A Simple Approximation for Calculating the Small-Angle X-ray and Neutron Scattering from Polydisperse Samples of Independently Scattering Uniform Spheres*

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Abstract

A convenient approximation has been obtained for the intensity of the small-angle X-ray or neutron scattering from an assembly of independently scattering spherical particles with constant density when the radius-distribution function is a Gaussian with a full width at half maximum which is not greater than 1.7 times the most probable radius. The approximation expresses the intensity in terms of elementary functions. Criteria are given for setting a bound on the error in the approximation.

1. Introduction

Two approaches can be employed to analyze small-angle X-ray or neutron scattering data from samples in which the scattering particles have the same shape but are not identical in size. In one method, an integral equation is solved numerically by use of measured scattering data (Schmidt, 1981; Fedorova & Schmidt, 1978; Vonk, 1976; Letcher & Schmidt, 1966). In the second procedure, a reasonable form is assumed for the distribution of particle dimensions, and after the intensity is calculated for this distribution, fitting techniques are used to determine the parameters in the distribution function (Hosemann & Motzkus, 1960; Motzkus & Hoseman, 1960; Wallace & Kratohvil, 1967). Although the first method may seem preferable, since no a priori assumptions must be made about the form of the distribution function, the solution of the integral equation is quite sensitive to small errors in the data and to the lack of scattering data at all scattering angles. Because of this sensitivity, fitting an intensity function calculated for a reasonable distribution function may often be the most practical way to analyze the scattering data from polydisperse systems.

Unfortunately, even for spherical particles, the intensity functions needed for these fits usually cannot be easily expressed in terms of elementary functions and so must be evaluated numerically. While numerical methods are adequate for analysis of most scattering data, a simple expression for the scattered intensity can often provide a clear picture of how the results depend on the parameters in the dimension distribution function and also can be employed for quick preliminary analyses of scattering curves and for investigating general properties of the scattering curves for a class of samples or dimension distribution functions.

In § 2, we develop an approximate expression for the scattered intensity for an assembly of independently scattering spherical particles with uniform electron density and a Gaussian radius-distribution function with a full width at half maximum which does not exceed approximately 1.7 times the most probable radius. With this distribution function, the scattered intensity can be approximated by a simple combination of elementary functions. This approximation gives the scattered intensity for relatively narrow radius distributions and thus is best suited for precisely the conditions for which Schmidt's (1958) exact expression for the scattered intensity for assemblies of uniform spherical particles with a broad distribution of particle radii becomes unwieldy.

Criteria for estimation of the error in the new expression are discussed in § 3.

2. Calculation of the scattered intensity

For a system of $N$ independently scattering spherical particles which have different radii $b$ and which, for X-ray or neutron scattering, respectively, have uniform electron or scattering-length density and are suspended in a solvent with a different but also constant electron or scattering-length density, the intensity $I(h)$ of X-ray or neutron scattering can be written (Guinier, Fournet, Walker & Yudowitch, 1955)

$$I(h) = I_0 \int_0^\infty \left( \frac{4 \pi b^3}{3} \right)^2 p(b) \phi^2(\beta b) \, db,$$

(1)

where $h = 4 \pi \lambda^{-1} \sin(\theta/2)$; $\lambda$ is the X-ray wavelength; $\theta$ is the scattering angle;

$$\phi^2(x) = \frac{9}{x^5} \left( \sin x - x \cos x \right)^2;$$

(2)

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and \( I_{00} \) is a constant, the value of which depends on whether the incident beam consists of X-rays or neutrons. For X-ray scattering, \( I_{00} = I_e \rho^2 \), where \( I_e \) is the intensity scattered by a single electron, and \( \rho \) is the difference between the electron densities of the particles and the solvent. For neutron scattering, \( I_{00} \) is proportional to the square of the scattering-length density. The radius-distribution function \( p(b) \) in (1) is defined to have the property that \( p(b) \, db \) is the probability that the observed X-ray has been scattered by a sphere with a radius in the interval between \( b \) and \( b + db \). The function \( p(b) \) is normalized so that
\[
\int_{-\infty}^{\infty} p(b) \, db = N. \tag{3}
\]
For the Gaussian distribution function
\[
p(b) = N \frac{1}{\sqrt{\pi}} \exp\left\{-\frac{[b-a]/(aa)^2}{4} \right\}, \tag{4}
\]
in which \( a \) is the most probable value of the radius and \( 2[\ln(2)]^{1/2} \sigma a \) is the full width at half maximum, (1) can be written
\[
I(h) = I(0) \frac{F(ha) - E(ha)}{1 - E(0)} \tag{5}
\]
where
\[
I(0) = I_{00} N \left(\frac{4 \pi}{3}\right)^2 \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left\{-\frac{[b-a]/(aa)^2}{4} \right\} \, db; \tag{6}
\]
\[
F(ha) = - \int_{-\infty}^{\infty} b^6 \exp\left\{-\frac{[b-a]/(aa)^2}{4} \right\} \Phi^2(hb) \, db \tag{7}
\]
and
\[
E(ha) = - \int_{-\infty}^{\infty} b^6 \exp\left\{-\frac{[b-a]/(aa)^2}{4} \right\} \Phi^2(hb) \, db \tag{8}
\]
Since \( \Phi^2(0) = 1 \),
\[
E(0) = G_0(\sigma) \left[ 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right] \tag{9}
\]
where
\[
G_0(\sigma) = \pi^{-1/2} \frac{1}{\Gamma(\sigma)} \left(\sigma t - 1\right)^n \exp\left(-t^2\right) \, dt, \tag{10}
\]
and \( n \) is zero or a positive integer.

When the distribution (4) is not broad – that is, when \( \sigma \) is not too large, \( E(ha) \) and \( E(0) \) in (5) will be negligible, and
\[
I(h) \approx I(0) F(ha). \tag{11}
\]
Bounds on the error in the approximation (11) are given in § 3.

An exact but relatively simple expression can be obtained for \( F(ha) \). The first and second derivatives of the integral (Gradshtein & Ryzhik, 1963)
\[
\int_{-\infty}^{\infty} \exp(-t^2) \cos[2x(1 + \sigma t)] \, dt = \pi^{1/2} \exp(-\sigma^2 t^2) \cos(2x), \tag{12}
\]
with respect to \( x \) yield the equations
\[
\int_{-\infty}^{\infty} (1 + \sigma t)^2 \exp(-t^2) \cos[2x(1 + \sigma t)] \, dt = -\pi^{1/2} \left[ (\sigma^2 x^2 - \sigma^2/2 - 1) \cos(2x) + 2x \sigma^2 \sin(2x) \right] \exp(-\sigma^2 t^2), \tag{13}
\]
By the change of variable
\[
i = \frac{b-a}{aa}, \tag{14}
\]
(7) can be written
\[
F(ha) = (9/2) \left( \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-t^2) \{1 + (1 + \sigma^2) \sigma^2(ha)^2 \}
- 2ha(1 + \sigma t) \sin[2ha(1 + \sigma t)] \right) \, dt
- \int_{-\infty}^{\infty} \exp(-t^2) \left[1 - (1 + \sigma^4) \sigma^2(ha)^2 \right] \times \cos[2ha(1 + \sigma t)] \, dt
\]
\times (ha)^{-6} \left[ \int_{-\infty}^{\infty} \left(1 + \sigma t\right)^6 \exp(-t^2) \, dt \right]^{-1}. \tag{15}
\]
With (12) and (13), (14) becomes
\[
F(ha) = (9/2) \left( 1 + \left(1 + \frac{1}{2} \sigma^2\right) (ha)^2 \right.
- 2ha(1 + (ha)^2) \sin(2ha) \exp[-(ha)^2]
\left. - \frac{1}{2}\left[1 + \left(\frac{3}{2} \sigma^2 - 1\right)(ha)^2 + (ha)^4\right]
\times \cos(2ha) \exp[-(ha)^2]\right)
\times \left[1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6\right]^{-1} \,(ha)^{-6}. \tag{16}
\]
Equation (15) is an exact expression for $F(ha)$ in terms of elementary functions.

A convenient equation can be obtained for the zero-angle scattered intensity $I(0)$ introduced in (5). From (6) and (10),

$$I(0) = I_{oo} N \left( \frac{4\pi^2 a^3}{3} \right)^2 \left( 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 \right) \left( 1 - \frac{E(0)}{1 - G_0(\sigma)} \right).$$

When $E(0)$ and $G_0(\sigma)$ in (16) are not negligible, they can be evaluated from tabulated integrals (Abramowitz & Stegun, 1965).

### 3. The error in the approximation

When $I(h)$ is approximated by (11), the quantities $E(ha)$ and $E(0)$ in (5) must be negligible with respect to $F(ha)$ and 1, respectively. As $\Phi^2(x)$ is never negative and has its maximum value of 1 at $x = 0$, $E(ha)$ will never be greater than $E(0)$. The approximation (11) thus can always be used when $E(0)$ is negligible with respect to $F(0)$. [As $0 \leq F(ha) \leq 1$, and $F(ha)$ is defined so that $F(0) = 1$, the condition that $E(0)$ is negligible with respect to $F(ha)$ guarantees that $E(0)$ will also be negligible with respect to 1.] This criterion for the use of (11) is convenient when $ha$ is not large with respect to 1 -- that is, when $F(ha)$ is not much smaller than 1. Tabulated values (Abramowitz & Stegun, 1965) of a function proportional to the $G_1(\sigma)$ can be used to calculate $E(0)$, which is given in Table 1 for several values of $\sigma$. As can be seen from the table, $E(0)$ is always less than 0.001 for all values of $\sigma$ which we consider and thus can normally be considered negligible with respect to 1.

For large $ha$, however, a more precise bound on $E(ha)$ than the condition $E(ha) \leq E(0)$ is necessary in order to avoid overestimation of the error. With the change of variable employed to obtain (14), (8) becomes

$$E(ha) = \left( \frac{9}{2} \right) \left( \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right) \left[ \frac{G_2(\sigma)}{(ha)^4} + \frac{G_3(\sigma)}{(ha)^6} \right]$$

After two integrations by parts, (17) can be written

$$E(ha) = \left( \frac{9}{2} \right) \left( \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right) \left[ \frac{G_2(\sigma)}{(ha)^4} + \frac{G_3(\sigma)}{(ha)^6} \right]$$

Integration of this expression by parts shows that

$$E(ha) \leq D(ha),$$

where

$$D(ha) = \frac{D_4(\sigma)}{(ha)^4} + \frac{D_6(\sigma)}{(ha)^6};$$

$$D_4(\sigma) = \left( \frac{9}{2} \right) G_2(\sigma) \left( \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right)$$

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$E(0)$</th>
<th>$D_4(\sigma)$</th>
<th>$D_6(\sigma)$</th>
<th>$(ha)_{a}$</th>
<th>$(ha)_{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/2$</td>
<td>$2.64 \times 10^{-7}$</td>
<td>$5.97 \times 10^{-5}$</td>
<td>0.0175</td>
<td>548</td>
<td>9.88</td>
</tr>
<tr>
<td>$5/9$</td>
<td>$1.351 \times 10^{-6}$</td>
<td>$1.609 \times 10^{-4}$</td>
<td>0.0332</td>
<td>467</td>
<td>8.29</td>
</tr>
<tr>
<td>$10/17$</td>
<td>$3.01 \times 10^{-5}$</td>
<td>$2.55 \times 10^{-3}$</td>
<td>0.0436</td>
<td>429</td>
<td>7.54</td>
</tr>
<tr>
<td>$2/3$</td>
<td>$1.461 \times 10^{-5}$</td>
<td>$5.97 \times 10^{-4}$</td>
<td>0.0681</td>
<td>358</td>
<td>6.16</td>
</tr>
<tr>
<td>$5/6$</td>
<td>$1.475 \times 10^{-4}$</td>
<td>$1.731 \times 10^{-3}$</td>
<td>0.0988</td>
<td>262</td>
<td>4.36</td>
</tr>
<tr>
<td>$1$</td>
<td>$6.67 \times 10^{-4}$</td>
<td>$2.95 \times 10^{-3}$</td>
<td>0.0982</td>
<td>205</td>
<td>3.33</td>
</tr>
</tbody>
</table>
and

\[ D_6(\sigma) = 27 \frac{G_0(\sigma)}{(1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6)}. \]

Some values of \( D_4(\sigma) \) and \( D_6(\sigma) \) calculated from the tables of Abramowitz & Stegun (1965) are included in Table 1.

Inequality (19) is convenient for setting a bound on the error in (11) for large \( ha \) that is, when \( ha \) exceeds about 10.

We now will develop an estimate of the error for use when \( ha \) is not large enough that (19) can be employed but still is not small enough that \( E(0) \) provides a useful limit on the error. To obtain this estimate, we integrate (17) by parts, obtaining

\[
E(ha) = (9/2) \left( \frac{ha}{a} \right)^{-(1/2)} \left( 1 + \sigma t \right)^2 \times \left\{ 1 + \cos[2ha(1 + \sigma t)] \right\} dt \\
- \left\{ \left. \frac{1}{1} \exp(-t^2) \right\} \right|_{-\infty}^{\infty} \\
\times \left\{ 2(1 + \sigma t) \exp(-t^2) \\
+ 2\sigma \left. \int_{-\infty}^{t} \exp(-u^2) du \right\} \right|_{-\infty}^{\infty} \\
\times \pi^{-1/2}(ha)^{-5} \left( 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right)^{-1}.
\]  

(21)

After another integration by parts, we find that

\[
E(ha) = (9/2) \left( \frac{ha}{a} \right)^{-(1/2)} \left( 1 + \sigma t \right)^2 \exp(-t^2) \\
\times \left\{ 1 + \cos[2ha(1 + \sigma t)] \right\} dt \\
- \left. \left. \frac{1}{1} \exp(-t^2) \right\} \right|_{-\infty}^{\infty} \\
- 4\sigma \left. \int_{-\infty}^{t} \left( 1 + \sigma t \right) \cos[2ha(1 + \sigma t)] \right|_{-\infty}^{\infty} \\
\times \left[ \left. \int_{-\infty}^{t} \exp(-u^2) du \right\} \right|_{-\infty}^{\infty} \\
\times \pi^{-1/2}(ha)^{-4} \left( 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right)^{-1}.
\]  

Since \( 1 + \sigma t \leq 0 \) for \( t \leq -1/\sigma \),

\[
E(ha) \leq (9/2) \left( \frac{ha}{a} \right)^{-(1/2)} \left\{ [2(1 + \sigma t)^2 \exp(-t^2)] - 4\sigma(1 + \sigma t) \\
\times \left[ \left. \int_{-\infty}^{t} \exp(-u^2) du \right\} \right|_{-\infty}^{\infty} \\
\times \pi^{-1/2}(ha)^{-4} \left( 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 + \frac{15}{8} \sigma^6 \right)^{-1}.
\]  

Integration by parts shows that

\[
E(ha) \leq \frac{4D_4(\sigma)}{(ha)^4},
\]  

(22)

where \( D_4(\sigma) \) is defined below (20).

Thus the error will not exceed \( E(0) \) for \( 0 \leq (ha) \leq (ha)_{ab} \), where

\[
(ha)_{ab} = \left[ \frac{4D_4(\sigma)}{E(0)} \right]^{1/4} = \left[ \frac{18G_2(\sigma)/G_6(\sigma)}{G_0(\sigma)} \right]^{1/4},
\]

while (22) gives a limit for the error when \( (ha)_{ab} \leq h \leq (ha)_{bc} \), where

\[
(ha)_{bc} = \left[ \frac{D_6(\sigma)/[3D_4(\sigma)]}{G_0(\sigma)/G_2(\sigma)} \right]^{1/2}.
\]

For \( h \geq (ha)_{bc} \), the error can be estimated from (19).

The quantities \( D_4(\sigma), D_6(\sigma), E(0), (ha)_{ab}, \) and \( (ha)_{bc} \) calculated from the tables of Abramowitz & Stegun (1965) are listed in Table 1 for several values of \( \sigma \).

From Table 1 and the values of \( F(ha) \) shown in Figs. 1 and 2, the relative error in the approximation (11) can be shown to be at most a few per cent for all values of \( ha \) for \( 0 \leq \sigma \leq 1 \). Except when \( \sigma \) is near 1, the error is considerably smaller. Thus, for all \( \sigma \) between 0 and 1, the error in the approximation (11) will not exceed the uncertainty in most experimental X-ray or neutron scattering data.
4. Discussion

As has been mentioned above, when both \( E(ha) \) and \( E(0) \) are negligible in (5), (11) and (16) give a simple and convenient expression for the intensity for a system of independently scattering uniform spherical particles with the radius distribution (4). This distribution, although it was selected primarily because it gives a convenient expression for the scattered intensity, can be used to approximate many other distribution functions by selection of the width parameter \( \sigma \) and the most probable radius \( a \). Since calculations (Schmidt, 1958; Mittelbach, 1965) suggest that the intensity is relatively insensitive to small changes in the form of the radius distribution function, little generality is lost by use of an approximate distribution function.

The full width of the distribution function (4) at half maximum is

\[
2(\ln(2))^{1/2} \sigma a \approx 1.7 \sigma a.
\]

As we have explained in § 3, the error in the approximation (11) is smaller than the uncertainty in most experimental scattering data when \( \sigma < 1 \). Thus, (16) will be a useful approximation when the width of the radius distribution function (4) does not exceed about \( 1.7 \) times the most probable radius \( a \).

Figs. 1 and 2 show the function \( F(ha) \) for several \( \sigma \) values between 0 and 1. When \( \sigma = 0 \), all particles have the same radius, and \( F(ha) = \Phi^3(ha) \), as can be verified from (2) and (15). For \( \sigma > 0 \), the subsidiary maxima and minima in \( F(ha) \) become washed out, and \( F(ha) \) has no maxima or minima when \( \sigma \geq 0.35 \).

The curves in Figs. 1 and 2 are similar to those which have been calculated numerically by Mittelbach (1965) for a distribution function equivalent to that employed by Schmidt (1958). (In Mittelbach’s distribution, the exponent \( m+3 \) corresponds to \( n \) in Schmidt’s calculations.) Mittelbach obtained subsidiary maxima and minima only for \( m > 50 \). Although Schmidt’s scattering equation for \( n = 53 \) gives an exact expression for the scattered intensity, the equation contains more than 50 terms. Thus, (11) has the advantage of being most accurate for precisely the conditions for which the results of Schmidt (1958) and those of Mittelbach (1965) become unwieldy.

When the term proportional to \( (ha)^{-6} \) in \( D(ha) \) in (20) is negligible,

\[
I(h) \approx (9/2)I(0) \left[ 1 + \frac{1}{2} \sigma^2 - G_2(\sigma) \right]
\times \left[ 1 - E(0) \right]^{-1} \left[ 1 + \frac{15}{2} \sigma^2 + \frac{45}{4} \sigma^4 
+ \frac{15}{8} \sigma^6 \right]^{-1} (ha)^{-4}.
\]  

(23)

When the integral \( G_2(\sigma) \) in (23) is not negligible, it can be evaluated with the tables of Abramowitz & Stegun (1963).

In analyses of small-angle scattering curves, the parameters \( \sigma \) and \( a \) can be calculated from a non-linear least-squares fit, such as CURFIT (Bevington, 1969). The same fit will normally give an amplitude parameter, and \( I(0) \) can be obtained from this parameter and the value of \( \sigma \) given by the fit.

As has been explained in § 3, the error in (11) will not exceed the smaller of the two quantities \( D(ha) \) and \( E(0) \). Since scattered intensities can rarely be measured with a relative uncertainty smaller than about 1%, the error estimates developed in § 3 show that when \( \sigma \leq 1 \), (11) is at least an adequate approximation for \( I(ha) \) for all \( ha \). Thus, for systems of spherical particles in which the radius distribution can be approximated by (4), (11) and (15) are reliable and convenient expressions for analysis of the scattering data when \( \sigma \leq 1 \).

References

SCATTERING FROM POLYDISPERSE SAMPLES


