Collimation Effects in Small-Angle X-ray and Neutron Scattering

BY PAUL W. SCHMIDT

Physics Department, University of Missouri, Columbia, MO 65211, USA

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Abstract

To obtain adequate intensity in small-angle X-ray and neutron scattering measurements, the apertures that define the incident and scattered beams often must be made so large that the measured intensity is an average over an appreciable interval of scattering angles. Allowance must frequently be made for the resulting distortion of the measured scattering curve. A technique previously developed by Hendricks & Schmidt [Acta Phys. Austriaca (1967), 26, 96–112; Acta Phys. Austriaca (1973), 37, 20–30] for describing collimation effects is outlined. This method makes use of a function called the ‘weighting function’, which specifies the width of the interval over which the intensity is averaged and indicates the emphasis given to scattering angles within this interval. A new calculation of the weighting function for ‘pinhole’ collimating systems, which employ circularly symmetric apertures instead of long narrow slits, is presented. Several techniques for performing collimation corrections are described, and a review is given of results that several workers have recently obtained in studies of collimation effects in pinhole systems.

I. Introduction

Even though many treatments of small-angle X-ray or neutron scattering theory assume that the measured scattering is the intensity at a single value of the scattering angle, this intensity cannot be directly measured. The reason that direct measurements are not possible is that adequate scattered intensity can be obtained only when the scattering system is designed to record the average intensity over an interval around the nominal scattering angle. The measured intensity therefore is often appreciably different from the intensity that would have been obtained if the scattering had been registered at only one scattering angle. This distortion is the subject of the present paper.

Fig. 1 shows an example of the large difference between the measured scattering and the scattered intensity that would have been obtained for perfect collimation (i.e. if the intensity had been measured only at the nominal scattering angle). My colleagues Mathias Steiner and Liu Baoren recently measured the lower curve with the Kratky camera (Kratky & Skala, 1958) in our laboratory at the University of Missouri. The sample was Vycor® 7930 porous glass. The upper (perfect-collimation) curve was calculated from the lower curve by use of the correction technique that we normally employ in our laboratory. (This correction procedure is outlined in § III.)

In many small-angle neutron scattering experiments, and also occasionally for small-angle X-ray scattering, allowance must be made for the fact that the system passes a band of wavelengths, rather than only one wavelength. This wavelength spread produces a distortion quite similar to collimation effects. In this paper, however, I consider only the effects produced by the finite size of the apertures.

In II I briefly review a procedure that Robert Hendricks and I have developed (Hendricks & Schmidt, 1967, 1973) for describing collimation effects. This procedure is based on the evaluation of a function called the weighting function, which specifies the interval of angles over which the scattered intensity is averaged and also describes the emphasis given to intensities at the angles within this interval.

Fig. 1. The relative scattered intensity before (lower curve) and after (upper curve) applying collimation corrections to the data for a sample of Vycor 7930 porous glass. The values of q are expressed in Å⁻¹. The scattering was measured with a Kratky camera.
In this section I also describe a new method that I have developed for calculating the weighting function for one example of the type of collimation systems often called 'pinhole' systems. In these systems, which have come into use after high-intensity sources became available, the intensity from an isotropic scatterer is averaged over a much narrower interval of scattering angles than is the case for instruments such as the Kratky camera, which use rectangular slits. Nevertheless, as I illustrate in § III, even with these so-called pinhole systems, collimation effects are not always negligible. Readers interested in the details of my calculation of the weighting function for a pinhole system can consult § IV.

In § II I also evaluate the weighting function for a pinhole system in which the width of the detector aperture can be considered negligible and the sensitivity of the detector and the distribution of the intensity over the source are uniform. This weighting function has a simple form and may be a useful approximation for studies of collimation effects in a number of pinhole collimation systems.

§ III begins with a summary of the material in a paper on collimation effects that I wrote over ten years ago (Schmidt, 1976). I also discuss some recent studies of collimation effects, including some procedures that can be employed with pinhole collimation systems. My choice of topics by no means implies that I consider these procedures to be the best ones. In fact, I doubt whether anyone can select the 'best' method for dealing with collimation effects, because the choice of how to handle these effects depends on a number of factors, including the types of scattering samples being investigated, the experimental scattering apparatus, and the computing facilities that are available. Finally, the user's preferences are always important and in many cases are the deciding factor.

II. The weighting function

A. The equation for the weighting function

Fig. 2 illustrates a technique which Robert Hendricks and I (Hendricks & Schmidt, 1967, 1973) have developed to describe collimation effects. The path of a single ray through the system is specified by the coordinates of three points, one in each of three planes. These planes are located at the source of the X-rays or neutrons, at the sample, and at the detector. The measured intensity \( I(q) \) is obtained by calculating the integral over the illuminated areas of these three planes. (The apertures that determine these illuminated areas are not always located at these planes. Often there are several apertures. The apertures that limit the ray often depend both on the nominal scattering angle and on the coordinates of the points through which the ray passes.) We have illustrated (Hendricks & Schmidt, 1967, 1973) how these ideas can be applied in some of the scattering systems often employed.

I will designate points in the detector, sample and source planes by the coordinate pairs \((x, x'), (y, y'), (z, z')\), respectively. I use primed and unprimed coordinates to specify points associated with the directions parallel respectively to the lengths and widths of the slits. The distances from the sample plane to the source and detector planes are \( L_s \) and \( L \), respectively. As Fig. 2 shows, the center of the detector plane is displaced by distances \( L_e \) and \( L_f \) from the axis of the collimation system in directions parallel respectively to the width and length of the slits, i.e. in the \(-x\) and \(x'\) directions. (The three planes are assumed always to be parallel, and all angles are considered small enough that either the sine or tangent of any angle can be considered equal to the angle expressed in radians.) With this notation, the measured intensity \( I_{\text{meas}}(\varepsilon, \gamma) \) can be written

\[
I_{\text{meas}}(\varepsilon, \gamma) = (1/A) \int_{-A}^{A} \int_{-A}^{A} I(z, z') I(\Omega) \, dz \, dz' \times \int_{-A_d}^{A_d} \int_{-A_d}^{A_d} e(x, x') f(z, z') \, dx \, dx'. \tag{1}
\]

In (1), \( I(\varepsilon) \) is the perfect-collimation scattered intensity at a scattering angle \( \varepsilon \),

\[
A = \int_{-A}^{A} f(z, z') \, dz' \int_{-A_d}^{A_d} e(x, x') \, dx' = \int_{-A_d}^{A_d} \int_{-A_d}^{A_d} e(x, x') f(z, z') dx \, dx',
\]

\[
\Omega = [(\varepsilon - u)^2 + (\gamma' - \gamma)^2]^{1/2},
\]

\[
u = -x/L - z/L_s + y(1/L + 1/L_s),
\]

\[
u' = -x'/L - z'/L_s + y'(1/L + 1/L_s),
\]

\( e(x, x') \) and \( f(z, z') \) are respectively the detector sensitivity and the distribution of intensity emitted by the

![Fig. 2. The path of rays through a small-angle scattering system. The detector plane, sample plane and source plane (referred to as the tube plane in the drawing) are shown, along with the true scattering angle \( \varepsilon \) (called \( \Omega \) in the text) and the nominal scattering angle \( \varepsilon \). [Reproduced by permission from Acta Physica Austrica, (1973). 37, 22.]](image-url)
source, and \( A_s, A_t \) and \( A_d \) are respectively the illuminated areas of the source, sample and detector planes. The scattering sample is assumed to be isotropic, and so the perfect-collimation intensity can be expressed by the even function \( I(e) \) of the scattering angle \( e \). Equation (1) is normalized so that if the perfect-collimation intensity is a constant, the measured intensity is equal to the same constant. In (2), the true scattering angle \( \Omega \) is expressed in terms of \( u, u' \) and the nominal scattering angles \( e \) and \( \gamma \).

Since the quantity \( \Omega \) defined in (2) depends only on the variables \( e, \gamma, u \) and \( u' \), the latter two variables can be chosen to replace \( \gamma \) and \( \gamma' \) as variables of integration in (1). Even though \( u \) and \( u' \) do not have a simple geometrical interpretation that can be easily shown in Fig. 2, they make it possible to obtain a very useful expression for \( I_{\text{meas}}(e, \gamma) \). After the order of integration is changed and the integration is performed over all variables except \( u \) and \( u' \), (1) can be expressed (Hendricks & Schmidt, 1967, 1973) as

\[
I(e, \gamma) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W(u, u') I(\Omega) \, du \, du'. \tag{4}
\]

The function \( W(u, u') \) is the weighting function. For convenience, infinite limits of integration are used in (4), even though \( W(u, u') \) is different from zero only for a finite region of \( u \) and \( u' \) around the origin. The weighting function has been defined to satisfy the normalization condition that

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W(u, u') \, du \, du' = 1.
\]

Equation (4) expresses the relation between the perfect-collimation and measured intensities when the detector sensitivity, the distribution of intensity of the source, and the location and dimensions of the aperture are known. This equation can be used to calculate the measured intensity from the perfect-collimation intensity. Alternatively, when the weighting function is known, the perfect-collimation intensity can, at least in principle, be obtained from experimental values of the measured intensity by solution of the integral equation (4), even though a solution of this integral equation may not always be practical.

**B. Collimation systems with rectangular slits**

Many small-angle scattering systems have apertures that are rectangular slits. [As I have mentioned, primed coordinates are used in (1) to specify points associated with the directions parallel to the lengths of the slits.] The lengths of the slits are assumed to be much greater than their widths. If the detector sensitivity and the distribution of the source intensity can be considered to be independent in the length and width directions, so that

\[
e(x, x') = e_w(x)e_l(x')
\]

and

\[
f(z, z') = f_w(z)f_l(z')
\]

the weighting function \( W(u, u') \) has the form

\[
W(u, u') = W_w(u)W_l(u'),
\]

and (4) can be written (Hendricks & Schmidt, 1967, 1973) as

\[
I_{\text{meas}}(e, \gamma) = \int_{-\infty}^{\infty} W_w(u)F(e - u, \gamma) \, du, \tag{5}
\]

where

\[
F(e, \gamma) = \int_{-\infty}^{\infty} W_l(u')I(\Omega') \, du',
\]

and

\[
\Omega' = [e^2 + (u' - \gamma)^2]^{1/2}. \tag{6}
\]

According to (5) and (6), for systems with rectangular slits, collimation correction can be done in two steps. First, corrections are made for the effect of the width of the slits. Corrections for length then are applied to the function \( F(e, \gamma) \) obtained from the width correction. The width correction must be done first.

Often, however, the slit width is so small that there is no need to make corrections for the effects of the widths of the slits, and \( I_{\text{meas}}(e, \gamma) \) can be considered equal to \( F(e, \gamma) \).

The slit-width weighting function \( W_w(u) \) can usually be quite easily determined experimentally. When there is no sample in the collimation system, the perfect-collimation intensity can be considered to be a delta function, and so, according to (6), \( F(e, \gamma) = W_l(\gamma)\delta(e) \). Thus, from (5),

\[
I_{\text{meas}}(e, \gamma) = W_l(\gamma)W_w(e).
\]

We have compared experimental and calculated slit-width weighting functions (for \( \gamma = 0 \)) (Hendricks & Schmidt, 1967, pp. 113, 119) for a Kratky collimation system (Kratky & Skala, 1958) and for a Beeman four-slit collimation system of the type developed by Anderegg, Beeman, Shulman & Kaesberg (1955).

The slit-length weighting function can in principle be evaluated in a similar way if the apparatus is constructed so that \( \gamma \) can be varied when \( e \) is set equal to zero. Although these variations are not possible on most slit systems, when they were carried out (Hendricks & Schmidt, 1967, pp. 116–117) on a Kratky camera (Kratky & Skala, 1958), the measured weighting function was found to be in quite good agreement with the calculated function.

I would like to mention that the weighting functions cannot be determined experimentally simply by placing a piece of film in the detector plane, because the film gives the weighting function that would have been obtained if the dimensions of the detector slit were negligible, while the weighting function allows for the finite size of this slit.
In § III, I discuss some techniques for correction of scattering data measured on a slit system.

C. Circularly symmetric collimation systems

In ‘pinhole’ collimation systems, the apertures are so small that the band of angles passed by the apertures is small compared with most or all of the scattering angles at which data are recorded, and the apertures are equidimensional (i.e. not elongated in any direction). Often the apertures are circularly symmetric.

For the isotropic scattering samples that I consider in this paper, the measured intensity from a pinhole system normally is obtained by averaging $I_{\text{meas}}(\varepsilon, \gamma)$ over the circle

$$
\varepsilon = \theta \cos \omega \\
\gamma = \theta \sin \omega.
$$

This circle contains all points in the detector plane that correspond to rays scattered at the nominal scattering angle $\theta$. The circular average $I_{\text{av}}(\theta)$ of $I_{\text{meas}}(\varepsilon, \gamma)$ then can be written

$$
I_{\text{av}}(\theta) = (1/2\pi) \int_0^{2\pi} I_{\text{meas}}(\theta \cos \omega, \theta \sin \omega) d\omega.
$$

Polar coordinates can be employed to rearrange the expression for $I_{\text{meas}}(\varepsilon, \gamma)$ so that this equation can be used to describe collimation effects for pinhole systems. Since six integrations are necessary to calculate $I_{\text{av}}(\theta)$, seven integrations must be performed to obtain $I_{\text{av}}(\theta)$.

As far as I know, the weighting functions for a pinhole collimation system have never been explicitly calculated. In this section I therefore outline a method by which the sixfold integral (1) can be expressed in a way that is convenient for collimation systems with circular symmetry. I then obtain an equation for $I_{\text{av}}(\theta)$. Although this equation is so new that it has not yet been applied, I believe that collimation effects can often be evaluated much more easily with this weighting function than by Monte Carlo techniques.

In this section I outline how the weighting function is calculated. The details of the calculation are given in § IV. Although § IV is quite condensed, it gives a complete description of the technique employed for calculating the weighting function.

In the calculation discussed below, I assume that the collimation system is circularly symmetric and that

$$
b(1/L_0 + 1/L) - c/L - a/L_0 > 0,
$$

where $a$, $b$ and $c$ are the radii of the apertures at the source, sample and detector, respectively. This assumption is fulfilled if $L$ and $L_0$ are of the same magnitude, $a$ is not a great deal larger than $b$, and $c$ is sufficiently small.

When the circular average of (1) is calculated and the Cartesian variables $x, x', y, y', z, z'$ in the integral in (1) are replaced by the polar coordinates $\rho, \delta, \sigma, \eta, \tau, \nu$ respectively, the equation

$$
I_{\text{av}}(\theta) = \frac{1}{\pi A} \int_0^{\pi} \int_0^{2\pi} \rho \, d\rho \int_0^{\pi} \sigma \, d\sigma \, d\eta \times \left[ \int_0^{2\pi} S(\rho, \delta, \sigma, \eta) I(\Omega_p) \, d\tau \, d\nu \right]
$$

is obtained. In (8),

$$
S(\rho, \delta, \sigma, \nu) = \epsilon(\rho \cos \delta, \rho \sin \delta) f(\tau \cos \nu, \tau \sin \nu),
$$

and

$$
\Omega_p = \left[ \theta^2 + r^2 - 2r\theta \cos \omega \right]^{1/2}.
$$

The quantity $\Omega_p$ in (8) is obtained by substitution of the variables

$$
\epsilon = \theta \cos (\omega + \beta), \\
\gamma = \theta \sin (\omega + \beta), \\
u = r \cos \beta,
$$

and

$$
u' = r \sin \beta
$$

in the equation

$$
\Omega = \left[ (\theta \cos \omega) - u + (u' - \theta \sin \omega) \right]^{1/2}.
$$

[To simplify the expression for $\Omega_p$, the angle $(\omega + \beta)$ has been used instead of $\omega$.] As is shown in § IV, (8) can be rearranged to give the expression

$$
I_{\text{av}}(\theta) = \int_0^R \int_0^{2\pi} W(r) I(\Omega) \, dr \, d\omega,
$$

where

$$
R = u/L_0 + b(1/L_0 + 1/L) + c/L,
$$

and

$$
W(r) = \frac{L_0^2(1/L_0 + 1/L)}{\pi A} \int_{\tau_{\text{min}}(r)}^{\tau_{\text{max}}(r)} K(\tau, r) \, d\tau.
$$

In (10),

$$
\tau_{\text{min}}(r) = \max \left[ 0, Lr - (a/L_0)L - b(L_1 + 1/L_0) \right],
$$

$$
\tau_{\text{max}}(r) = \min \left[ y, x \right],
$$

$$
K(\tau, r) = \int_{\tau_{\text{min}}(r)}^{\tau_{\text{max}}(r)} s \, ds \int_{L_0}^{L_0/L_0} A(z, \tau) I(\Omega_p) \, dz \\
\times \int_{-A(z, \tau)}^{A(z, \tau)} G(r, s, \tau, z, \beta) \, d\beta,
$$

where

$$
A(z, \tau) = 1 - A(z, \tau) I(\Omega_p) \\
A(z, \tau) = A(z, \tau) I(\Omega_p)
$$

and

$$
G(r, s, \tau, z, \beta) \\
G(r, s, \tau, z, \beta)
$$
A(x, y, z) = 0 \quad 0 \leq z \leq |x - y|
A(x, y, z) = \cos^{-1} \left[ \frac{(x^2 + y^2 - z^2)/2}{xy} \right] \quad |y - y| \leq z \leq x + y
A(x, y, z) = \pi \quad x + y \leq z,
\begin{align*}
s_{\text{ma}}(r, \tau) &= \min [r + a/L_0, b(1/L_0 + 1/L) + \tau/L], \\
s_{\text{ma}}(r) &= \max [0, r - a/L_0], \\
\min (x, y) &= x \quad x \leq y, \\
\min (x, y) &= y \quad x \geq y,
\end{align*}
\begin{align*}
G(r, s, \tau, \alpha, \beta) &= \int_0^{2\pi} e(\tau \cos \nu, \tau \sin \nu) f_\alpha(r, s, \alpha, \beta, \nu) d\nu, \\
f_\alpha(r, s, \alpha, \beta, \nu) &= f[F_\alpha(\alpha, \beta, \nu), F_\beta(\alpha, \beta, \nu)], \\
F_\alpha(\alpha, \beta, \nu) &= L_0[-r \cos(\alpha + \beta + v) + s \cos(\alpha + \nu)], \\
F_\beta(\alpha, \beta, \nu) &= L_0[-r \sin(\alpha + \beta + v) + s \sin(\alpha + \nu)].
\end{align*}

Although the weighting function (10) may seem very complicated, evaluation of this weighting function on a computer and use of the function for collimation corrections and studies of collimation effects probably will often be easier than making Monte Carlo calculations like those by which Barker & Weertman (1987) computed $I_{\text{meas}}^\varphi(\theta)$ from a theoretical expression for $I(\varphi)$ (see §III A)

When the width $c$ of the detector aperture is small enough that it can be considered to be zero, and when the detector sensitivity $e(x, x')$ and the distribution $f(z, z')$ of the intensity emitted by the source have the constant values $e$ and $f$, respectively, (9) and (10) reduce to
\begin{align*}
W_0(r) &= \frac{1}{2\pi^2 ef} \left( \frac{L_0}{ab_L} \right)^2 K(0, r), \\
K(0, r) &= 8\pi e f \int_{s_{\text{ma}}}^{s_{\text{max}}(r, 0)} A(s, 0, b_L) A(r, s, a/L_0) s ds \\
&= 8\pi^2 ef \int_{s_{\text{ma}}}^{s_{\text{max}}(r, 0)} A(r, s, a/L_0) s ds.
\end{align*}

Therefore
\begin{align*}
W_0(r) &= 4(L_0/\pi ab_L)^2 U(r), \\
U(r) &= (a/L_0)^2 \\
&= (1/L + 1/L_0), \\
U(r) &= \pi(a/L_0)^2 \quad 0 \leq r \leq b_L - a/L_0, \\
U(r) &= (a/L_0)^2 \cos^{-1} \left[ \frac{r^2 + (a/L_0)^2 - b_L^2}{2r(a/L_0)} \right] \quad r \geq b_L + a/L_0.
\end{align*}

When $b_L - a/L_0 \leq r \leq b_L + a/L_0$. For $r \geq b_L + a/L_0$, $U(r) = 0$.

Miller, Cooper, Han & Pruckmayr (1984), who were among the first people to use the weighting function method described by (9) for correction of small-angle scattering data obtained on a pinhole system, calculated an approximate weighting function for a special case of the conditions for which the weighting function $W_0(r)$ was obtained.

Equation (9) can be further rearranged by replacing $\omega$ by $s = \theta - \Omega_p$, where
\begin{align*}
\Omega_p &= \left[ \theta^2 + r^2 - 2r \cos \varphi \right]^{1/2},
\end{align*}

and (9) can be written
\begin{align*}
I_{\text{meas}}^\varphi(\theta) &= \int_{\varphi}^{r} \frac{(\varphi - s)^{1/2}}{\theta^{1/2}} I(\varphi - s) W_p(s, \varphi) ds, \quad (11)
\end{align*}

where
\begin{align*}
W_p(s, \varphi) &= \frac{(R^2 - s^2)^{1/2}}{1 - y^2/[4\theta(\theta - s)]^{1/2}} dy. \quad (12)
\end{align*}

(The conditions $\theta > s$ and $\theta > R$ must be satisfied, because otherwise at the smallest scattering angles the detector would be struck by the direct beam.)

According to (11) and (12), for pinhole systems, $\theta^{1/2} I_{\text{meas}}^\varphi(\theta)$ is obtained from $\theta^{1/2} I(\theta)$ and the weighting function $W_p(s, \varphi)$ by a relation analogous to (5). However, with pinhole systems there are two differences. First, the factor $\theta^{1/2}$ multiplies the measured and perfect-collimation intensities in the equation corresponding to the convolution integral (5). Second, the weighting function $W_p(s, \varphi)$ in general depends on both $s$ and $\varphi$. The dependence on $\varphi$ disappears, however, when powers of $(s/\varphi)$ higher than 1 can be neglected. If first-order terms also are negligible, (11) states that $I_{\text{meas}}^\varphi(\theta)$ and $I(\theta)$ are related by a convolution integral like (5).

Equations (11) and (12) provide a derivation for the expression given (without proof) by Moore [1980, equation (16)] and show the conditions under which his equation (16) applies.

## III. Some techniques for collimation correction

### A. Introductory comments

Two methods, which are sometimes called 'smearing' and 'unsmeearing' or 'desmearing', have been used to take account of collimation effects. [The expressions may come from the German words verschmieren and entschmieren sometimes employed (e.g. Kratky, Porod & Skala, 1960).] In smearing, the
measured intensity is calculated from the properties of the collimation system and an assumed theoretical expression for the perfect-collimation intensity. De-smearing, on the other hand, computes the perfect-collimation intensity from the measured intensity. An example of smearing is shown in Fig. 3, which illustrates Barker's calculation of the measured intensity expected from the D11 small-angle scattering system at the Institut Laue–Langevin in Grenoble, France when the perfect-collimation intensity is proportional to \( q^{-4} \), where \( q = 4\pi\lambda^{-1}\sin(\theta/2) \); \( \lambda \) is the scattered wavelength, and \( \theta \) is the nominal scattering angle. In his calculation, which takes account of the spread in the neutron wavelengths, Barker used a Monte Carlo technique to find the approximate weighting function for the D11 system. The triangles in Fig. 3 show the products of \( q^{4} \) and the 'smeared' intensities computed with this approximate weighting function and a perfect-collimation intensity that was assumed to be proportional to \( q^{-4} \). To verify this smearing calculation, the product of \( q^{4} \) and the scattered intensity measured for a sample that was expected to give a perfect-collimation intensity proportional to \( q^{-4} \) was divided at each value of \( q \) by the quantities shown by the triangles in Fig. 3. The results, which are indicated by squares in Fig. 3, can be seen to give reasonably constant values, as is expected when the perfect-collimation scattering from the experimental sample is proportional to \( q^{-4} \).

As I mentioned in § I, Fig. 1 compares the scattering curve recorded on a Kratky camera (Kratky & Skala, 1958) at the University of Missouri for a sample of Vycor 7930 porous glass with the curve corrected for collimation effects by the slit-function method that my colleagues and I routinely use in our laboratory and which is described below in § III B. As can be seen, the measured and corrected curves differ appreciably, as is normal for collimation systems which employ rectangular collimating slits. However, the corrected curve shown in Fig. 1 is in quite good agreement with the uncorrected scattering curves obtained for the same sample on the pinhole neutron and X-ray small-angle scattering systems at the National Center for Small-Angle Scattering Research at Oak Ridge, Tennessee, USA.

Both 'smearing' (i.e. calculation of the measured intensity from the properties of the scattering system and a theoretical expression for the perfect-collimation scattering) and collimation correction have advantages and disadvantages as techniques for taking account of collimation effects. At first sight, collimation correction might appear to be preferable to smearing because no knowledge of the perfect-collimation scattering curve is required. However, people who calculate collimation correction calculations are faced with many of the problems encountered in other relatively complex mathematical analyses of measured data. Many of these difficulties are connected with the fact that experimental data cannot be measured with arbitrarily high precision and do not extend over an infinite interval of scattering angles. Normally, as the name suggests, the smearing process tends to smooth any features present in the perfect-collimation scattering curve. Collimation correction must restore this lost structure. However, a collimation correction method normally has no a priori way of 'knowing' whether small fluctuations in the measured intensity are due to features reflecting the structure in the sample or are merely the result of experimental artifacts. While careful smoothing of the measured curve can minimize these difficulties, the uncertainty can never be completely eliminated, and so any collimation correction will tend to magnify the errors or uncertainties in the measured curve. Although collimation correction procedures can be designed so that they minimize these effects, this problem can never be completely overcome.

While a smearing calculation avoids the difficulties associated with errors in the intensities or with the restricted interval of scattering angles at which the intensity is measured, the experimenter in general has no way of knowing the form of the perfect-collimation intensity. Nevertheless, in many investigations, knowledge about the sample and its structure can suggest adequate information for analysis of the data, as was the case in the scattering measurements shown in Fig. 3.

Often the collimating slits of a Kratky camera (Kratky & Skala, 1958) can be considered to be infinitely long. For infinite slits, the slit-length weighting function is a constant. (Because of the infinite slit
length, the slit-length weighting function cannot satisfy the normalizing condition.) For small-angle scattering curves measured with infinitely long collimating slits, both the smearing and unsmearing calculations are relatively simple, and smeared intensities are often especially convenient for analysis of the scattering data. For example, if the perfect-collimation intensity is proportional to $q^{-3}$, the measured scattering curve is proportional to $q^{-3}$. In many experiments, the decision about whether to analyze the scattering data by smearing or by collimation correction depends on how much is known about the sample, on the facilities available for data analysis, and to some extent on the investigator’s preference as a result of earlier experience.

Collimation correction procedures can be divided into two classes. The first group consists of exact solutions of the integral equations. These solutions are probably most useful for correcting data from collimation systems which have rectangular slits, since for these collimation systems the correction can be broken into two steps, in each of which the integral equation has only one independent variable. This simplification has made it possible to obtain exact solutions for many of the integral equations encountered with slit systems. (For brevity, in the discussion below, I refer to collimation systems with rectangular slits as 'slit systems'. I call systems with circular symmetry ‘pinhole systems’.)

B. Collimation correction for slit systems

For slit systems, $\gamma$ is usually zero, and (5) and (6) can be written

$$I_{\text{meas}}(\epsilon, 0) = \int_{-\infty}^{\infty} W_w(u) F(\epsilon - u, 0) \, du \quad (13)$$

and

$$F(\epsilon, 0) = \int_{-\infty}^{\infty} W_l(v) I([(\epsilon^2 + v^2)]^{1/2} \, dv. \quad (14)$$

As I mentioned in § II, usually the slit-width weighting function $W_w(u)$ and sometimes also the slit-length weighting function $W_l(v)$ can be evaluated from experimental measurements. Although direct measurements of the weighting functions are normally preferable to calculations of these functions, often there is no alternative to a calculation. Exact expressions for the weighting functions for the Kratky camera (Kratky & Skala, 1958) and the Beeman four-slit scattering system (Anderegg et al., 1955) have been calculated (Hendricks & Schmidt, 1967), although these functions are often not easy to use.

Another possibility is to calculate weighting functions numerically from the dimensions of the collimation system. A computer program is available for these calculations (Buchanan & Hendricks, 1971). Information about this program is available from Dr J. S. Lin, National Center for Small-Angle Scattering Research, PO Box X, Oak Ridge, Tennessee 37831, USA.

Many weighting functions can be satisfactorily approximated by a Gaussian. A convenient technique is to assume that the weighting function (for either slit lengths or slit widths) has the form (Hendricks & Schmidt, 1967, pp. 120–121)

$$W_g(u) = p(\pi)^{-1/2} \exp(-p^2u^2), \quad (15)$$

where

$$p = (\pi)^{1/2} W(0).$$

This approximate weighting function $W_g(u)$ has the property that it equals the exact weighting function $W(u)$ at $u = 0$. It also satisfies the normalization convention that, as I mentioned in § II,

$$\int_{-\infty}^{\infty} W_g(u) \, du = 1.$$

[Although the variable $u$ in (15) for the Gaussian approximation suggests that the Gaussian is a slit-width function, the Gaussian approximation can also be used as a slit-length weighting function when, as is usually true, the length weighting function cannot be directly measured.]

In our laboratory at the University of Missouri, we have used the Gaussian approximation (15) for our slit-length weighting function for many years and have never had any evidence that the approximation was not satisfactory. Several times we have compared corrected scattering curves obtained from data for the same scattering sample measured with two quite different collimation systems. The fact that the two corrected curves were in excellent agreement supports our assumption that our collimation corrections are reliable. For example, when we recently measured the scattering from a porous silica gel both with our Kratky X-ray scattering system and the pinhole system at the University of Missouri Research Reactor, the two corrected curves were essentially equivalent. Our experience thus suggests that collimation corrections are probably not highly sensitive to small changes in the form of the weighting function.

As Guinier, Fournet, Walker & Yudowitch (1955, pp. 112–114) pointed out some years ago, slit-width corrections can be made by a method based on Fourier cosine transforms. In practice, however, this technique has not turned out to be very useful.

Since slit-width effects are usually small, approximate correction techniques are often useful. For many years, we have been using a width correction method (Taylor & Schmidt, 1967) which is based on a procedure suggested by Kratky, Porod & Skala (1960, pp. 99–101). In this method,

$$F(\theta, \gamma) = I_{\text{meas}}(\epsilon, \gamma) - (M/2)I_{\text{meas}}(\epsilon, \gamma)$$
where

\[ M_2 = \int_{-\infty}^{\infty} u^2 W_w(u) \, du, \]

and \( I''_{\text{meas}}(\varepsilon, \gamma) \) is the second derivative of the measured intensity with respect to \( \varepsilon \).

Normally we find that this correction technique is satisfactory. Recently, however, we have noticed that at scattering angles smaller than about 0.005 rad (with copper K\(\alpha\) X-rays), rapidly varying scattering curves are not corrected accurately. This effect is noticeable, for example, for perfect collimation intensities proportional to \( q^{-4} \).

Since slit-width effects can be described by the convolution integral (6), deconvolution procedures developed in other fields, such as optical spectroscopy, can be applied in small-angle scattering. For example, Sauder (1966) has described a method which can be considered to be a generalization of the technique of Kratky, Porod & Skala (1960).

Bale (1987) has employed Sauder’s method to correct for the analog of slit-width effects which he observed in a position-sensitive detector. In these detectors, the resolution of the detector along the counter wire can be described by a function like the slit-width weighting function. This function has both a narrow peak centered at a position on the counter wire corresponding to the nominal scattering angle and also a weaker but much broader shoulder, which has been ascribed to fluorescence photons which move parallel to the counter wire before they are detected (Kopp, 1987). The behavior of the detector used by Bale and his co-workers can be approximately simulated by the function

\[ F(x) = 0.9985 \exp(-x^2) + 0.0015 \exp\left(-\frac{x}{20}\right)^2, \]

where \( x \) specifies the scattering angle or the position where the X-ray quantum is registered in the position-sensitive detector. Similar shoulders can be expected in other position-sensitive detectors. The intensity of the shoulder is so low that it cannot be seen in Fig. 4(a), which is a plot of \( F(x) \) for all \( x \), but is visible only in Fig. 4(b), which shows values of \( F(x) \) smaller than 0.1. Bale found that the shoulder, which has an area only about 3% of that of the main peak, was still intense enough to have a small but easily detectable effect on the values of the exponents calculated from scattering curves proportional to negative powers of \( q \). He was able to obtain the correct exponents by use of a generalization of Sauder’s (1966) method.

I would now like to illustrate slit-length corrections by reviewing a technique known as the slit-function method. In this correction procedure, which was suggested by Kratky, Porod & Kahovec (1951), an approximate Gaussian slit-length weighting function \( W_l(x) \) is used to obtain the function \( H(x) \) which is the solution of the integral equation

\[ 1 = \int_{-\infty}^{\infty} \frac{W_l[(x-t)^{1/2}] + W_l[-(x-t)^{1/2}]}{2(x-t)^{1/2}} H(t) \, dt. \]

The function \( H(x) \), which is called the slit function, has the property that

\[ I(\varepsilon) = \frac{1}{2} \int_{-\infty}^{\infty} \frac{F[(\varepsilon^2 + t)^{1/2}, 0]}{[\varepsilon^2 + t]^{1/2}} H(t) \, dt. \]

Thus when the slit function \( H(x) \) is known, an exact solution of the slit-length weighting function can be obtained.

Of course, one might first get the impression that this technique merely substitutes one unsolvable integral equation for another for which no easy solution is available. However, the slit function equation must be solved only once for each setting of the collimation system, rather than for each measured curve.

![Fig. 4](image-url)
About ten years ago, Fedorov & Schmidt (1978) developed some procedures for using slit functions for routine collimation corrections. (Earlier studies of the slit function are summarized in my 1976 review and in Fedorov’s and my 1978 paper.) We devised (Fedorov & Schmidt, 1978) a method for calculating \( H(x) \) for larger \( x \) from an exact solution which was assumed to be known for smaller \( x \). [A technique for finding this small-\( x \) solution has recently been described by Deutsch & Luban (1987).] Fedorov & Schmidt (1978) derived expressions for the slit function for a trapezoidal weighting function often obtained with the Kratky camera (Hendricks & Schmidt, 1967, p. 116).

The slit function for the normalized Gaussian weighting function

\[
W_g(u) = \pi^{-1/2} p \exp(-u^2) \exp(-u^2/2)
\]

is (Fedorov & Schmidt, 1978)

\[
H(x) = \pi^{-1/2} \left[ \frac{\exp(-p^2 x)}{px^{1/2}} + 2 \int_0^{px^{1/2}} \exp(-u^2) \, du \right].
\]

This equation shows that the slit function can be expressed as a function of the quantity \( px^{1/2} \). [Equation (17) has been corrected for an error in equation (11) of our 1978 paper. Similarly, in the lower part of the left column of p. 413, the integral in the definition of \( g(i) \) should be multiplied by \( 2\pi^{-1/2} \). Finally, the lower limit in equation (4) on p. 411 should be \( -\infty \).]

For several years, my colleagues and I at the University of Missouri have used a Gaussian approximate slit-length weighting function and the associated slit function for correcting our scattering curves by the slit-function method. The necessary integral for calculating \( I(\theta) \) is evaluated numerically, and the result is put in a form similar to that employed in another correction technique that we used previously (Lin, Von Bastian & Schmidt, 1974). With both correction methods, the statistical uncertainty in the corrected data can be estimated by propagation of the uncertainty in the data points.

An important advantage of the slit-function method is that it can be easily adapted to give an approximation for the contribution to the integral in (16) from values of the integrand corresponding to scattering angles so large that no experimental data points are available. (These contributions are calculated only for scattering angles at which data have been recorded.) This approximation is possible because

\[
\lim_{x \to \infty} H(x) = 1.
\]

The slit function given by (17) for a Gaussian weighting function has this property.] If one assumes that \( H(x) \leq 0 \) for \( x \leq x_m \) and that \( F(\varepsilon, 0) \to 0 \) when \( \varepsilon \to \infty \), the contribution to the integral (16) from \( x \) values larger than \( x_m \) is \( F(\varepsilon^2 + x_m^2, 0)^1/2 \). In our analyses of measured data from many samples, we have found that this procedure is preferable to the assumption that values of the integrand for \( x \geq x_m \) do not contribute appreciably to the integral.

C. Series expansion techniques

In this class of collimation correction techniques, the measured intensity \( I_{\text{meas}}(\theta_i) \) at the scattering angle \( \theta_i \) is expressed by the series

\[
I(\theta_i) = 4 \sum_{n=1}^{\infty} a_n B(n, i),
\]

where the \( B(n, i) \) are known functions. As the \( B(n, i) \) are chosen to be relatively simple functions, the mathematical operations necessary for data analysis can be performed exactly on the \( B(n, i) \). For example, a series expansion for the measured intensity can be easily obtained. After the coefficients \( a_n \) have been evaluated by a fit of this series to the measured data, the coefficients can be used to calculate the perfect-collimation intensity.

Probable the first series expansion method to be widely used in small-angle scattering was Glatter’s (1977a, b, 1982) indirect expansion technique. Glatter has employed this method in many analyses of small-angle scattering data.

Moore (1980) has developed a different series expansion technique for collimation correction. Series expansions have also been employed by Müller & Damaschun (1979), Luzzati (1980), Taupin & Luzzati (1982), and Gerber & Schmidt (1983).

D. Pinhole collimation systems

Moore’s (1980) expansion technique is well suited for use with circularly symmetric collimation systems. By extension of Moore’s series expansion technique for collimation correction, Ramakrishnan (1985) has developed another procedure for correcting small-angle scattering data measured by use of a spherically symmetric collimation system. Both Moore’s and Ramakrishnan’s methods begin with an expansion of the correlation (distance distribution) function \( p(r) \), which has the property that

\[
I(\theta) = \int_0^d \frac{p(r) \sin qr}{qr} \, dr,
\]

where \( q = 4\pi\lambda^{-1} \sin(\varepsilon/2) \), \( \lambda \) is the wavelength, and \( d \) is a length that is not smaller than the largest distance separating two points in the scatterer. Moore expresses the function

\[
Q(r) = p(r)/r
\]

by the Fourier sine series

\[
Q(r) = 8\pi \sum_{n=1}^{\infty} a_n \sin(\pi nr/d)
\]
for \( r < d \) and sets \( Q(r) = 0 \) for \( r > d \). Then for the angle \( \theta_i \) corresponding to \( q_i \),

\[
I(\theta_i) = \int_0^d Q(r) \sin q_i r \, dr
\]

\[
= 4 \sum_{n=1}^{\infty} a_n B(n, i).
\]  

(18)

When the functions \( B(n, i) \) are evaluated by substitution into the above equations, the expression

\[
B(n, i) = 2\pi^2 n d (\frac{\sin (dq_i)}{(\pi n)^2 - (q_i d)^2})^{-1}.
\]

is obtained.

Ramkrishnan's (1985) adaptation of Moore's (1980) method for use with isotropic scattering samples employs Bessel functions instead of sines in the series for \( Q(r) \).

The coefficients \( a_n \) must be determined with care, in order to avoid instabilities in the calculations. Particular attention must be paid to the choice of the length \( d \), which should be as small as possible while not being smaller than the largest distance separating two points in the sample. Further information about fitting techniques is given by Moore (1980), Glatter (1977a, b, 1982) and Ramakrishnan (1985). In his integral transform method, Glatter (1977a, b, 1982) employs cubic spline functions in place of sines in the series expansion of \( Q(r) \) and has a somewhat different criterion for the choice of the length \( d \). All of these methods have been successfully used for making collimation corrections.

Wignall, Christen & Ramakrishnan (1988) have employed Moore's (1980) technique to investigate collimation effects on the 30 m small-angle neutron scattering system at Oak Ridge, Tennessee, USA. Their calculations included corrections for wavelength effects. Collimation effects were always appreciable, although the effects could often be minimized by suitable choice of the experimental geometry, including the sample-detector distance and the sizes of the slits. Fig. 5 shows the results Wignall, Christen & Ramakrishnan (1988) obtained when they used Moore's (1980) method to correct the scattering curve for a system of spherical particles. The spheres had radii of about 490 Å. Measured data points and intensities corrected for collimation effects are indicated by open and closed circles, respectively. The line is drawn through the corrected points. Since the series coefficients \( a_n \) were evaluated by a fit of a 'smeared' scattering curve obtained from an equation like (18), and the corrected curve was calculated from these \( a_n \) and the corresponding perfect-collimation \( B(n, i) \), the corrected curve is smooth and does not show the scatter in the measured data points.

Seeger & Pynn (1986) have described a way to allow for resolution effects in a circularly symmetric pulsed neutron source. In their work they concentrate on the wavelength spread inherent in a pulsed system. Their work is not directly applicable to the purely geometrical effects that I have discussed.

IV. Calculation of the weighting function for a circularly symmetric scattering system

From (8) and the definitions of \( u, u' \), and the polar coordinates \( \rho, \sigma, \eta, \tau \) and \( \nu \) introduced below (8),

\[
u = -\rho \cos \delta/L_0 - \tau \cos \nu/L + \sigma(1/L_0 + 1/L) \cos \eta \]

and

\[
u' = -\rho \sin \delta/L_0 - \tau \sin \nu/L + \sigma(1/L_0 + 1/L) \sin \eta.\]

By introduction of the variables

\[
u = r \cos \beta, \quad \nu' = r \sin \beta,\]

\[
s \cos \alpha = -\tau \cos \nu/L + \sigma(1/L_0 + 1/L) \cos \eta \]

\[
s \sin \alpha = -\tau \sin \nu/L + \sigma(1/L_0 + 1/L) \sin \eta,\]

the equations

\[
u = r \cos \beta = -(\rho/L_0) \cos \delta + s \cos \alpha \]

and

\[
u' = r \sin \beta = -(\rho/L_0) \sin \delta + s \sin \alpha \]

are obtained. When the pairs of variables \( \rho, \delta \) and \( \sigma, \eta \) are replaced respectively by the pairs \( r, \beta \) and \( s, \alpha \), (8)
can be written

\[
I_{\text{meas}}(\theta) = (L_0^2 / \pi A)(1/L_0 + 1/L)^{-2} \int \frac{d\omega}{\omega} \int \frac{d\tau}{\tau} 
\times \int_0^{2\pi} K(\tau, \nu, \theta, \omega) e^{i(\tau \cos \nu, \tau \sin \nu)} d\nu,
\]

where

\[
K(\tau, \nu, \theta, \omega) = \int_0^{s_{\text{max}}} s ds 
\times \left( J(\omega, s, \alpha + \nu + \pi, \theta) - A(s, t/L, bL) \right) dz,
\]

\[
b_L = b(1/L_0 + 1/L),
\]

\[
s_{\text{max}}(r/L) = \tau/L + b_L,
\]

the function \( A(x, y, z) \) is defined below (8), \( \max(x, y) \) is given by (10),

\[
J(\omega, s, \alpha, \theta) = \int_{r_{\min}(s)}^{r_{\max}(s)} H(r, s, \alpha) \Omega_p r dr,
\]

\[
r_{\max}(s) = s + a/L_0
\]

\[
r_{\min}(s) = \max(0, s - a/L_0),
\]

\[
H(r, s, \alpha) = \int_{-rL_0 \cos(\alpha + \beta) + sL_0 \cos \alpha} \int_{-rL_0 \sin(\alpha + \beta) + sL_0 \sin \alpha} f \, d\beta, d\alpha,
\]

and

\[
\Omega_p = (r^2 + \theta^2 - 2r \theta \cos \omega)^{1/2}.
\]

Equation (9) is obtained from (19) by changing the order of integration over \( r, s \) and \( \tau \).

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References


Further information about this work can be obtained from John Barker, Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA.


