths,

$$F(l_n)=\frac{\int_0^{l_n}\exp(-\Sigma_T l)\mathrm{d}l}{\int_0^{t_n}\exp(-\Sigma_T l)\mathrm{d}l}. \tag{5}$$

That is, the scattering event is forced to occur at a distance $l_n < t_n$ from $\mathbf{r}_{n-1}$ in the direction $\mathbf{\Omega}_n$ by selecting a random number R_{ln} in the interval (0,1), such that the distance l_n is chosen from the modified exponential distribution

$$R_{ln}=F(l_n)=\frac{1-\exp(-\Sigma_T l_n)}{1-\exp(-\Sigma_T t_n)}. \tag{6}$$

The distance l_n may be obtained easily from the above expression, *viz.*

$$l_n=-\frac{1}{\Sigma_T}\log\{1-R_{ln}[1-\exp(-\Sigma_T t_n)]\}, \tag{7}$$

which is analogous to equation (3) for the non-optimized program. This is shown schematically in Fig. 2.

The use of statistical weights takes into account the probability of absorption and escape of neutrons, and allows the consideration only of scattered neutrons. The statistical weight of the neutron is altered by factors

(1) $1-\exp(-\Sigma_T t_n)$, to allow for the probability that neutrons may not have interacted within the sample;

(2) Σ_s/Σ_T, to allow for the probability that neutrons may have been absorbed within the sample.

Consequently the statistical weight of the neutron at the nth scatter is given by

$$W_n=W_{n-1}\frac{\Sigma_s}{\Sigma_T}[1-\exp(-\Sigma_T t_n)], \tag{8}$$

where W_{n-1} is the neutron weight at the previous scatter, so that the weight of the neutron at the nth scattering event is simply given by

$$W_n=W_0\prod_{j=1}^{n}\left\{\frac{\Sigma_s}{\Sigma_T}[1-\exp(-\Sigma_T t_j)]\right\} \tag{9}$$

where W_0 is the initial neutron weight.

B. Scattering angle distributions

Angles of scatter are selected at each scattering event

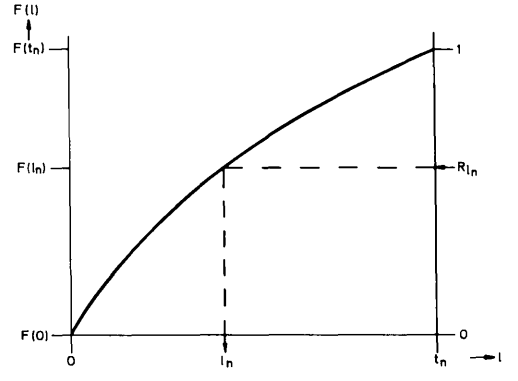

Fig. 2. A schematic drawing of the random selection of a path length l_n from the cumulative distribution function $F(l)$.

from the cumulative distribution of scattering angles,

$$f(\theta_n)=\frac{\int_0^{\theta_n}\frac{\partial\sigma}{\partial\Omega}(\theta',\lambda)\sin\theta'\mathrm{d}\theta'}{\int_0^{\pi}\frac{\partial\sigma}{\partial\Omega}(\theta',\lambda)\sin\theta'\mathrm{d}\theta'}. \tag{10}$$

The distribution of azimuthal angles is uniform, of course, since the scattering for isotropic systems is independent of azimuth; that is

$$f'(\varphi_n)=\varphi_n/2\pi. \tag{11}$$

Hence the selection of a random number $R_{\theta n}$ in the interval (0,1) produces a scattering angle θ_n given by

$$R_{\theta n}=f(\theta_n)=\frac{\int_0^{\theta_n}\frac{\partial\sigma}{\partial\Omega}(\theta',\lambda)\sin\theta'\mathrm{d}\theta'}{\int_0^{\pi}\frac{\partial\Omega}{\partial\Omega}(\theta',\lambda)\sin\theta'\mathrm{d}\theta'}. \tag{12}$$

From the elastic scattering equation

$$Q=4\pi/\lambda\sin\theta/2 \tag{13}$$

a corresponding scattering vector Q_n may alternatively be selected from the diffraction pattern $S(Q)$; here we use the convention

$$\frac{\partial\sigma}{\partial\Omega}(\theta,\lambda)=S(Q).$$

$$R_{\theta n}=f(Q_n)=\frac{\int_0^{Q_n}S(Q)Q\mathrm{d}Q}{\int_0^{2k}S(Q)Q\mathrm{d}Q} \tag{14}$$

where $k=2\pi/\lambda$ is the neutron wavevector. This is shown schematically in Fig. 3.

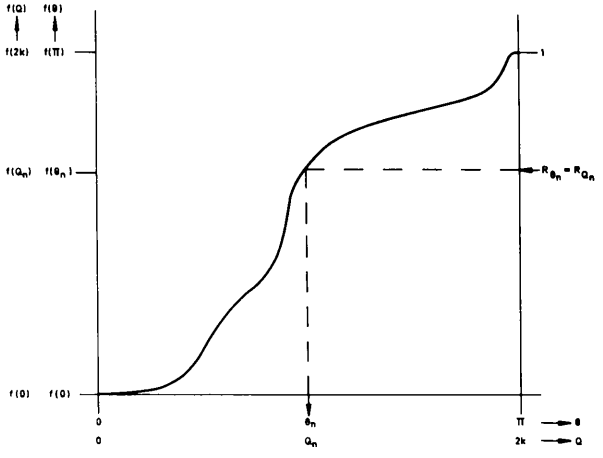

Fig. 3. A schematic drawing of the random selection of a scattering angle θ_n (and hence a corresponding wave vector transfer Q_n) from the cumulative distribution function $f(\theta)$.

The selection of a random number $R_{\varphi n}$ in the interval (0,1) produces an azimuthal scattering angle φ_n given by

$$R_{\varphi n}=f'(\varphi_n)=\varphi_n/2\pi. \tag{15}$$

Once these angles of scatter are chosen, then the new direction $\mathbf{\Omega}_{n+1}$ of the neutron is computed from

$$\mathbf{\Omega}_{n+1}\cdot\mathbf{\Omega}_n=\cos\theta_n. \tag{16}$$

For the case of isotropic scattering where $\partial\sigma/\partial\Omega$ is independent of scattering angle, or $S(Q)$ is constant, then equation (14) reduces to

$$R_{Qn}=Q_n^2/4k^2. \tag{17}$$

Again, from the elastic scattering equation (13), the scattering angle θ_n is given by

$$\cos\theta_n=(1-2R_{Qn}). \tag{18}$$

In general, the structure factor $S(Q)$ is not given in analytic form, and consequently the determination of the scattering angle is not as easy as the selection of the collision distance. Prior to the running of the neutron histories, an array $t(Q)$ must be set up with the values

$$t(Q_m)=\sum_{j=1}^{m}S(Q_j)Q_j\Delta Q_j, \tag{19}$$

where ΔQ_j is the equal-step incremental value of Q. The maximum value is $t(2k)$ which is simply

$$t(2k)=\int_0^{2k}S(Q)Q\mathrm{d}Q. \tag{20}$$

Since in the approximation of elastic scattering the cross section may be obtained from

$$\sigma_s(k)=\frac{2\pi}{k^2}\int_0^{2k}S(Q)Q\mathrm{d}Q, \tag{21}$$

then

$$t(2k)=\frac{\sigma_s(k)k^2}{2\pi}=\frac{2\pi\sigma_s(\lambda)}{\lambda^2}. \tag{22}$$

After a random number R_{Qn} has been selected, the determination of the scattering vector Q_n is performed by searching through $t(Q)$ until

$$t(Q_m)\le R_{Qn}t(2k)<t(Q_{m+1})=t(Q_m+\Delta Q_m). \tag{23}$$

That is,

$$f(Q_m)\le R_{Qn}<f(Q_{m+1}). \tag{24}$$

Then the scattering vector is given by

$$Q_m\le Q_n<Q_{m+1}, \tag{25}$$

and, by linear interpolation,

$$Q_n=Q_m+\Delta Q_m\frac{R_{Qn}t(2k)-t(Q_m)}{t(Q_{m+1})-t(Q_m)}. \tag{26}$$

C. *Detector scoring*

When interaction points and scattering angles are chosen as described in §§ 3*A* and 3*B* above, the simula-

tion is optimized in the sense that the simulated paths are truly characteristic of the paths travelled in the real case. Direct simulations have this property also. However, the continuation of histories by forcing scattering collisions in the specimen further optimizes the simulation by sampling events which have relatively low probability, without the need for tracing large numbers of histories.

After the nth scattering point has been selected, but before the angle of scatter has been chosen, a score $\mathscr{S}_n(\mathbf{\Omega}_D)$ is computed for each detector in turn. The distance $L_{Dn}(\mathbf{r}_n, \mathbf{\Omega}_D)$ from the scattering point $\mathbf{r}_n$ to the surface of the sample in the detector direction $\mathbf{\Omega}_D$ is found in order to compute an escape probability. The scattering angle θ_{Dn} from the direction $\mathbf{\Omega}_n$ to $\mathbf{\Omega}_D$ (and hence the corresponding scattering vector Q_{Dn}) is found in order to compute the differential scattering probability,

$$P_{Dn} = \frac{\Delta\Omega_D}{\sigma_s} \frac{\partial\sigma}{\partial\Omega}(\theta_{Dn}) = \frac{\Delta\Omega_D}{\sigma_s} S(Q_{Dn}), \qquad (27)$$

where $\Delta\Omega_D$ is the solid angle subtended by the detector at the sample.

The score is also dependent on the statistical weight of the neutron at the nth scattering event, so that

$$\mathscr{S}_n(\mathbf{\Omega}_D) = W_n P_{Dn} \exp(-\Sigma_T L_{Dn}). \qquad (28)$$

In practice there is no differentiation among the scores $\mathscr{S}_2, \mathscr{S}_3, \ldots$ *etc.*, since all the scores are due to multiply scattered neutrons. This simulation with scores computed for each detector according to a neutron transport escape calculation (and with weights adjusted at each collision) significantly reduces the computational effort compared to a direct simulation wherein only those neutrons which actually escape to a detector are counted.

D. Neutron initialization

In general, the incident beam distribution is not a separable function of direction, position and wavelength. While it is a useful approximation to assume separability, the correct method is to account for the correlation among angles, positions and wavelengths in the actual joint probability distribution describing the incident neutron beam. Consequently it would be correct to assign an initial weight $W_0(\mathbf{\Omega}, \mathbf{r}, \lambda)$ according to this probability distribution. In our simplified program each neutron is given an initial weight of unity and an initial direction identical to the nominal incident beam direction. The position coordinates of the neutron in the incident beam are chosen at random from a uniform distribution. Furthermore, the beam is assumed to be monochromatic.

It is worth pointing out that these simplifications preclude a complete simulation of resolution effects due to wavelength and angular spread in the incident beam, which we have ignored. In a subsequent paper (Mildner & Carpenter, 1977) we describe an efficient method for treating many wavelengths in a single simulation. That program can also be used for a 'monochromatic' beam experiment with a large wavelength spread $\Delta\lambda$. In this paper, however, we assume that the wavelength resolution is such that it is negligible compared with the angular resolution. Additionally it is useful in many experiments to have a simple program which is more easily operable and much less costly than programs designed to simulate inelastic scattering (Copley, 1974; Johnson, 1974), in which the wavelength spread of the incoming neutron beam is considered.

E. Sample geometries

The program has been written so that one subroutine defines the incoming neutron beam profile and the diffractometer geometry with the direction cosines of the particular detectors. Another subroutine gives the sample configuration, such as vertical cylinder centrally located in the beam, or a slab placed at an angle in the beam, or some other geometry as suggested by Copley (1974). In addition, this subroutine has been written for complicated sample geometries, such as a number of cylindrical tubes placed in the neutron beam, and therefore the program may be used in situations where no analytic approximation is available. These subroutines can readily be changed to accommodate the needs of a specific measurement.

F. Structure factor input data

A calculation of the multiple scattering in a diffraction experiment of course requires an estimate of the structure factor $S(Q)$ for the specimen, which is used in generating the scattering angle distribution (equation 14). Since $S(Q)$ is what we wish to measure, its estimation is usually the greatest difficulty in multiple scattering calculations. $S(Q)$ may be available from models, or other sources, but in many cases is not. In such situations the uncorrected data themselves may be employed, provided that the multiple scattering corrections are not too great. Then it may be asserted with some confidence that the computed corrections are adequate. In principle, the once-corrected data might then again be used to generate a second multiple scattering correction, and so on *ad infinitum*. In cases where multiple scattering is not too important, the first iteration should be adequate. This method should be superior to one using a structure factor derived from some model independent of the particular experiment since the results will tend to be biased toward the model.

4. Cumulative scoring

The purpose of the Monte Carlo simulation is to provide values of $P_1(\theta)$ and $P_M(\theta)$, the probabilities of single and multiple scattering into a detector bank at an angle θ, which are given by the average values of the scores $\mathscr{S}_1^k(\theta)$ and $\mathscr{S}_M^k(\theta)$, where k labels the individual neutron history,

$$\mathscr{S}_1^k(\theta)=\sum_{D(\theta)} U_D \frac{\Sigma_s}{\Sigma_T} \times[1-\exp(-\Sigma_T t_1)]P_{D1}\exp[-\Sigma_T L_D(\mathbf{r}_1,\mathbf{\Omega}_D)] \quad (29)$$

and

$$\mathscr{S}_M^k(\theta)=\sum_{N=2}^{\infty}\mathscr{S}_N^k(\theta), \quad (30)$$

where

$$\mathscr{S}_N^k(\theta)=\sum_{D(\theta)} U_D \prod_{n=1}^{N}\left\{\frac{\Sigma_s}{\Sigma_T}[1-\exp(-\Sigma_T t_n)]\right\} \times P_{DN}\exp[-\Sigma_T L_D(\mathbf{r}_N,\mathbf{\Omega}_D)]. \quad (31)$$

The summation accounts for the finite extent of detectors by treating them as points at different azimuthal angles with suitable weightings U_D to account for the azimuthal location of a group of detectors which may be arranged at a given θ. (The solid angle subtended by each azimuthal detector is incorporated in P_{D1} and P_{DN}.) Several azimuthal detectors may be equivalent so that $U_D=1,2,etc.$, according to the number of symmetrically equivalent azimuthal detectors.

Simulation statistics

We assume that each individual score $\mathscr{S}_N^k(\theta)$ is selected independently and randomly from an unknown probability distribution with a mean $P_N(\theta)$ and variance σ_N^2. Summations of the scores $\mathscr{S}_N^k(\theta)$ over the total number K of neutron histories will yield average values of the scores

$$\mathscr{S}_N(\theta)=\frac{1}{K}\sum_{k=1}^{K}\mathscr{S}_N^k(\theta). \quad (32)$$

The sample mean $\mathscr{S}_N(\theta)$ is the simulation estimate of $P_N(\theta)$, and provided K is large enough, the average value of $\mathscr{S}_N(\theta)$ approaches $P_N(\theta)$. That is

$$P_1(\theta)=\lim_{K\to\infty}\frac{1}{K}\sum_{k=1}^{K}\mathscr{S}_1^k(\theta) \quad (33)$$

$$P_M(\theta)=\lim_{K\to\infty}\frac{1}{K}\sum_{k=1}^{K}\sum_{N=2}^{\infty}\mathscr{S}_N^k(\theta). \quad (34)$$

An estimate of the variance σ_N^2 of the distribution of simulated scores $\mathscr{S}_N(\theta)$ is given by

$$\sigma_{NK}^2=\frac{1}{K-1}\left\{\sum_{k=1}^{K}[\mathscr{S}_N^k(\theta)-\mathscr{S}_N(\theta)]^2\right\} \quad (35)$$

where $N=1$ or M. Then σ_{NK}^2/K is an estimate of the variance σ_{NP}^2 of the probability distribution of $\mathscr{S}_N(\theta)$ about the mean value $P_N(\theta)$. This estimate however is subject to the difficulties associated with sampling from an unknown (presumably non-Gaussian) distribution. A method of grouping data to determine confidence limits to the estimated mean $\mathscr{S}_N(\theta)$ has been used to overcome this problem.

The independent samples are divided into K_G groups of K_{Hi} histories in the ith group. Each group $i(1\le i\le K_G)$ is regarded as an independent sample of the probability distribution, and the average scores for single and multiple scattering for the ith group are

$$\mathscr{S}_1^i(\theta)=\frac{1}{K_{Hi}}\sum_{k\in\{k\}_i}\mathscr{S}_1^k(\theta) \quad (36)$$

and

$$\mathscr{S}_M^i(\theta)=\frac{1}{K_{Hi}}\sum_{k\in\{k\}_i}\sum_{N=2}^{\infty}\mathscr{S}_N^k(\theta). \quad (37)$$

If the K_{Hi} are large enough (~ 100), the distribution of the means of these samples becomes approximately normal by the central limit theorem. Then for K_G groups, the average scores for single and multiple scatterings are given by the group means,

$$\overline{\mathscr{S}_1}(\theta)=\frac{1}{K_G}\sum_{i=1}^{K_G}\mathscr{S}_1^i(\theta) \quad (38)$$

and

$$\overline{\mathscr{S}_M}(\theta)=\frac{1}{K_G}\sum_{i=1}^{K_G}\mathscr{S}_M^i(\theta). \quad (39)$$

The variance of the distribution of group-averaged score $\mathscr{S}_N^i(\theta)$ is estimated by

$$\sigma_{NZG}^2=\frac{1}{K_G-1}\left\{\sum_{i=1}^{K_G}[\mathscr{S}_N^i(\theta)-\overline{\mathscr{S}_N}(\theta)]^2\right\}. \quad (40)$$

Then the measure of the deviation of the sample mean $\overline{\mathscr{S}_N}(\theta)$ from the probability distribution mean $P_N(\theta)$ is the standard deviation σ_N of the group-averaged scores

$$\sigma_N=\frac{1}{K_G^{1/2}}\sigma_{NK_G}, \quad (41)$$

where $N=1$ or M.

5. Multiple scattering correction

It is interesting to compute the probability $P_I(\theta)$ in the 'ideal' scattering experiment where there is no beam attenuation and no multiple scattering. The effective thickness $\bar{t}$ of the target as seen by the incoming beam in the $\mathbf{\Omega}_0$ direction is the value of t_1 averaged over the beam profile. For thin samples the probability of a scattering event is $\Sigma_s\bar{t}$, and in the absence of finite target corrections, the score would be

$$\mathscr{S}_I(\theta)=\sum_{D(\theta)} U_D\Sigma_s\bar{t}P_{D0}. \quad (42)$$

With the substitution of equation (27) and of

$$\Sigma_s\bar{t}=\mathscr{N}\sigma \quad (43)$$

where $\mathscr{N}$ is the number of scattering atoms per unit area, and after summation over all detectors at a particular scattering angle, the ideal probability $P_I(\theta)$ of scattering (that is, with no finite target effects) becomes

$$P_I(\theta)=\mathscr{S}_I(\theta)=\mathscr{N}\sigma P_{D0}=\mathscr{N}S(Q)\Delta\Omega_D. \quad (44)$$

The multiplicative correction factor that is necessary to be applied to the ideal scattered intensity to account

for the finite thickness of the specimen is $(P_1+P_M)/P_I$. This factor may be separated into two, *viz.*

(1) the attenuation correction factor:

$$C_A \equiv P_1/P_I \text{ and;}$$

(2) the multiple scattering correction factor:

$$C_M \equiv (1+P_M/P_1) = P_T/P_1 .$$

Then the overall correction factor is

$$C_0 = \frac{P_T}{P_I} = \frac{P_1}{P_I}\frac{P_T}{P_1} = \frac{P_1}{P_I}(1+P_M/P_1) = C_A C_M . \quad (45)$$

This factor is to be divided out of the measured data to obtain the ideal scattered intensity.

There may be an advantage in smoothing certain of the computed functions which are expected not to exhibit strong variations with Q, in order to diminish computational statistical errors. The multiple scattering probability $P_M(Q)$ is expected to be rather smoothly varying [this is a somewhat relaxed version of Vineyard's (1954) arguments] so that $P_M(Q)$ is a candidate for smoothing. Also, to a crude approximation, the attenuation correction factor $C_A(Q)$ may be expressed as

$$C_A(Q) = \frac{P_1(Q)}{P_I(Q)} \simeq \exp\left[-\Sigma_T(k)t(\theta)\right], \quad (46)$$

where $t(\theta)$ is the mean distance through the sample to reach a detector at angle θ. Therefore

$$\eta(Q) \equiv \frac{1}{\Sigma_T(k)t(\theta)} \ln \frac{P_1(Q)}{P_I(Q)} \quad (47)$$

is expected to be a smooth function and a candidate for smoothing even though $\Sigma_T(k)$ and $t(\theta)$ may vary. The variation of $\Sigma_T(k)$ is potentially important in a variable-wavelength (*i.e.* time-of-flight) measurement, as the variation of $t(\theta)$ with scattering angle may be in a fixed-wavelength measurement.

Error estimates δP_1 and δP_M are generated in the calculation. The errors $\delta\eta(Q)$ in $\eta(Q)$ are

$$\delta\eta(Q) = \frac{1}{\Sigma_T(k)t(\theta)} \frac{\delta P_1(Q)}{P_1(Q)} . \quad (48)$$

These estimates may be used in generating smoothed versions (such as might be calculated by spline function fitting) of $P_M(Q)$ and $\eta(Q)$. If the smoothed versions of $P_M(Q)$ and $\eta(Q)$ are denoted by $\bar{P}_M(Q)$ and $\bar{\eta}(Q)$, the attenuation correction factor is

$$C_A(Q) = \exp\left[-\bar{\eta}(Q)\Sigma_T(k)t(\theta)\right] \quad (49)$$

and the overall correction factor is

$$C_O(Q) = C_A(Q)\left[1+\frac{\bar{P}_M(Q)}{P_1(Q)}\right] . \quad (50)$$

Since $P_1(Q)$ is subject to computational statistical error while $P_I(Q)$ is not, it may be further advantageous to compute

$$C_O(Q) = C_A(Q) + \frac{\bar{P}_M(Q)}{P_I(Q)} . \quad (51)$$

It is a matter of taste whether the multiple scattering is applied as a correction factor or as an additive correction. An advantage of the former method is that the attenuation factor C_A can sometimes be computed accurately by means other than a Monte Carlo simulation, and the separately calculated C_A can either be applied to check the simulation, or used instead of the simulation to improve accuracy, as suggested earlier (Mildner, Carpenter & Pelizzari, 1974). Consequently it is the efficiency of obtaining the function P_T/P_1 that makes the optimized technique more useful than the direct simulation for the correction of measured data as a function of scattering angle. (Moreover in the case of computing multiple scattering corrections to data obtained on neutron time-of-flight diffractometers with their relatively few scattering angles, the cost of the direct simulation becomes prohibitive). Among the various combinations of functions we have found the ratio P_T/P_1 to be the most smoothly varying with Q.

Fig. 4 shows a cubic spline smoothing function fitted

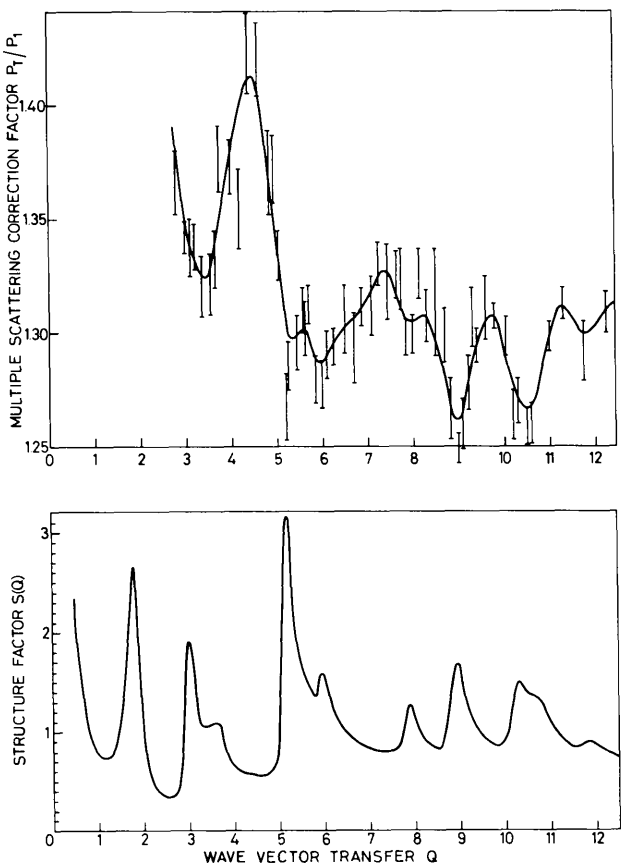

Fig. 4. The smoothing of the multiple scattering correction factor as a function of wave vector transfer using spline functions for time-of-flight diffraction data of a glassy carbon. The fluctuations in this function can be seen to correlate with the features in the structure factor (below) of the material.

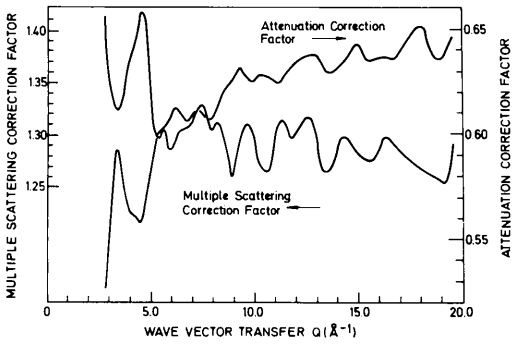

Fig. 5. The multiple scattering and attenuation correction factors at 90° scattering for time-of-flight diffraction data of a cylindrical sample of a glassy carbon.

to the multiple scattering correction factor of a neutron time-of-flight diffraction experiment on a sample of glassy carbon which exhibits intense small-angle scattering (Mildner & Carpenter, 1974). The structure factor of the sample is greatly varying, and the peaks and valleys of the multiple-scattering correction factor can be correlated with those of the structure factor as should be expected, for the correction factor is greatest for those values of Q for which the structure factor is low, and *vice versa*. Hence, the effect of multiple scattering is to decrease the peaks in the measured spectrum and to fill in the minima, and the application of the correction is such that the peaks are enhanced in the true structure factor.

Fig. 5 shows the results of the Monte Carlo simulation, namely the attenuation and multiple-scattering correction factors for data taken at a scattering angle of 90°. The sample was a long cylinder of diameter 2 cm and density 0·075 atom b^{-1} cm^{-1}, with the axis perpendicular to the scattering plane. The diameter was thus about a half-scattering mean free path, assuming 5·5 b $atom^{-1}$ scattering. It can be seen that these corrections vary greatly so that they need to be computed in detail to obtain accurate results of the diffraction measurement.

6. Conclusion

Monte Carlo methods for correcting diffraction measurements can be wasteful if optimized techniques such as those introduced by Bischoff are not used. A simple program for a monochromatic source has been presented in which successive scattering events are forced to occur within the sample, and each simulated path, weighted by its relative probability, contributes to the scattered intensity measured by a detector. A method of grouping the neutron histories is used to determine the statistics of a particular simulation. The most useful result is the multiple-scattering correction factor which may be obtained easily from the simulation, and is not featureless, especially when the structure factor of the sample modulates considerably.

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