Intersect Distributions and Small-Angle X-ray Scattering Theory*

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A new method has been developed for calculating the intersect distribution function \( G(M) \) which is used in the theory of the small-angle X-ray scattering from suspensions of identical non-interacting randomly oriented particles with uniform electron density. Intersects, or chords, are straight lines which have both ends on the particle boundary, and \( G(M) \) is the probability that an intersect has a length between \( M \) and \( M + dM \). Since \( G(M) \) can be shown to contain all information about these suspensions which is obtainable from small-angle X-ray scattering measurements, the intersect distribution function can be used to study the relation between the scattered intensity and the particle shape and dimensions. The new calculation technique, which employs some results from integral geometry, is much simpler than methods previously used to find \( G(M) \) or the characteristic function \( \gamma_0(r) \), which contains essentially equivalent information. For particles with a smooth convex boundary, the first two terms are obtained in the expansion of \( G(M) \) in powers of \( M \) and are evaluated for a plane lamina and a three-dimensional particle. The approximate expressions for \( G(M) \) are used to determine some properties of the scattered intensity in the outer part of the scattering curve.

Introduction

Small-angle X-ray scattering is often used to study the form and dimensions of the particles in colloidal suspensions. The relation between the scattered intensity and the particle structure must be known before the scattering data can be interpreted. Although this relation is now well enough understood to permit analysis of most scattering data from dilute suspensions of colloidal particles, a more detailed knowledge of the relationship will allow more information to be obtained from experimental scattering curves and thus will permit small-angle X-ray scattering studies to give more details about the particles in a colloidal suspension.

The scattered intensity from a dilute suspension of randomly oriented identical particles is proportional to the intensity scattered by a single randomly-oriented particle, with the intensity being averaged over all particle orientations. Thus, in discussions of the angular dependence of the scattering, only a single particle need be considered. Also, at scattering angles of a few degrees or less, the X-ray scattering is determined by the overall configuration of the particle and is not affected by structure with dimensions of the magnitude of interatomic spacings. The particles can therefore be considered to have a uniform electron density. For similar reasons the solvent electron density can be taken to be constant. The scattering from a particle then is determined only by the form and dimensions of the surface which is the boundary of the particle.

Under these conditions, all information about the particle shape which is obtainable from scattering measurements is contained in a function called the characteristic function \( \gamma_0(r) \) (Guinier, Fournet, Walker & Yudowitch, 1955, pp. 12-16), which is a measure of the average probability that if a point is in the particle, a second point will also be in the particle when the two points are separated by a distance \( r \).

Porod (1967) has shown that essentially the same information can be obtained from a related function called the intersect distribution function \( G(M) \). An intersect, or chord, is a line which has both ends lying on the boundary of the particle. The intersect distribution function \( G(M) \) gives the probability that an intersect will have a length in the interval between \( M \) and \( M + dM \). Often the intersect distribution function is easier to calculate than the characteristic function.

Recently we described a technique (Schmidt, 1967a; Wu & Schmidt, 1968) for finding the intersect distribution function for plane laminas with a smooth convex boundary curve. We have now used some results from integral geometry to simplify the calculation considerably. Also, we now are able to deal with three-dimensional particles bounded by a smooth convex surface. While the results for two-dimensional laminas were useful for showing some properties of the intersect distribution and for indicating how the calculation could be extended to three-dimensions, our new results for three-dimensional particles should have considerably greater application in analysis and interpretation of experimental scattering curves.

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The relation between the characteristic function and the intersect distribution

The average intensity $I(h)$ scattered by a single randomly oriented particle can be written (Guinier et al., 1955, p. 12, equation 21)

$$I(h) = 4\pi I_e V^2 \int_0^\infty \gamma_0(r)^2 \sin hr \frac{dr}{hr}$$

where $V$ is the particle volume, $I_e$ is the intensity scattered by a single electron, $\rho$ is the difference in the electron densities of the particle and the solvent, $h = 4\pi\lambda^{-1} \sin(\theta/2)$, $\lambda$ is the X-ray wavelength, and $\theta$ is the scattering angle. For a three-dimensional particle (Porod, 1967)

$$G(M) = \bar{M} \gamma_0(M)$$

where $\bar{M}$, the average length of an intersect, is given by (Wu & Schmidt, 1968; Guinier et al., 1955, p. 15, equation 24)

$$\bar{M} = -1/\gamma_0(0) = 4V/S$$

and where $S$ is the surface area of the particle.

In two dimensions there is a similar relation (Wu & Schmidt, 1968, equation 9)

$$G(M) = \bar{M} \beta_0(M)$$

between $G(M)$ and the characteristic function $\beta_0(r)$ for a plane lamina, with (Wu & Schmidt, 1968, equation 8; Schmidt & Hight, 1959)

$$\bar{M} = -1/\beta_0(0) = \pi A/L$$

where $A$ and $L$ are the area and perimeter of the lamina.

Since $\gamma_0(0) = 1$ (Guinier et al., 1955, p. 15) and, as mentioned above, $\gamma_0(0) = -S/(4V)$, $G(M)$ and $\gamma_0(r)$ contain equivalent information. If $\gamma_0(r)$ is known, $G(M)$ can be calculated from (1), and the equation (Porod, 1967)

$$\gamma_0(r) = (1/\bar{M}) \int_r^\infty dM(M-r)G(M)$$

can be used to obtain the characteristic function from the intersect distribution.

Calculation of the intersect distribution

(a) Two dimensions

The intersect distribution $G(M)$ has been defined so that $G(M)dM$ is equal to the probability that an intersect will have a length between $M$ and $M + dM$. The line density $dg$ used in integral geometry (Blaschke, 1955, p. 8, equation 38) therefore can serve as a starting point for calculating $G(M)$. Blaschke establishes the validity of $dg$ as a measure of the probability that a line will pass through a given point in a plane and will be directed so that the angle between the $x$ axis and a unit vector $p_1$ normal to the line will have a value between $\phi$ and $\phi + d\phi$. By modification of Blaschke's notation, $dg$ can be expressed

$$dg = |dpd\phi|$$

where $dp$ represents a displacement parallel to $p_1$. This form of $dg$ can be interpreted as a statement that $dg$ is proportional to the product of the probabilities that (a) the line will pass through the neighborhood of a given point and that (b) the unit vector normal to the line will have a given orientation. These two probabilities are proportional to $dp$ and $d\phi$, respectively.

To specify points on the boundary of a two-dimensional plane lamina with a smooth convex boundary, we will use the arc length $t$ from a reference point. A point on the boundary will be called 'point $t$' when this arc length is equal to $t$.

Consider an intersect with length $M$ and with one of its ends at point $t$. Let $\alpha$ be the angle between the $x$ axis and the unit tangent vector at point $t$, with the unit tangent vector being oriented in the direction in increasing $t$. Then $\mu = \phi - \alpha - \pi/2$ is the angle between the intersect and the tangent vector. (Fig. 1) Also

$$dp = -\sin \mu dt .$$

Let $D$ be the length of the longest line that can be contained in the lamina. Then $0 \leq M \leq D$, and from the definition of $G(M)$,

$$\int_0^D G(M)dM = 1 .$$

Also, all lines passing through point $t$ will be intersects, and so, where $a$ is a constant of proportionality

$$\int_0^D G(M)dM = a \int_0^\infty dg = 1 .$$

All lines crossing the boundary of the lamina will be accounted for when

$$\int_0^L dt \int_{\alpha + \pi/2}^{\alpha + 3\pi/2} \sin(\phi - \alpha - \pi/2)d\phi = 2L$$

where $L$ is the length of the perimeter of the lamina. Thus, from (2), $a = 1/(2L)$.

For each value of $M$ in the interval $0 \leq M \leq M_m(t)$,
we assume that there will be two values of \( \mu \). (Our calculations show that this assumption is verified for small \( M \) and in certain other cases. The calculation can be modified when this assumption is not valid.) When \( M \) replaces \( \varphi \) as a variable of integration,

\[
\int_0^D G(M) \, dM = \frac{1}{2L} \sum_{i=1}^2 \int_0^L \frac{d\mu_i}{dM} | \cos \mu_i | \, dM
\]

where the \( \mu_i \) are the two values of \( \mu \) corresponding to a given value of \( M \), and \( M_{\text{max}}(t) \) is the largest value of \( M \) at point \( t \). By changing the order of integration over \( M \) and \( t \), we obtain

\[
G(M) = \frac{1}{2L} \sum_{i=1}^2 \int_0^L \frac{d\mu}{dM} | \cos \mu_i | \, dt.
\]  

(3)

For each value of \( i \), the integration in (3) is carried out over all \( t \) values for which intersects with length \( M \) can be drawn.

According to (3), for a plane lamina the calculation of \( G(M) \) reduces to expressing \( \cos \mu_i \) as a function of \( M \) and \( t \).

For example, a short calculation shows that at any point on the boundary of a circle with radius \( R \),

\[
\cos \mu_i = (-1)^i \left[ 1 - \frac{M^2}{4R^2} \right]^{1/2}.
\]

Then, from (3),

\[
G(M) = \frac{M}{2R(4R^2 - M^2)^{1/2}}.
\]

This expression is equivalent to our previous result (Schmidt, 1967a, p. 477), since, as mentioned in the preceding section, for a circle, \( M = \pi A/L = \frac{1}{2} \pi R \).

For small \( M \), the Frenet–Serret equations (Widder, 1947) can be used to extend our previous calculations (Schmidt, 1967b) to give the approximate expressions

\[
M \cos \mu_i = \frac{k^2 u^3}{12} - \frac{kk' u^4}{8} - \frac{4kk'' + 3(k')^2 - k^4}{120} u^5
\]

and

\[
M^2 = u^2 - \frac{k^2 u^4}{12} - \frac{kk' u^5}{12} - \frac{9k'' + 8(k')^2 - k^4}{360} u^6
\]

(4)

where the two ends of the intersect are at points \( t \) and \( t + u \), and where \( k \), \( k' \), and \( k'' \) are respectively the curvature, \( dk/dt \), and \( d^2k/dt^2 \) at point \( t \). By successive approximations (5) can be solved for \( M \), giving

\[
u = (-1)^i \left[ M + \frac{k^2 M^3}{24} + (-1)^i \frac{kk' M^4}{24} + \frac{27k'' + 72kk'' + 64(k')^2}{5760} M^5 \right].
\]

Thus, \( u \) is positive for \( i = 2 \) and negative for \( i = 1 \). By substituting this expression in (4), one obtains

\[
\cos \mu_i = (-1)^i \left[ 1 - \frac{k^2 M^2}{8} - (-1)^i \frac{kk' M^3}{12} \right]^{1/2}.
\]

Then

\[
G(M) = \frac{1}{L} \int_0^L \frac{d\mu}{dM} \left[ \frac{k^2 M^2}{4} - \frac{9k^4 + 16(k')^2 + 24kk''}{288} M^4 \right].
\]

But by partial integration

\[
\int_0^L \frac{d\mu}{dM} \, dM = -\int_0^L \frac{d(k')^2}{dM} \, dt
\]

since the quantity \( (kk') \) has the same value at point \( 0 \) and point \( L \). Therefore, for small \( M \), \( G(M) \) can be written

\[
G(M) = \frac{(k^2)}{4} M + \left[ \frac{k^4}{32} - \frac{(k')^2}{36} \right] M^3 + \ldots
\]

(6)

where bars indicate averages over the boundary of the lamina. For example,

\[
\bar{k}^2 = \frac{1}{L} \int_0^L d(k^2).
\]

Equation (6) is equivalent to our previous result (Wu & Schmidt, 1968, equation 26). The calculation of \( G(M) \) is considerably easier with (6) than with our earlier method.

(b) Three dimensions

In three dimensions, the line density \( dg \) can be written (Blaschke, 1955, p. 65, equation 50)

\[
dg = dA \cos \omega \, dS
\]

where \( dA \) is a surface area element on the smooth convex boundary surface, \( \omega \) is the angle between the intersect and the normal to the surface, and \( dS \) is an element of area on a spherical surface with unit radius and center at the area element \( dA \). The two ends of the intersect are at \( dA \) and \( dS \). The expression for \( dg \) can be interpreted as a statement of the probability that the intersect \( (a) \) will pass through \( dA \) and also \( (b) \) will have a given orientation. The first probability is proportional to the projection of \( dA \) normal to \( M \) and thus is proportional to \( dA \cos \omega \), while the second probability is proportional to \( dS \).

Just as for two dimensions

\[
\int_0^D G(M) \, dM = 1 = \frac{1}{a} \int_0 a \, dg
\]

where \( D \) is the length of the longest intersect, and \( a \) is a proportionality constant. For the area element \( dS \), a spherical coordinate system can be used with origin at \( dA \) and with the inward normal as the \( z \) axis. Then all intersects are accounted for when

\[
\int_0^{\pi/2} \int_0^{2\pi} \cos \omega \, d\omega \, d\varphi \int_0^{\pi/2} \cos \omega \, dS = \pi A
\]

where \( \omega \) and \( \varphi \) are the polar and azimuth angles in the spherical coordinate system. \( A \) is the surface area of the particle, and the surface integration extends over the entire convex boundary surface. Thus \( a = 1/(\pi A) \).
An explicit expression for \( G(M) \) can be obtained by using \( M \) as a variable of integration instead of \( \varphi \). Let \( p \) be a vector specifying a point on the boundary surface, and let \( M_0(p) \) be the length of the intersect which coincides with the inward normal at \( p \). (For this intersect, \( \varphi = 0 \).) Then for small \( M \), our calculations show that for a given value of \( \varphi \), in the interval \( 0 < \varphi < \pi/2 \) there will be only one value \( \omega_1 \) of \( \omega \) corresponding to a given value of \( M \), and \( \partial \omega_1/\partial M \leq 0 \). We will assume that there will be only one \( \omega \) value for \( 0 \leq M \leq M_0(p) \) and that when \( M_0(p) \leq M \leq D \), there will be two \( \omega \) values \( \omega_1 \) and \( \omega_2 \) for each \( \varphi \) value, with \( \partial \omega_1/\partial M \geq 0 \) and \( \partial \omega_2/\partial M \leq 0 \). For \( M \leq M_0(p) \), we assume that \( 0 < \varphi \leq \pi/2 \) and that for \( M > M_0(p) \), intersects with length \( M \) will exist for an interval which may be smaller. The limits of the integration over \( \varphi \) will be written \( \varphi_a < \varphi < \varphi_b \), with the quantities \( \varphi_a \) and \( \varphi_b \) depending on \( p \) and \( M \). Then, when \( M \) is used as a variable of integration, \( G(M) \) can be expressed

\[
G(M) = \frac{1}{2\pi A} \int_{\varphi_a}^{\varphi_b} \left[ \frac{\partial \cos^2 \varphi_1}{\partial M} - \frac{\partial \cos^2 \varphi_2}{\partial M} \right] d\varphi . \tag{7}
\]

In (7), the convention is used that \( \cos^2 \omega_2 \) is set equal to zero when there is only one value of \( \omega \) corresponding to a given value of \( M \). The surface integration in (7) extends only over the portion of the boundary surface for which intersects with length \( M \) exist.

If \( D_0 \) is the smallest value of \( M_0(p) \), for \( 0 \leq M \leq D_0 \), \( \varphi_b = 2\pi \), \( \varphi_a = 0 \), and the surface integration is carried out over the entire boundary.

When \( M \geq D \), \( G(M) = 0 \).

For a sphere with radius \( R \), \( D = D_0 = 2R \), and for \( 0 \leq M \leq 2R \), \( \cos \omega_1 = M/(2R) \), and

\[
G(M) = \frac{M}{2R^2} . \tag{8}
\]

An approximate expression for \( G(M) \) will now be obtained for small \( M \) for an arbitrary smooth convex boundary surface. Points \( p \) on the boundary surface will be expressed by two parameters \( u \) and \( v \). These parameters are chosen so that the lines on the surface for which \( u \) and \( v \) are constant are lines of curvature, and therefore the lines along which \( u \) is constant will be orthogonal to the lines for which \( v \) is constant (Struik, 1950, p. 80). At each point \( p \) on the surface, a cylindrical coordinate system is constructed, with coordinates \( r \), \( \varphi \) and \( z \) and with the \( z \) axis being the inward normal at \( p \). As shown in the Appendix, points on the surface near \( p \) can be expressed

\[
z = \sum_{i=2}^{\infty} Z_i(\varphi)r^i . \tag{9}
\]

(The \( Z_i(\varphi) \) also depend on \( u \) and \( v \), although this dependence is not explicitly indicated). In (9), \( z \) is the distance from a point on the surface to the tangent plane at \( p \). The \( Z_i(\varphi) \) which have been evaluated are expressible in the form

\[
Z_i(\varphi) = \sum_{j=0}^{i} Z_{ij} \cos^{i-j} \varphi \sin^j \varphi . \tag{10}
\]

The \( Z_{ij} \) in (10) are functions of \( u \) and \( v \) but are independent of \( \varphi \). Values of the \( Z_{ij} \) for \( i = 2, 3, \) and 4 are listed in Table 1.

**Table 1. Values of the \( Z_{ij} \) in equation (10)**

<table>
<thead>
<tr>
<th>( i )</th>
<th>( j )</th>
<th>( Z_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>( k_1/2 )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>( k_2/2 )</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>( E^{-1/2}k_1(u) )</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>( G(u)k_1(u) )</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>( k_3/2 )</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>( G(u)k_2(u) )</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>( E^{-1/2}k_2(u) )</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>( E^{-1/2}Gk_2(u) )</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>( k_4/2 )</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>( G(u)v )</td>
</tr>
</tbody>
</table>

The coordinate system has been chosen so that \( \cos \omega_1 = z/M \) and \( M^2 = r^2 + z^2 \). Thus, from (9),

\[
\cos^2 \omega_1 = \sum_{i=2}^{\infty} M^i \sin^{i+2} \omega_1 \sum_{i=2}^{i} Z_{i-j+2}(\varphi)Z_j(\varphi) = \sum_{i=2}^{\infty} Y_i(\varphi)M^i . \tag{11}
\]

with

\[
Y_2(\varphi) = [Z_2(\varphi)]^2 ,
Y_3(\varphi) = 2Z_2(\varphi)Z_3(\varphi) ,
Y_4(\varphi) = [Z_3(\varphi)]^2 + 2Z_2(\varphi)Z_4(\varphi) - 2[Z_2(\varphi)]^4 .
\]

From (7) and (11), for \( M \leq D_0 \),

\[
G(M) = \sum_{i=1}^{\infty} g_i M_i . \tag{12}
\]

where

\[
g_i = \frac{i+1}{2\pi A} \int dA \int_0^{2\pi} d\varphi Y_{i+1}(\varphi)
\]

with the surface integration extending over the entire boundary surface.

When the integration over \( \varphi \) is carried out, the \( g_i \) can be expressed

\[
g_1 = \frac{3k_1^2 + 2k_1k_2 + 3k_3^2}{16} ,
g_2 = 0 ,
g_3 = g_{31} + g_{32} - g_{33} . \tag{13}
\]
where bars over quantities indicate values averaged over the boundary surface, and

\[ \begin{align*}
\overline{g_{31}} &= \frac{3(Z_{30})^2 + (Z_{33})^2 + (Z_{31})^2 + (Z_{32})^2 + 2(Z_{31}Z_{31} + Z_{30}Z_{32})}{4} \\
\overline{g_{32}} &= \frac{(k_1 + k_2)(3Z_{40} + Z_{42} + 3Z_{44}) + (k_1 - k_2)(Z_{40} - Z_{44})}{4} \\
\overline{g_{33}} &= \frac{35k_4^4 + 20k_1^2k_2 + 18k_1k_2^2 + 20k_1k_2^2 + 35k_2^4}{256}
\end{align*} \]

By use of the Gauss–Codazzi equations (A20)–(A22) (see Appendix), \( g_{31} \) can be written

\[ g_{31} = \frac{(k_1 - k_2)^2 k_1 k_2}{48} + 2g_5^b + B_1 \]

where

\[ g_5^b = \frac{5}{288} \left[ \frac{[(k_1)_{u_1}^2 + 3(k_2)_{u_1}^2]}{E} + \frac{[(k_2)_{u_1}^2 + 3(k_1)_{u_1}^2]}{G} \right] \]

\[ B_1 = \frac{[(G/E)^{1/2}(k_1 - k_2)(k_2)_{u_1} + [(E/G)^{1/2}(k_1 - k_1)(k_1)_{u_1}]}{48(EG)^{1/2}} \]

Also, (A20)–(A22) can be used to show that

\[ \frac{(k_1 + k_2)(3Z_{40} + Z_{42} + 3Z_{44})}{4} = C - \frac{9}{5} g_5^b + B_2 \]

and

\[ \frac{(k_1 - k_2)(Z_{40} - Z_{44})}{2} = \frac{(k_1 - k_2)^2 (k_1 k_2 + k_2^2)}{16} - \frac{6}{5} g_5^b + B_3 \]

where \( B_2 = B_{21} - B_{22} \), and

\[ C = \frac{3k_4^4 + 3k_1^2k_2 + 4k_1k_2^2 + 3k_1^2 + 3k_2^2}{32} \]

\[ B_{21} = \frac{[(G/E)^{1/2}(k_1 + k_2)(k_1 + k_2)_{u_1} + [(E/G)^{1/2}(k_1 + k_2)(k_1 + k_2)_{u_1}]}{32(EG)^{1/2}} \]

\[ B_{22} = \frac{[(G/E)^{1/2}(k_1 - k_2)(k_2)_{u_1} + [(E/G)^{1/2}(k_1 - k_1)(k_1)_{u_1}]}{32(EG)^{1/2}} \]

\[ B_3 = \frac{[(G/E)^{1/2}(k_1 - k_2)(k_1)_{u_1} + [(E/G)^{1/2}(k_1 - k_1)(k_1)_{u_1}]}{48(EG)^{1/2}} \]

Although we have not yet obtained a completely rigorous proof, our calculations strongly suggest that \( B_1 \), \( B_2 \), and \( B_3 \) will be zero for any smooth convex surface. With this assumption, \( g_3 \) can be expressed

\[ g_3 = g_5^b - g_3^b \quad (15) \]

where \( g_3^b \) is given by (14), and

\[ g_3^b = \frac{5(k_1 - k_2)^2 (3k_1^2 + 2k_1k_2 + 3k_2^2)}{768} \]

Thus, for small \( M \), \( G(M) \) can be approximated by

\[ G(M) = \frac{3k_1^2 + 2k_1k_2 + 3k_2^2}{16} M \]

\[ + [g_3^b - g_3^b] M^3 + \ldots \quad (16) \]

Discussion

The expressions for the intersect distributions are valid for any convex boundary and can be used to obtain properties of the scattered intensity that are independent of a particular particle shape.

The intersect distribution function for a plane lamina can be calculated much more easily by (3) than by the method which we used previously. In the earlier calculation, for a given intersect length, an average was computed over all points of the lamina through which intersects passed, both interior points and points on the boundary. In (3), however, only boundary points need be considered, and as a result, the calculation is shortened appreciably. Also, in (3) there is no need to employ the weighting factor which had to be evaluated in our earlier procedure for finding \( G(M) \).

The simplification is at least as great for three dimensional particles as for plane laminas. We have generalized the earlier method to compute \( G(M) \) for three-dimensional particles with a smooth convex boundary surface and have found that this calculation is considerably more complicated than use of (7).

The coefficient of the term proportional to \( M \) in (16) contains the same information as the coefficient of the term proportional to \( r^3 \) in the expression for the characteristic function calculated by Kirste & Porod (1962). This term can be computed from (7) more easily than by the method which Kirste & Porod employed.

Our calculation shows that in (16) there is no constant term and no term proportional to \( M^2 \). This result
suggestions that for a smooth convex boundary surface, in (16) all coefficients of terms with even powers of $M$ may be zero. The vanishing terms with even powers of $M$ may be a consequence of the smoothness of the boundary surface, since when the boundary has sharp corners, as in the case of right cylinders, the characteristic function contains a term proportional to $r^2$, corresponding to a constant term in $G(M)$. (Porod, 1967; Méring & Tchoubar, 1968; Tchoubar & Méring, 1965).

Because of the relation between $G(M)$ and the characteristic function $y_0(r)$, the scattered intensity $I(h)$ can be written

$$I(h) = \frac{\pi I_0 q^2 S}{h} \sum_{r=0}^{\infty} H(r) \sin hrdr$$  \hspace{1cm} (17)

where

$$H(r) = r \int_{r}^{\infty} (M - r)G(M)dM.$$  \hspace{1cm} (18)

According to the theory of asymptotic expansion of Fourier integrals (Erdelyi, 1956), the form of $I(h)$ for large $h$ will depend on the behavior of $H(r)$ in the neighborhood of $r=0$ and near points at which there are discontinuities in the second or higher-order derivatives of $H(r)$. [From (18), $H(r)$ and its first derivative must be continuous, assuming that $G(M)$ is integrable.] Points at which derivatives of $H(r)$ have discontinuities will contribute damped oscillatory terms to the asymptotic expansion of $I(h)$. These terms may be difficult to observe experimentally, especially in polydisperse systems, in which the terms from particles with different diameters will occur at different scattering angles and thus will tend to average to zero. [This averaging effect has been demonstrated for polydisperse assemblies of spherical particles (Mittelbach, 1965).] The most important and easily observable contribution to the asymptotic expression for the intensity at large $h$ thus comes from the form of $H(r)$ near $r=0$. According to Erdélyi's expression for the asymptotic expansion of Fourier integrals, the contribution to the asymptotic expansion of (17) from the behavior of $H(r)$ for small $r$ is

$$I(h) \approx \pi I_0 q^2 S \sum_{i=0}^{N-1} \frac{(-1)^{i} H^{(2i)}(0)}{h^{2i+2}},$$

where $N$ is the number of terms used in the asymptotic expansion, and

$$H^i(r) = \frac{d^i H}{dr^i}.$$  \hspace{1cm} (19)

According to (19), the $g_{2N}$ do not affect the asymptotic expansion of the intensity for large $h$. Also, since $g_1$ is always positive, (19) indicates that $I(h)$ will always approach its limiting $h^{-4}$ dependence from above, rather than below. This property is to be expected for dilute samples composed of identical particles and also for dilute polydisperse samples. It also should be found for more concentrated samples, since compared with the inner part of the scattering curve, the outer portion, which is given by the asymptotic expressions, is relatively insensitive to interparticle interactions.

For spheres, $g_3=0$. We have found that $g_3$ is also zero for ellipsoids of revolution. The form of (15) suggests that $g_3$ can be positive, or negative, or zero.

We will mention the similarity of $g_3$ and the term proportional to $M^3$ in (6). Both terms are the sum of a positive term which is a quartic polynomial function of curvatures and a negative term involving an average of squares of first derivatives of curvatures.

From the expression for the intensity scattered by a plane lamina with a smooth convex boundary (Wu & Schmidt, 1968, equation 7), the analogue of (17) is

$$I(h) = \frac{2\pi q^2 L}{h} \int_{0}^{\infty} H_2(r) \sin hrdr,$$

where $\sigma$ is the number of electrons per unit area of the lamina, $L$ is the length of the lamina perimeter, and

$$H_2(r) = \int_{r}^{\infty} (M - r)G(M)dM.$$  \hspace{1cm} (18)

When the lamina has a smooth boundary, without kinks or bends, the series expansion (6) possibly may have no terms with even powers of $M$. In this case, for large $h$,

$$I(h) \approx \frac{2\pi q^2 A}{h^2 - I_e}.$$  \hspace{1cm} (20)

Then the asymptotic expression for $I(h)$ for a plane lamina gives no information about the form of $G(M)$ for small $M$. However, if there are even-order terms in the power-series expansion of $G(M)$ for small $M$, the coefficients of these terms would appear in an asymptotic expansion like (20).

Since for a smooth boundary (20) contains no terms proportional to $h^{-4}$ or $h^{-6}$, the intensity for a plane lamina ordinarily can be expected to be approximated by the limiting form (20) over a wider range of angles than for the corresponding scattering from three-dimensional particles.

Although experimental techniques are not at present sufficiently developed to justify the additional effort, in principle (6) and (19) could be extended to obtain higher-order terms.

In addition, (3) and (7) can be used to study the form of $G(M)$ in the neighborhood of points where its derivatives are discontinuous. In our earlier work, we have discussed these discontinuities for a plane lamina (Wu & Schmidt, 1968). We are now investigating some of the corresponding discontinuities for three-dimensional particles.

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APPENDIX

Let \( x \) be a vector representing a point on a smooth convex surface, with \( u \) and \( v \) being the two parameters used to specify the point. The parameters are chosen so that the parametric lines, along which one of the parameters \( u \) or \( v \) is constant, are also lines of curvature. Then (Struik, 1950, pp. 80-81) the lines for which \( u \) is constant will be orthogonal to the lines along which \( v \) is constant. The normal curvatures in the directions in which \( v \) and \( u \) are constant will be called \( k_1 \) and \( k_2 \), respectively.

If \( x + \Delta x \) denotes a point on the surface near \( x \), with the parameters having the values \( u + \Delta u \) and \( v + \Delta v \) then \( \Delta x \) can be represented by the Taylor series

\[
\Delta x = \sum_{i=0}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^i j!}{j! (i-j)!} x_{ij} \tag{A1}
\]

where

\[
x_{ij} = \frac{\partial x}{\partial u^i \partial v^j}
\]

and where the partial derivatives \( x_{ij} \) are evaluated at \( x \).

The vectors

\[
x_u = \frac{\partial x}{\partial u}
\]

and

\[
x_v = \frac{\partial x}{\partial v}
\]

will be tangent to the surface at \( x \) and will be directed along the parametric lines. Thus they will be orthogonal. From these vectors, two unit vectors \( \mathbf{l} = E^{-1/2} x_u \) and \( \mathbf{m} = G^{-1/2} x_v \) can be constructed, where \( x_u \cdot x_u = E \) and \( x_v \cdot x_v = G \). The unit vector \( \mathbf{n} = \mathbf{l} \times \mathbf{m} \) then is normal to the surface at \( x \). For \( i = 2 \), the expressions for the \( x_{ij} \) (Struik, 1950, pp. 106-108) can be written

\[
x_{20} = \frac{E_v}{2E^{1/2}} 1 - \frac{E_u}{2G^{1/2}} \mathbf{m} + k_1 E \mathbf{n} \tag{A2}
\]

\[
x_{21} = \frac{E_v}{2E^{1/2}} 1 + \frac{G_u}{2G^{1/2}} \mathbf{m} \tag{A3}
\]

\[
x_{22} = - \frac{G_u}{2G^{1/2}} 1 + \frac{G_v}{2G^{1/2}} \mathbf{m} + k_2 G \mathbf{n} \tag{A4}
\]

where the subscripts \( u \) and \( v \) denote partial differentiation with respect to \( u \) and \( v \).

From the definition of the unit vector \( \mathbf{l} \),

\[
\mathbf{l}_u = (x_u E^{-1/2})_u = x_{20} E^{-1/2} - (\frac{1}{2}) E^{-3/2} x_u E_u
\]

Then from (A2),

\[
\mathbf{l}_u = \frac{E_v}{2(GE)^{1/2}} \mathbf{m} + k_1 E^{1/2} \mathbf{n} \tag{A5}
\]

Similarly

\[
\mathbf{l}_v = \frac{G_u}{2(EG)^{1/2}} \mathbf{m} \tag{A6}
\]

From (A3) and (A5),

\[
\mathbf{n}_u = (l_u \times \mathbf{m}) + (l \times \mathbf{m}_u) = -k_1 E^{1/2} \mathbf{l} \tag{A7}
\]

Also

\[
\mathbf{n}_v = -k_2 G^{1/2} \mathbf{m} \tag{A8}
\]

When \( \Delta x \) in (A1) is expressed in terms of cylindrical coordinates \( r, \varphi, z \) to give

\[
\Delta x = r \cos \varphi \mathbf{l} + r \sin \varphi \mathbf{m} + z \mathbf{n}
\]

(A1) yields the three equations

\[
r \cos \varphi = \sum_{i=1}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^i j!}{j! (i-j)!} L_{ij} \tag{A9}
\]

\[
r \sin \varphi = \sum_{i=1}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^i j!}{j! (i-j)!} M_{ij} \tag{A10}
\]

\[
z = \sum_{i=2}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^i j!}{j! (i-j)!} N_{ij} \tag{A11}
\]

where

\[
x_{ij} = L_{ij} \mathbf{l} + M_{ij} \mathbf{m} + N_{ij} \mathbf{n} \tag{A12}
\]

Since \( x_u \) and \( x_v \) lie in the tangent plane at \( x \), the \( x_{ij} \) have no components parallel to \( \mathbf{n} \), and both \( N_{ij} \) are zero. Thus, in (A11) the summation over \( i \) begins with \( i=2 \).

From (A12),

\[
x_{i+1,j} = (x_{ij})_u = (L_{ij})_u + (M_{ij})_u \mathbf{m} + (N_{ij})_u \mathbf{n} + L_{ij} \mathbf{l}_u + M_{ij} \mathbf{m}_u + N_{ij} \mathbf{n}_u
\]

Thus, from (A3), (A5) and (A7),

\[
L_{i+1,j} = (L_{ij})_u + \frac{E_v}{2(EG)^{1/2}} M_{ij} - k_1 E^{1/2} N_{ij}
\]

\[
M_{i+1,j} = (M_{ij})_u - \frac{E_v}{2(EG)^{1/2}} L_{ij}
\]

\[
N_{i+1,j} = (N_{ij})_u + k_1 E^{1/2} L_{ij}
\]

Also, since

\[
x_{i+1,j+1} = (x_{ij})_v
\]

\[
L_{i+1,j+1} = (L_{ij})_v - \frac{G_u}{2(EG)^{1/2}} M_{ij}
\]

\[
M_{i+1,j+1} = (M_{ij})_v - \frac{G_u}{2(EG)^{1/2}} L_{ij} - k_2 G^{1/2} N_{ij}
\]

\[
N_{i+1,j+1} = (N_{ij})_v + k_2 G^{1/2} M_{ij}
\]

The \( x_{ij} \) can be obtained from (A2) by repeated application of (A13) and (A14).
Equations (A9) and (A10) can be written
\[\Delta u = E^{-1/2} \cos \varphi - E^{-1/2} \sum_{i=2}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^{i-j}(\Delta v)^j}{j!(i-j)!} L_{ij},\] (A15)
\[\Delta v = G^{-1/2} \sin \varphi - G^{-1/2} \sum_{i=2}^{\infty} \sum_{j=0}^{i} \frac{(\Delta u)^{i-j}(\Delta v)^j}{j!(i-j)!} M_{ij}.\] (A16)

By successive approximations, (A15) and (A16) can be used to obtain the expressions
\[\Delta u = \sum_{i=1}^{\infty} U_i(\varphi) r^i,\] (A17)
\[\Delta v = \sum_{i=1}^{\infty} V_i(\varphi) r^i.\] (A18)

With these equations, (A11) can be written
\[z = \sum_{i=2}^{\infty} Z_i(\varphi) r^i.\] (A19)

The calculation is somewhat simplified by the fact that evaluation of \(Z_k(\varphi)\) requires \(U_i(\varphi)\) and \(V_i(\varphi)\) only for \(i=1, \ldots, k-1\).

The quantity \(x_{11}\) can be obtained from equations (A2) both by differentiating \(x_{20}\) with respect to \(v\) and also by differentiating \(x_{31}\) with respect to \(u\). Since the expressions for \(x_{11}\) must be equal, the relations
\[k_1k_2 = -\frac{1}{2(EG)^{1/2}} \left[ \frac{\partial}{\partial v} (\frac{E_v}{(EG)^{1/2}}) + \frac{\partial}{\partial u} (\frac{G_u}{(EG)^{1/2}}) \right]\] (A20)
and
\[(k_1)_u = \frac{E_e}{2E} (k_2 - k_1)\] (A21)
are obtained. Also, the equation
\[(k_2)_u = \frac{G_v}{2G} (k_1 - k_2)\] (A22)
results from equating the expressions for \(x_{12}\) obtained by differentiating the second and third of equations (A2) with respect to \(v\) and \(u\), respectively. Equations (A20)–(A22) are the Gauss–Codazzi equations (Struik, 1950, pp. 110-113). They are useful in evaluating the \(Z_k(\varphi)\).

Table 1 gives values of \(Z_2(\varphi), Z_3(\varphi),\) and \(Z_4(\varphi)\). Although the calculation would be tedious, in principle it could be continued to give the \(Z_k(\varphi)\) for larger \(k\) values.

Equation (A19) is a generalization of the well-known parabolic approximation \(z = Z_2(\varphi) r^2\) for a surface in the neighborhood of a point (Struik, p. 81, equations 6–10).

References