Efficient implementation of multiple scattering Monte Carlo estimates in time-of-flight neutron spectrometry exploiting wide-area detectors

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Abstract. The substantial upgrade in new-generation reactor-based time-of-flight spectrometers lies in their hugely increased detection area ensuring high neutron-collection power and remarkably good count statistics in relatively short times. Dealing with thousands of time channels and several tens of thousands of detection pixels is, however, quite punishing for data handling and correction. Real-geometry multiple scattering evaluation, even in an approximate way, is often the most demanding step in the treatment of inelastic neutron data, and becomes a very hard task in widely-extended detection geometries, as those of spectrometers like BRISP, IN4 or IN5 at the Institut Laue Langevin in Grenoble. We refreshed our approach to multiple scattering calculations, in order to obtain reasonably accurate real-geometry results in nearly real-time conditions. Our new code, originating from a long standing experience in the application of Monte Carlo (MC) integration techniques to multiple scattering calculations, is now made particularly efficient in computing time both by a careful application of the MC importance sampling method, and by the use of programming languages allowing for an efficient use of matrix algebra to avoid the far slower nested-loop logic of more traditional languages. The concepts at the basis of the algorithm and several implementation details are presented, together with the application to a real experimental test case.

1. Introduction
Multiple scattering is an unavoidable phenomenon in all situations where a radiation or particle beam is scattered upon interaction with a matter specimen. In the case of neutron diffraction or spectroscopy, multiple scattering plays a particularly important role due to weakness of the probe, which imposes the use of larger samples (volumes in the cm³ range) and beam cross-sections (of the order of cm²) than with other scattering techniques.

The common experimental practice looks for a compromise between the need of a sufficiently strong scattering signal making experiments feasible in a reasonable time, and the requirement to keep multiple scattering and other phenomena, such as attenuation, resolution loss, and others,
at an acceptable level. It is generally considered as a reasonable compromise to make the sample scatter a fraction of the order of 10 to 20% of the incoming neutrons, which is also the order of magnitude of the expected multiple-to-single signal ratio. However, in particular cases, for instance when a high-scattering or thick-walled container is needed, it can be even larger.

Excluding the lucky and few cases when it can just be neglected, or treated simply as a flat background, multiple scattering is a typical effect that needs to be corrected for to access the sought-for structural or dynamical quantities (related to the single-scattering component only) from the experimental raw data. In no way multiple scattering contributions to the total signal can be measured independently, therefore they need to be estimated otherwise.

Much effort has been devoted in the past to multiple scattering evaluation in neutron diffraction [1, 2, 3, 4, 5]. In the case of inelastic scattering, with which we are concerned here, an essential point is that the simple knowledge of the multiple-to-single scattering ratio, in terms of just one number telling us the strength of this effect, is not at all sufficient for an appropriate correction of the experimental spectra, since the spectral distributions of multiple and single scattering signals are substantially different. This can be intuitively understood considering that, roughly speaking, the energy transferred from the neutron to the sample after \( p \) scattering events covers a range at least as broad as the \( p \)-fold convolution with itself of the one-scattering energy transfer probability distribution.

Therefore, multiple scattering evaluation in inelastic experiments is quite harder than in diffraction measurements, requiring the consideration of each energy change along the neutron zig-zag paths in the sample, ruled by the (unknown) sample-specific, anisotropic, and inelastic scattering law, and giving rise to different attenuation effects. It is then clear that a reasonable estimate of multiple inelastic scattering requires to follow, in some way, the “history” of a neutron from its arrival at the sample to its absorption into a detector, during which a number of scattering events may take place.

Two main routes of approach have been traditionally followed to tackle this problem from the computational point of view, both relying on the application of random Monte Carlo (MC) statistical methods. One, the most frequently applied [6, 7, 8, 9, 10], treats the problem as one of “neutron histories simulation” which, in a very recent development [11], becomes a part of an overall simulation of the spectrometer-plus-sample system in a virtual experiment. In this type of algorithms, a scattering event is forced to take place along a straight path of the neutron into the material system, and the new energy and direction of the emerging neutron are chosen according to a joint probability distribution function determined by the scattering law assumed as a model. Along the new path a second scattering is considered and so on, until the neutron is forced to fly to the detector carrying with itself as a label the product of all the attenuation factors along the travelled path and all the scattering strengths due to the various events. This approach is very efficient but rather heavy in terms of computer time and of programming for different sample geometries. In particular the choice of energy and vector momentum transfer at every scattering point requires a sampling from a four-dimensional probability distribution which can only be done in a numerically approximate and slow way.

Much less attention [12, 13, 14] has so far received an alternative route based on using MC techniques to calculate multiple scattering intensities as multidimensional integrals of appropriate functions. Though in principle less efficient because a certain number of samplings of the integration variables has to be discarded, this approach is characterised by a much simpler implementation and turns out to be more easily optimized as far as the statistical accuracy is concerned, thus allowing for a fast computation.

In this paper we show that this second way of facing the problem of the multiple inelastic scattering correction can be successfully applied to new-generation instruments which, with their extremely high space and time resolution and their very wide detection areas, still challenge neutronists aiming at a quick, statistically accurate, and reasonable estimate of the quoted effects.
in real-geometry conditions. In particular, we will consider time-of-flight (ToF) experiments, where each detection element records a full inelastic scattering spectrum.

We show that good estimates of multiple scattering can be obtained in time of the order of minutes with standard “off-the-shelf” computers. This renders an algorithm as the one described here a tool not only useful for the analysis of neutron data but also suitable to a real-time monitoring of the experiment. On ToF instruments this strongly suggests that the multiple scattering signal can be usefully evaluated as a function of flight time, so that it can be directly subtracted without converting it into a more usual energy distribution.

The intensity of inelastic scattering in a neutron experiment is, in fact, customarily described in terms of an energy distribution for a given angle $\theta_D$ defined by the position $P_D$ of a detector element with respect to the sample position. (In this paper an energy $E$ or the corresponding frequency $\omega = E/\hbar$, where $\hbar$ is the Planck constant, will be used equivalently.) As explained before, however, calculating scattering intensities directly on the flight time scale of the measurements is quite a natural choice for a ToF experiment. We therefore select a suitable set of time values, and for each of them we calculate the intensity due to scattering sequences where the neutron arrives at the detector at time $\tau$ having been scattered a fixed number of times. We assume a common start time for all neutrons, neglecting the neutron pulse duration.

In this paper we limit ourselves to double scattering only, since higher-order scattering sequences add to the total signal a contribution which is usually little, if not negligible at all, and increasingly structureless and similar to a flat background that can be more easily modelled and subtracted in other ways, while, on the other hand, its computation becomes more time-consuming. If necessary, however, the computation of higher-order processes is a lengthy but in principle straightforward task.

2. Single and double scattering

A set of orthogonal cartesian axes having its origin $O$ at the centre of the sample position is used to define the geometry of the system (see figures 1 and 2), with the $y$-axis in the direction of the incident beam. To simplify the description, we consider here a somewhat idealized situation. The actual implementation, still in progress, takes care of further details of a realistic case. We assume an incident non-diverging neutron beam which illuminates the sample with a uniform intensity. Moreover, we neglect the presence of a container and consider only the bare sample in the form of a slab perpendicular to the beam, with its vertical axis along the $z$ direction, and a $(x,z)$-plane two-dimensional position-sensitive detector facing the beam at a distance $L_0$ from the sample center. The distance between $O$ and the detector element is $L_D = L_0/\cos \theta_D$. The flight time start $\tau = 0$ is taken here to coincide with the instant when the neutron pulse arrives at the beam cross-section plane $y = 0$, although an instrument-dependent offset may be present in the definition of the ToF frame. In the following, we will make use of the well-known relationships among energy, wave vector $k$, and speed $v$ of a neutron, namely

$$\omega = \frac{\hbar k^2}{2m},$$

and

$$v = \frac{\hbar k}{m},$$

where $m$ is the neutron mass.

For single-scattering calculations, we consider an event where a neutron with fixed energy $\omega_0$ enters the sample material crossing its surface at a point $A$, is inelastically scattered in $P$ at an angle $\theta$, and travels in the direction of $P_D$ crossing again the sample surface at point $B$. The path travelled inside the material is made of two line segments of lengths $\ell_{AP}$ and $\ell_{PB}$. The
vector positions of $P$ and $P_0$ are $r$ and $r_D$ with $|r_D| = L_D$. The situation is depicted in figure 1. Upon scattering, the neutron energy changes to $\omega_1$, with an energy transfer $\omega = \omega_0 - \omega_1$.

The quantity to be calculated is the scattering intensity distribution per unit time of flight

$$\frac{dI_1}{d\tau}(\theta_D, \tau) = \Phi_0 n \int_V dr \exp[-\mu_{\text{tot}}(k_0)\ell_{AP}] \frac{d^2\sigma}{d\Omega d\omega}(\theta, \omega) \exp[-\mu_{\text{tot}}(k_1)\ell_{PB}] \frac{\Delta_D \cos \theta}{L^2} \eta(k_1) \frac{d\omega}{d\tau}$$

(3)

where $\Phi_0$ is the incident flux, $n$ is the number density of scattering units, the exponentials are the attenuation factors along the incident- and scattered-neutron path, $\mu_{\text{tot}} = n(\sigma_{\text{scat}} + \sigma_{\text{abs}})$ is the attenuation coefficient due to both scattering and absorption cross sections, and $\eta$ is the detector efficiency. Both $\mu_{\text{tot}}$ and $\eta$ depend, in general, on the neutron speed. $\ell_{AP}$ is a function of $r$, while $\ell_{PB}$, the distance $L$ between $P$ and $P_D$, and the actual scattering angle $\theta$ depend on both $r$ and $r_D$. Moreover, in equation (3) $\frac{d^2\sigma}{d\Omega d\omega}$ is the double-differential cross section, $\Delta_D$ is a surface element on the detector around $P_D$, and the actual scattering is performed over the whole illuminated sample. The function $\omega' = \omega_0 - \omega_1(\tau)$ is obtained from (1) with

$$k_1(\tau) = \frac{mL}{\hbar \left( \tau - \frac{r \cdot \mathbf{y}}{v_0} \right)}.$$

(4)

where $\mathbf{y}$ is the unit vector in the $y$ direction. Equation (4), in turn, is derived from the imposed total flight time

$$\tau = \frac{r \cdot \mathbf{y}}{v_0} + \frac{L}{v_1}.$$

(5)

In (3) is also used the derivative

$$\frac{d\omega}{d\tau} = \frac{\hbar^2}{m^2L} k_1^2(\tau).$$

(6)

In the case of double scattering, the neutron is inelastically scattered twice, first in $P_1$ at an angle $\theta_1$ and then in $P_2$ at an angle $\theta_2$. $P_1$ and $P_2$ have vector positions $r_1$ and $r_2$, and $r_{12}$ is the vector distance between the two points. The path travelled inside the material is now made of three straight parts of lengths $\ell_{AP_1}$, $\ell_{P_1P_2} = r_{12}$, and $\ell_{P_2B}$. The energy transfers are $\omega' = \omega_0 - \omega_1$ and $\omega'' = \omega_1 - \omega_2$. The geometry of a double-scattering process is schematically represented in figure 2.

Now the specified (i.e. pertaining to a given time channel of the acquisition time frame) flight time $\tau$ and the positions of the scattering centres do not determine $\omega'$ in a unique way, as this quantity can assume any value such that the time of flight up to the second scattering point does not exceed the value prescribed for the whole path to the detector. Then $\omega'$ can vary between $-\infty$ and $\omega'_{\text{max}} = \omega_0 - mr_{12}^2/[2\hbar(\tau - r \cdot \mathbf{y}/v_0)^2]$. The calculation has therefore to include the integration over one energy variable, in our case $\omega'$ between the given limits. However, when $\omega'$ is chosen, $\omega''$ is fixed by the constraint on the total flight time, so that $\omega'' = \omega''(\omega', \tau)$.

The double-scattering ToF intensity can be written as

$$\frac{dI_2}{d\tau}(\theta_D, \tau) = \Phi_0 n^2 \int_{V_1} dr_1 \int_{V_2} dr_2 \exp[-\mu_{\text{tot}}(k_0)\ell_{AP_1}] \int_{-\infty}^{\omega_{12}^\text{max}} d\omega' \frac{d^2\sigma}{d\Omega d\omega'}(\theta_1, \omega') \times \frac{\Delta_D \cos \psi}{L^2} \eta(k_1) \frac{d\omega''}{d\tau}$$

(7)
where now \( k_1 = k_1(\omega') \) and \( k_2 = k_2(\omega', \tau) \). In (7) there appear three attenuation exponential factors, two double-differential cross sections, and the six-dimensional integration over the coordinates of the two scattering points. \( \ell_{\text{AP}_1} \) is a function of \( r_1 \), while \( \ell_{\text{r}_12 \theta_1} \) depend on \( r_1, r_2, \) and \( r_D \). The path lengths \( \ell_{\text{P}_2\text{B}} \) and \( L \) are functions of \( r_2 \) and \( r_D \), and \( \theta_2 \) depends on \( r_1, r_2, \) and \( r_D \). \( \psi(r_2, r_D) \) is the angle between the directions of \( \text{P}_2 \text{P}_D \) and the \( y \) axis. The integration volumes \( V_1 \) and \( V_2 \) do not coincide if the second scattering can occur in a region of the sample not directly illuminated by the incident beam but from which the detector can be reached. The calculation of (7) is performed with the help of the following relationships. For a given \( \omega' \) one has

\[
k_1(\omega') = \sqrt{\frac{2m}{h} (\omega_0 - \omega')}
\]  

and the corresponding \( v_1(\omega') \). From the total time of flight

\[
\tau = \frac{r_1 \cdot \hat{y}}{v_0} + \frac{r_{12}}{v_1} + \frac{L}{v_2}
\]  

one has

\[
k_2(\omega', \tau) = \frac{mL}{h \left[ \tau - \frac{r_1 \cdot \hat{y}}{v_0} - \frac{r_{12}}{v_1(\omega')} \right]},
\]  

\[
\omega''(\omega', \tau) = \omega_0 - \omega' - \omega_2(\omega', \tau),
\]  

and

\[
\frac{d\omega''}{d\tau}(\omega', \tau) = \frac{h^2}{m^2 L} k_2^2(\omega', \tau).
\]  

In our case the multiple scattering evaluation is essentially given by the calculation of (7), since, as said before, we are neglecting higher-order scattering contributions. However, the
calculated \( \frac{dI}{d\tau} (\theta_D, \tau) \) cannot be usefully applied to the correction of experimental data unless first normalized in a consistent way. This problem, unsolvable in practice, can be circumvented by calculating, with a negligible extra cost in computing time, the single-scattering intensity \( \frac{dI}{d\tau} (\theta_D, \tau) \) and taking the double-to-single scattering intensities ratio, which is independent of any instrumental or experimental normalization, and of undetermined arbitrary quantities such as \( \Phi_0 \) and \( \Delta_D \) as well. In this way, to each point in the experimental ToF spectrum the correct single-scattering intensity can be assigned, resulting in an effective subtraction of double-scattering contributions.

An essential ingredient for these calculations is the scattering law expressed through the double-differential cross section. For simplicity, we discuss this issue with reference to a situation typical of a small-angle spectrometer like BRISP [15] having as one of the main fields of application the investigation of liquid-state dynamics. Assuming for simplicity a monatomic sample characterised by both coherent and incoherent scattering, with the respective bound-atom cross-sections denoted as \( \sigma_{coh} \) and \( \sigma_{incoh} \), the scattering process is ruled by

\[
\frac{d^2 \sigma}{d\Omega d\omega} (\theta, \omega) = \frac{k'}{4\pi k} [\sigma_{coh} S(Q, \omega) + \sigma_{incoh} S_s(Q, \omega)]
\]

(13)

where \( Q = |k - k'| \) is the momentum transfer, in units of \( \hbar \), in a generic event where the neutron wave vector changes from \( k \) to \( k' \), \( S(Q, \omega) \) is the dynamic structure factor describing the spectrum of density fluctuations with wave vector \( Q \), and \( S_s(Q, \omega) \) is its self part.

A typical \( Q \) range of interest for such experiments, relevant for the study of collective dynamics, is around \( 1 \leq Q/\text{nm}^{-1} \leq 10 \), where \( S(Q, \omega) \) is well described by model line shapes, based on hydrodynamic or viscoelastic concepts [16], which usually display a central peak plus more or less broad inelastic contributions related to the presence of excitation modes. On the other hand, \( S_s(Q, \omega) \) describes the single-particle motions reflecting some kind of diffusive-like dynamics and is usually given by a quasielastic spectral line, often modelled as a Lorentzian curve [17, 18]. These models provide suitable inputs for a scattering law to be used in the MC calculation of single scattering, at least as an initial guess to be refined later.

On the other hand, the same models do not, generally, describe correctly the multiple scattering situation. To see why, we first recall that the total, i.e. frequency-integrated, coherent scattering intensity reflects, although is not exactly proportional to, the static structure factor

\[
S(Q) = \int_{-\infty}^{+\infty} d\omega S(Q, \omega)
\]

(14)

while the frequency integral of \( S_s(Q, \omega) \) is just unity.

At a small angle \( \theta_D \), the detector collects neutron scattered once at actual angles \( \theta \approx \theta_D \), so that the low-\( Q \) dynamic structure factor is to be modelled. Multiple-scattering processes, instead, can end with the neutron travelling in a direction close to that of the incoming beam after having been scattered more than once at any angle. Indeed, the most common situation for double scattering is that a small \( \theta_D \) is obtained with two large-angle, and therefore large-\( Q \), processes, as the scattering sample usually extends much more transversally than in the beam direction, the sample thickness being typically of the order of a few mm. In figure 3 we show that in the MC evaluation of (7) most double-scattering sequences are characterised by angles distributed around the value \( \pi/2 \). As a consequence, a reasonable model for double-scattering calculations should be one that represents the dynamical properties at a rather large \( Q \), in a region, typically beyond the position of the main peak of the static structure factor, where the differences between \( S(Q, \omega) \) and \( S_s(Q, \omega) \) are greatly reduced and \( S(Q) \) oscillates around unity.
The above considerations suggest that even in condensed samples, a reasonable, easy-to-use and very general scattering law to be applied in the evaluation of \( \frac{dI_2}{d\tau}(\theta_D, \tau) \) is provided by the well-known free-particle dynamic structure factor

\[
S(Q, \omega) = S_s(Q, \omega) = \frac{1}{s\sqrt{2\pi}} \exp \left[ -\frac{(\omega - \omega_r)^2}{2s^2} \right] \tag{15}
\]

where \( s = Q\sqrt{k_B T/M} \), \( k_B \) is the Boltzmann constant, \( T \) is the temperature of the sample, \( M \) is the atomic mass, \( \omega_r = hQ^2/(2M) \) is the so-called recoil frequency, and \( S(Q) = 1 \). Equation (15) gives the correct limit form of \( S(Q, \omega) \) for very large \( Q \). In this paper we refer to calculation of \( \frac{dI_2}{d\tau}(\theta_D, \tau) \) performed with a double-differential cross-section defined by (13) in the ‘self approximation’ \( S(Q, \omega) = S_s(Q, \omega) \) defined by (15), which turns out to be very convenient for an efficient application of MC integration, as shown below.

3. Monte Carlo integration

The MC method of integration [19, 20] is based on the fact that the integral

\[
I = \int_V dx \, dy \cdots dz \, f(x, y, \cdots, z) \tag{16}
\]

can be estimated as

\[
I_{MC}(N) = \frac{V}{N} \sum_{i=1}^{N} f(x_i, y_i, \cdots, z_i) \tag{17}
\]

if a set \((x_i, y_i, \cdots, z_i)\) is randomly and uniformly sampled \( N \) times in the integration domain \( V \) of volume \( V \). \( I_{MC}(N) \) is a random variable with mean \( I \) and variance

\[
\text{var} I_{MC}(N) = \frac{V^2}{N} \text{var} f = \frac{1}{N} \left[ \left( V \int_V dx \, dy \cdots dz \, f^2(x, y, \cdots, z) \right) - f^2 \right] \tag{18}
\]

where \( \text{var} f = \langle f^2 \rangle - \langle f \rangle^2 \) is the variance of the function \( f \) in \( V \), required to be finite.

The deviations of \( I_{MC}(N) \) from the true value \( I \) are of order of the standard deviation given by the square root of (18), which implies that, with increasing \( N \), the rate of convergence of \( I_{MC}(N) \) is \( 1/\sqrt{N} \), a fundamental property of MC integration. This very slow convergence...
makes the method inefficient for integrating functions of one variable, if compared with common
deterministic quadrature algorithms [19], but the power of the method appears clearly when
applied to the integration in more dimensions, since the $1/\sqrt{N}$ convergence rate is independent
of the number of dimensions. Therefore, MC integration is the best choice for the evaluation of
quantities as those in (3) and (7) where a three- and a seven-dimensional integral needs to be
computed, respectively.

Equation (18) shows that the statistical accuracy of MC integration depends on two factors,
the variance of the integrand function over the integration domain and the number of samplings
(i.e. of function evaluations). This has led to the development of variance-reduction techniques,
in order to allow for the desired accuracy while keeping $N$, and therefore the computation
load, at a minimum. A general approach to this problem is the so-called method of importance
sampling (IS) based on the use of non-uniform distributions of random numbers and aiming
at the application of the intuitive idea that a greater efficiency is achieved by evaluating the
function $f$ the more often in ranges where it contributes the more to the integral $I$. Limiting
ourselves to only quoting the results, the method consists of replacing (17) with [19, 20]

$$I_{MC}(N) = \frac{1}{N} \sum_{i=1}^{N} \frac{f(x_i, y_i, \ldots, z_i)}{w(x_i, y_i, \ldots, z_i)}$$  \hspace{1cm} (19)

where $w$ is a weight function required to be strictly positive and normalized to unity in V,
and the set $(x_i, y_i, \ldots, z_i)$ is randomly sampled according to a joint probability distribution
given by $w$. In the case of interest here, only one variable, say $z$, is sampled non-uniformly,
and $w(x, y, \ldots, z)$ splits into the product $w(x, y, \ldots)w_z(x, y, \ldots, z)$ where the first term
is a constant in the volume spanned by $x, y, \ldots$ and the second rules the IS of $z$ according
to the conditioned probability distribution of $z$ given $x, y, \ldots$. The method is most easily
implemented when a generator of random numbers distributed according to $w$ is available.
The purpose of using (19) lies in the fact that a variance reduction may be achieved if $w$ can be
chosen to be similar in shape to $f$, so that the ratio $f/w$ has a smaller variance than $f$ alone,
improving the convergence of the MC estimate of $I$. Since IS is exploited in the calculation of
the double-scattering intensity, we report here for later reference the corresponding expression
of the variance, given by

$$\text{var } I_{MC}(N) = \frac{1}{N} \left[ \int_V \frac{f^2(x, y, \ldots, z)}{w(x, y, \ldots, z)} - \left( \int_V \frac{f(x, y, \ldots, z)}{w(x, y, \ldots, z)} \right)^2 \right]$$  \hspace{1cm} (20)

which replaces the one given in (18).

For the MC calculation of the integral in (3) we use (17) where the integration variables are
the coordinates of the scattering point $P$. For a slab sample having its sides parallel to the
coordinate axes, the obvious choice is to use cartesian coordinates $x, y$, and $z$, obtained from
uniform random sampling in the ranges corresponding to the volume directly exposed to the
beam. From the coordinates of $P$ and those, known, of $P_D$ at the detector, it is immediate to
derive the positions of $A$ and $B$, the distances $\ell_{AP}$, $\ell_{PB}$, and $L$, and the angle $\theta$. From equations
(4)-(6), the known scattering properties of the material, and the detector efficiency, the values
of the integrand function are readily calculated for each of the $N$ iterations and finally averaged.

The MC calculation of (7) presents particular features to be dealt with, concerning the
integration over both space and energy variables. As far as the spatial integration is concerned,
one has to consider the presence of the term $1/r_{12}^2$ which makes the function to be integrated to
have an infinite variance, rendering a direct calculation subject to wild fluctuations depending
on whether the points $P_1$ and $P_2$ happen to be sampled very close to each other or not. We are
in fact dealing with a function presenting a singularity in $r_{12} = 0$, though its volume integral
remains finite (obviously, since otherwise the multiple scattering intensity would be infinite).
The standard approach to this problem is to look for a change of variables that removes the singularity. For example, a procedure based on this idea has been mentioned in Ref. [13].

In this case an effective solution is found passing from the set of variables \((r_1, r_{12})\) to the set \((r_{12}, \theta_{12})\) where \(r_{12}\) is defined in spherical coordinates \((r_{12}, \theta_{12}, \phi_{12})\) with \(dr_{12} = d\theta_{12} r_{12}^2 d\phi_{12} \sin \theta_{12} d\phi_{12} \). In this way, the factor \(r_{12}^2 \sin \theta_{12}\) is included into the integrand function compensating \(1/r_{12}^2\) and removing the singularity and the diverging variance. It is convenient to choose the polar axis along the \(y\) direction so that \(\theta_{12}\) coincides with the first scattering angle \(\theta_1\). The integral over \(r_{12}\) can be written in the form

\[
\int dr_{12} f(r_{12}) = \int_0^{r_{12}} r_{12} d\theta_{12} \int_0^{2\pi} d\phi_{12} [r_{12}^2 \sin \theta_{12} f(r_{12})].
\]

The meaning of the upper limit \(r_{12}^*\) for the variable \(r_{12}\) is understood by observing that, once \(r_1\) is determined as in the calculation of single scattering, the sampling of \((r_{12}, \theta_{12}, \phi_{12})\) selects a random point within a sphere of radius \(r_{12}^*\) around \(P_1\). Such a point however can be a valid choice for \(P_2\) only if it lies inside the scattering material, otherwise it needs to be discarded.

On the other hand, if the distance between \(P_1\) and \(P_2\) is kept above a certain minimum the singularity does not show up and the variance of the integrand function is greatly reduced even when the choice of the two scattering points is made by a standard uniform sampling of \(r_1\) and \(r_2\) in their respective volumes.

One is then led to find an optimum strategy in the splitting of the integral in (7) into the sum of two parts: one, \(I_{\text{short}}\), ‘at short distances’, is performed as described above using as variables \(r_1\) and \(r_{12}\) with spherical coordinates for the latter, and one, \(I_{\text{long}}\), ‘at long distances’, is carried out with uniform sampling of \(r_1\) and \(r_2\). The first computation requires to discard the whole sampling when \(P_2\) falls outside \(V_2\), the second one requires discarding pairs which are at distances less than \(r_{12}^\ast\). Therefore, \(r_{12}^\ast\) is a parameter to be optimized with the criterion of obtaining the smallest variance for the total \(I_{\text{MC}} = I_{\text{short}} + I_{\text{long}}\). In fact, with a larger \(r_{12}^\ast\) more samplings are to be discarded in the computation of both \(I_{\text{short}}\) and \(I_{\text{long}}\), but this loss of efficiency is more than compensated by the fact that a larger \(r_{12}^\ast\) increases the integration domain of a function with an intrinsically lower variance due to the compensation of the factor \(1/r_{12}^2\), and also reduces the variance of the function to be integrated in \(I_{\text{long}}\). On the other hand too large an \(r_{12}^\ast\) makes the loss of samplings too great to be compensated.

The integration volume \(V_1\) is the same as for single scattering. As for \(V_2\), in the calculation of \(I_{\text{short}}\) it is given by the volume of \([0, r_{12}^\ast] \times [0, \pi] \times [0, 2\pi]\), that is \(V_2 = 2\pi^2 r_{12}^\ast\), while it equals the real sample volume when \(I_{\text{long}}\) is also computed with cartesian coordinates for \(P_2\).

We next discuss the integration over the energy transfer \(\omega'\) contained in (7). The integrand function, denoted here for short as \(F(\omega')\), depends strongly on \(\tau\) and on the actual \(Q\) values involved in the two scattering events. With a dynamic structure factor in the form (15), one can write both double-differential cross sections as functions of \(\omega'\) as

\[
\frac{d^2\sigma}{d\Omega d\omega'}(\omega') = \frac{k_1(\omega')}{k_0} \frac{\sigma_{\text{scat}}}{s(Q_1)^{1/2}} \frac{1}{2\pi} \exp \left[ -\frac{(\omega' - \omega_1(Q_1))^2}{2s^2(Q_1)} \right]
\]

and

\[
\frac{d^2\sigma}{d\Omega d\omega''}(\omega'') = \frac{k_2(\omega'')}{k_1(\omega'')} \frac{\sigma_{\text{scat}}}{s(Q_2)^{1/2}} \frac{1}{2\pi} \exp \left[ -\frac{(\omega'' - \omega_2(Q_2) - \omega_1(Q_2))^2}{2s^2(Q_2)} \right],
\]

where the dependence of the various quantities on \(\tau, r_1, r_2,\) and \(r_D\) is not indicated to simplify the notation, and \(\sigma_{\text{scat}} = \sigma_{\text{coh}} + \sigma_{\text{incoh}}\). Here,

\[
Q_1(\omega') = k_0^2 + k_1(\omega')^2 - 2k_0 k_1(\omega') \cos \theta_1,
\]
\begin{equation}
Q_2(\omega') = k_1(\omega')^2 + k_2(\omega')^2 - 2k_1(\omega')k_2(\omega')\cos \theta_2,
\end{equation}

and (11) has been used. Expressions (21) and (22) are bell-shaped curves centred at two, in general different, values of \( \omega' \) and having different widths. Although, due to the \( \omega' \) dependence of \( Q_1, Q_2, k_1/k_0, \) and \( k_2/k_1, \) they do not have a Gaussian shape, they do not differ strongly from it and so neither does their product. Adding to this that all the other \( \omega' \)-depending terms in (7) are very smooth functions of \( \omega' \) leads one to conclude that what is to be performed is the integration of a function \( F(\omega') \) rather similar to a Gaussian one.

This situation, together with the property of the integration domain of being unbounded on one side, lends itself naturally to the application of the IS technique using a suitable Gaussian weight function \( w(r_1,r_2;\omega') \), or \( w(\omega') \) for short. This choice exploits the availability in many software programs of generators of normally-distributed random numbers.

The actual implementation of the IS integration over \( \omega' \) proceeds as follows. Once the scattering points are sampled as described before, while retaining the explicit dependence on \( \omega' \) in the exponentials of (21) and (22), we choose a value of \( \omega' \) only for the purpose of fixing \( Q_1, Q_2, \) and the derived quantities. A convenient choice turns out to be \( \omega' = 0 \). Then, the product of the two exponentials, so modified into true Gaussian curves, is also a Gaussian function of \( \omega' \) with peak position and width that are immediately calculated. However, for the width it is advisable to take a slightly larger value, in order to ensure that the tails of \( w(\omega') \) always decay to zero more slowly than those of \( F(\omega') \), preventing problems of divergence in the ratios \( F(\omega')/w(\omega') \) of (19) or \( F^2(\omega')/w(\omega') \) of (20). The actual sampling of \( \omega' \) is then obtained according to the so-defined \( w(\omega') \) by means of the normally-distributed random number generator and, together with the spatial variables already determined, allows for the calculation of \( F(\omega') \) and the entire function to be integrated in (7). The rare case in which the value of \( \omega' \) is larger than \( \omega'_\text{max} \) requires the sampling of all variables to be discarded.

The effectiveness of this IS implementation has been estimated in a simplified situation where we consider only that part of \( F(\omega') \) that contributes most to its variance, namely the product \( \frac{d^2\sigma}{d\Omega d\omega'}(\omega') \cdot \frac{d^2\sigma}{d\Omega d\omega'}(\omega') \), and using (18) and (20) to calculate the expected variances in the \( \omega' \) integration alone, for some random choices of the other spatial variables. This has been done with the actual instrumental setup and the same sample properties of an experiment described later as a test case for the comparison with calculated scattering intensities. The typical variance reduction factor, shown in figure 4, is of the order of a few tens, which translates immediately into the same factor of computer time saving for a given required statistical accuracy.

4. Calculations and results

Turning to the real case, where the above MC integrations have to be performed efficiently for ToF instruments using thousands of detection pixels and time-channels, it is necessary to adopt programming methods ensuring an extremely fast computation of the integrands in (3) and (7) for all samplings and, ideally, all pixels and all time-channels. However, it is immediate to realize that, even by exploiting the IS method and other tools, such an ambitious project is still out of reach of medium-performance ‘normal’ personal computers, unless weeks or months of computing time are accepted.

To obtain real-time double scattering results, it is thus unavoidable to reduce the number of evaluations by reasonably decreasing, in the calculations, the spatial and time resolution with respect to that of the real instrument. As common practice also in the gathering of experimental data, spatial resolution is reduced by grouping ‘equivalent’ pixels, i.e. those pixels corresponding to the same nominal scattering angle \( \theta_D \) within an appropriate step \( \Delta \theta_D \). In the case of flat two-dimensional detectors as the BRISP one, this corresponds to grouping the detector pixels into a limited number of rings, each delimited by the intersections of the detector surface with
Figure 4. Ratio of the standard variance (18) to the IS variance (20) in the integration over \( \omega' \) of the product \( \frac{d^2\sigma}{d\Omega_d d\omega'}(\omega') \frac{d^2\sigma}{d\Omega_d d\omega''}(\omega') \), for three random samplings of the spatial coordinates performed in the ‘short distance’ (left) and ‘long distance’ (right) modes. The horizontal scale gives the flight time \( \tau \), the vertical line marks the position of the ‘elastic channel’, i.e. the flight time of a neutron undergoing one elastic scattering at the origin \( O \). The data refer to a detector element at \( \theta_D = 6.5^\circ \) with \( L_0 = 4 \text{ m} \).

the Debye-Scherrer cones [18] of semiaperture \( \theta_D - \Delta\theta_D/2 \) and \( \theta_D + \Delta\theta_D/2 \), respectively. In this way the integrand evaluation is performed not for all available pixels, but only for few tens of scattering angle values.

Moreover a further reduction of computing time is achieved by limiting the double scattering calculation to far less and more widely spaced time channels than those set through the detector electronics in the real-instrument acquisition configuration. Such a choice is well justified by the rather flat and structureless profile typical of double scattering intensities (see below), which does not require a high time resolution.

This is not the case for single scattering evaluations, due to the much narrower and sometimes structured corresponding ToF spectrum. However, computing time is saved in this case not at the expenses of the time resolution, but by the fact that the spectrum is concentrated in a much narrower time window than that actually provided by the whole ToF frame. In any case, the evaluation of (3) for one time value is much faster than that of (7).

The above reasonable approximations of the detection geometry and time-acquisition properties of the instrument are enough to ensure the wanted performances in terms of computing time, if of course used in connection with a modern programming approach, based on row-by-column matrix products in place of nested loops. Suitable commercial software efficiently allows for large-size matrix handling and multiplication, and therefore for single and double scattering evaluations in real-time conditions.

In particular, for each nominal scattering angle \( \theta_D \), the random coordinates of \( P_1 \) and \( P_2 \), within their scattering volumes, are initially stored in \( N \times 3 \) matrices, and the whole MC computation, including the IS of \( \omega' \), is carried out simultaneously for all \( n_{\text{ch}} \) time channels and all samplings, thanks to the possibility of calculating the needed quantities in the form of \( N \times n_{\text{ch}} \) matrices, which can be properly combined in an extremely fast way. As a final output we arrive at an \( N \times n_{\text{ch}} \) matrix containing the integrand of (3) or (7) for each sampling (rows of the final matrix) and for each time channel (columns of the final matrix). To obtain the MC integral at
Figure 5. Calculated ToF spectra. The double-scattering intensity (red dots with error bars and red line interpolated through the calculated points) is shown in the top frames and compared with single scattering in the bottom ones. The blue dots and the black line show the tails of single scattering spectrum before and after the convolution with the experimental resolution. The data refer to $\theta_D = 3.3^\circ$ (left) and $6.5^\circ$ (right). The vertical lines mark the positions of the ‘elastic channel’ as in figure 4.

As an example of the application of this computer program to the correction of multiple scattering effects, we refer to measurements recently performed [21] on BRISP with an incident neutron wavelength of 0.988 Å and $L_0 = 4$ m. The sample was liquid D$_2$S at a temperature of 205 K in a slab-shaped container, with a sample thickness of 6 mm. The calculation of single scattering has been carried out assuming a scattering law of the type shown in (13), with $S(Q, \omega)$ given by the Rayleigh-Brillouin three-line spectrum [16] and the simple Lorentzian line...
of the Fick’s law [17] describing the self diffusion dynamics. Both models are derived within hydrodynamics concepts. However, the presence of incoherent scattering cross-sections and the fact that $S(Q)$ is much smaller than unity due to the low compressibility of the liquid [17] make incoherent scattering dominate.

As already said, double scattering was calculated with the free-particle $S(Q, \omega)$ of (15). The calculations were obtained with rather small values of $N$. The double scattering was evaluated at 128 time channels with 500 samplings for $I_{\text{long}}$ and only 70 for $I_{\text{short}}$, where $r_{12}^* = 3 \text{ mm}$, i.e. half the sample thickness. The single scattering was computed at 800 time channels with $N = 500$. At each scattering angle, 5 and 3 cycles were performed for double and single scattering, respectively.

We present preliminary results at two scattering angles, namely $\theta_D = 3.3^\circ$ and $6.5^\circ$. In figure 5 we show the intensity of double scattering, which appears to be distributed over a very large time range. In fact, in the range where the experimental spectrum is appreciably different from zero, the double scattering is rather flat and low, as seen in the bottom frames of the figure. In order to allow for a meaningful comparison with the experiment, the calculated single scattering intensity must be convoluted with the experimental resolution, which, on the other hand, has a negligible effect on the double scattering spectrum. The comparison is displayed in figure 6, where the lower line gives $\frac{dI_1}{d\tau}$ and the upper line is the sum of $\frac{dI_1}{d\tau}$ and $\frac{dI_2}{d\tau}$. Both calculated lines are arbitrarily but consistently scaled to be plotted together with the measured spectra, which are, in turn, not yet normalized in absolute units. The experimental data shown here are obtained after subtraction of the container scattering, where the attenuation due to the presence of the sample has been properly accounted for.

From figure 6 it appears that the calculated total spectra are in rather good agreement with the experiment. However, we remind that it is not the purpose of this algorithm to simulate the correct scattering law. Instead, the use of very simple, though reasonably realistic, models for $\frac{d^2\sigma}{d\Omega d\omega}$ is aimed at an estimate of the multiple-to-single scattering ratio which is believed to be
**Figure 7.** BRISP spectra of D$_2$S (blue dots) at the same angles as in figure 5, together with the results of the multiple scattering subtraction (red dots) performed as described in the text.

a good approximation to the real one, only weakly dependent on the adopted $S(Q, \omega)$ model. Indeed, the agreement between the calculation and the measurement is better at the lower angle, according to the fact that hydrodynamic models are known to be valid only at very low $Q$.

The subtraction of multiple scattering from the experimental signal proceeds then from the assumption that

$$
\frac{dI_1/d\tau}{dI_1/d\tau + dI_2/d\tau}_{\text{exp}} \simeq \frac{dI_1/d\tau}{dI_1/d\tau + dI_2/d\tau}_{\text{calc}},
$$

so that, to a good approximation, the single-scattering experimental spectrum is obtained from the measured one by multiplication for the right-hand-side quantity, which is close to one in the peak region and decreases to zero in the tails. The application of this procedure leads to the results shown in figure 7.

We conclude by noting that, once the feasibility of such computations is demonstrated, further improvements can be easily envisaged in order to bring a program of this kind to the level of a reliable real-time tool for both planning and checking experimental work in the field of inelastic neutron scattering, besides of course helping in the analysis of data already collected. In this direction, foreseeable steps are, for example, the extension to the more realistic case of a scattering system inside a container, and the availability of a variety of models for the scattering law of different types of samples, starting from the schematization of molecular systems based on effective-mass approaches [22].

**Acknowledgments**

Useful discussions with R. Mancinelli on the application of the IS method are gratefully acknowledged.

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