Interpretation of Small-Angle Scattering Curves Proportional to a Negative Power of the Scattering Vector*

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(Received 20 March 1982; accepted 28 May 1982)

Dedicated to Professor Dr O. Kratky on his 80th birthday (8 March 1982)

Abstract

The intensity of the small-angle X-ray and neutron scattering from a polydisperse system of randomly oriented independently scattering particles is shown to be proportional to $h^{-\alpha}$ for all values of the scattering vector $h$ when the distribution of particle dimensions is proportional to $r^{-d+1-\alpha}$, where $h = \frac{4\pi\lambda^{-1}}{\sin(\theta/2)}$; $\theta$ is the scattering angle; $\lambda$ is the wavelength; $r$ is the maximum dimension of a particle; and $d$ is the number of dimensions of the particles. The value of $\alpha$ lies in the interval $0 < \alpha < \omega$, where $\omega = 4, 2, 1$ for $d = 3, 2, 1$, respectively. This relationship between the scattered intensity and the particle-dimension distribution does not depend on the shape of the particles in the polydisperse system, provided that the particle-shape distribution is independent of the distribution of particle dimensions.

The intensity of small-angle X-ray and neutron scattering is often proportional to a negative power of the scattering angle. For example, for three-dimensional scattering centers bounded by well-defined surfaces, the outer part of the small-angle scattering curve is proportional to the inverse fourth power of the scattering angle $\theta$ (Porod, 1951; Schmidt & Hight, 1965). The outer portion of the averaged scattering curve from randomly oriented platelets is proportional to $\theta^{-2}$ (Schmidt & Hight, 1965, p. 870). For randomly oriented thin rods, the corresponding part of the scattering curve is inversely proportional to $\theta$ (Guinier, Fournet, Walker & Yudowitch, 1955, p. 20). Thus, for all three of these scattering systems there will be a region of scattering angles in which the scattered intensity is proportional to $\theta^{-\alpha}$ and thus to $h^{-\alpha}$, where $h = \frac{4\pi\lambda^{-1}}{\sin(\theta/2)}$, and $\lambda$ is the X-ray wavelength. The value of the exponent $\alpha$ obtained from a measured scattering curve can often be used to determine whether the scatterers in the sample are three-dimensional, with $\alpha = 4$, or whether they can be considered to be platelets or rods, for which the exponent $\alpha$ is 2 or 1, respectively.

As yet, however, almost no interpretations have been proposed for scattering curves proportional to $h^{-\alpha}$ when $\alpha$ is not equal to 4, 2, or 1. The purpose of this note is to point out that values of $\alpha$ between 1 and 4 can be obtained from polydisperse systems of randomly oriented, independently scattering particles for a rather broad class of particle-dimension distributions. This result is independent of the shape of the particles and is true for all values of the scattering vector $h$.

The average scattered intensity $I(h)$ for perfect collimation that will be obtained from a system of independently scattering randomly oriented particles with different sizes and shapes can be written

\[ I(h) = \int_{0}^{\omega} \int_{0}^{\infty} \rho(r, \beta) I_0(hr, r, \beta) \, dr \, d\beta. \]  

(1)

In (1), the maximum dimension $r$ is used to describe the size of the particle, $\beta$ is a parameter characterizing the particle shape; $I_0(hr, r, \beta)$ is the intensity scattered at an angle corresponding to this value of $h$ by a particle with a maximum dimension $r$ and shape parameter $\beta$; and $\rho(r, \beta)drd\beta$ is the probability that the maximum dimension is between $r$ and $r + dr$ while the shape parameter lies in the interval between $\beta$ and $\beta + d\beta$. A single quantity $\beta$ is assumed to be sufficient to describe the variation of the shape of the particles. One example of this type of variation is a system of ellipsoids of revolution with varying elongation. Equation (1) can be generalized to include systems which require consideration of more than one shape parameter.

When the variations in the maximum dimension and the shape are independent, $\rho(r, \beta)$ can be written

\[ \rho(r, \beta) = \rho(r) g(\beta). \]  

(2)

With (2), (1) becomes

\[ I(h) = \int_{0}^{\omega} \rho(r) r^{2d} I_0 F(hr) \, dr, \]  

(3)

where $d$ is the number of dimensions of the scattering...
particle, and
\[ r^{2d}I_{00}F(hr) = \int_0^\infty g(\beta)I_\theta(hr, r, \beta) \, d\beta. \] (4)

The function \( F(x) \) in (4) is defined to have the property \( F(0) = 1 \). Then (4) has the proper \( r \) dependence for \( h = 0 \), since \( I_\theta(0, r, \beta) \) is proportional to the square of the number of electrons in the particle (Guinier, Fournet, Walker & Yudowitch, 1955, p. 16) and thus is proportional to \( r^{2d} \). For three-dimensional particles, for example, \( I_\theta(0, r, \beta) \) is proportional to the square of the particle volume and so to \( r^6 \), while, for platelets and rods, \( I_\theta(0, r, \beta) \) is proportional to the square of the area and the length, respectively, or to \( r^4 \) and \( r^2 \). The constant \( I_{00} \) in (4) depends on the type of particle shape (whether the particles are spherical, cylindrical, or ellipsoidal, for example) but not on \( \beta \). As has been mentioned, for large \( x \), \( I_\theta(x, r, \beta) \) and thus \( F(x) \) will be proportional to \( x^{-\omega} \), where \( \omega = 1, 2, \) and 4 for \( d = 1, 2, \) and 3, respectively.

If the dimension distribution \( \rho(r) \) can be expressed as
\[ \rho(r) = Ar^{-\gamma}, \] (5)
where \( A \) and \( \gamma \) are constants, (3) becomes
\[ I(h) = I_{00}AB h^{-(2d + 1 - \gamma)}, \] (6)
where the constant \( B \) is defined as
\[ B = \int_0^\infty x^{2d - \gamma}F(x) \, dx. \] (7)

Equation (6) holds for all values of \( h \) and is true regardless of the shape of the particles. For the integral in (7) to converge absolutely when the function \( F(x) \) has the small-\( x \) and large-\( x \) behavior which has been assumed above,
\[ 2d + 1 > \gamma > 2d + 1 - \omega. \] (8)

According to (6) and (8), when \( \rho(r) \) is given by (5), \( I(h) \) is proportional to \( h^{-\omega} \), where
\[ \omega > \alpha > 0, \] (9)
and
\[ \alpha = 2d + 1 - \gamma. \] (10)

An intensity proportional to \( h^{-\omega} \) thus will be obtained from a dimension-distribution function
\[ \rho(r) = Ar^{-(2d + 1 - \omega)}. \]

For this distribution function,
\[ \int_0^\infty \rho(r) \, dr \] (11)
does not converge, since there are so many particles with small \( r \) that the total number of particles in the system is not finite. This unrealistic behavior can be avoided by postulating that (5) gives the distribution function only when \( r \) is not less than some minimum dimension \( r_{\text{min}} \). For \( r < r_{\text{min}} \), the distribution function can have a form which makes the integral (11) converge. The intensity from this modified distribution function will differ from that given by (6), but the difference can be expected to be small when \( hr_{\text{min}} \) is small – that is, when the scattering vector \( h \) is not large enough to permit resolution of structures with dimensions \( r_{\text{min}} \). The difference between the intensity from the dimension distribution (5) and the modified distribution thus would be observable only at \( h \) values greater than those for which (6) is assumed to describe the measured intensity.

Deviations from a scattered intensity proportional to \( h^{-\omega} \) in systems of three-dimensional scatterers have been discussed by several authors (Ruland, 1971, 1974; Rathje & Ruland, 1976; Vonk, 1973; Koberstein, Morra & Stein, 1980). These deviations can be the result of density fluctuations or of the fact that the scattering centers have a diffuse boundary, rather than being bounded by a sharp surface. The deviations also may be caused by the small-angle tail of the large-angle scattering pattern. The scattered intensity observed when any of these effects are appreciable, however, does not follow a power law over the entire interval of scattering angles for which the intensity is recorded. This scattering thus is different from that given by (6), which describes the whole scattering curve, rather than just its outer part.

For example, the scattered intensity \( I_{\text{diff}}(h) \) from a system of particles with diffuse boundaries can be written (Ruland, 1971, p. 71)
\[ I_{\text{diff}}(h) = I_{\text{sharp}}(h) H^2(h), \]
where \( I_{\text{sharp}}(h) \) is the scattered intensity that would be observed if the particles had sharp boundaries, and \( H^2(h) \) is a function describing the effects of the diffuse boundary. Although, as the above equation states, the diffuse boundary affects \( I_{\text{diff}}(h) \) at all scattering angles, usually \( I_{\text{diff}}(h) \) will not be proportional to \( h^{-\omega} \) at all \( h \) values for which scattering data are recorded. The scattering from systems of particles with diffuse boundaries thus can be expected to be different from that given by (6), since this equation has been assumed to describe the entire scattering curve, rather than just its outer part.

The effect of a diffuse particle boundary ordinarily is to cause the outer part of the scattering curve to decrease more rapidly than \( h^{-\omega} \) (Ruland, 1971). On the other hand, according to inequality (9), for polydisperse systems of independently scattering three-dimensional particles with sharp boundary surfaces, \( \omega = 4 \), and so the scattered intensity is proportional to \( h^{-\omega} \), with the exponent \( \alpha \) being less than 4. The scattering from systems of particles with sharp boundaries and with dimension distributions like (5) thus is quite different from that expected for scattering particles with diffuse boundaries. This difference may be
useful in the interpretation of scattering data from systems of particles.

The scattered intensity

\[ I(h) = \frac{I(0)}{(1 + b^2 h^2)^2}, \]  

(12)

where \( I(0) \) is the zero-angle scattered intensity and \( b \) is a constant, is produced by a random distribution of scattering material in a system composed of two phases, each of which has a constant electron density (Debye, Anderson & Brumberger, 1957). If this intensity is considered to be due to a polydisperse assembly of independently scattering spheres with uniform electron density, the diameter distribution \( \rho(a) \) which gives the intensity (12) can be conveniently calculated (Letcher & Schmidt, 1966, p. 650) from the characteristic function \( g(a) \) for the polydisperse system. [Some properties of this function, which sometimes is called the correlation function and which is referred to as \( \gamma(r) \) by Letcher & Schmidt (1966), are discussed by Guinier, Fournet, Walker & Yudowitch (1955, ch. II).] The function \( g(a) \) corresponding to the intensity (12) is (Debye, Anderson & Brumberger, 1957, p. 682)

\[ g(a) = e^{-(a/b)}. \]  

(13)

The diameter distribution \( \rho(a) \) calculated from (13) for a polydisperse system of uniform independently scattering spheres which gives the intensity (12) is (Letcher & Schmidt, 1966, p. 650)

\[ \rho(a) = -\frac{2 \bar{V}}{\pi} \frac{d}{da} \left[ \frac{g'(a)}{a} \right] = \frac{2 \bar{V}}{\pi} \frac{a + b}{a^2 b^3} e^{-(a/b)}, \]  

(14)

where \( a \) is the diameter of a sphere, and \( \bar{V} \), the average volume of a particle in the polydisperse system, is

\[ \bar{V} = \frac{\pi}{6} \int_0^\infty a^3 \rho(a) \, da. \]

The integral (11) does not converge for the diameter distribution (14). Thus, neither of the scattered intensities (6) and (12) can be obtained from a polydisperse assembly of a finite number of spheres with uniform electron density.

Although the observation of a scattered intensity proportional to \( h^{-2} \) is certainly not sufficient to guarantee that the scattering sample is a polydisperse system of particles in which \( \rho(r) \) is proportional to \( r^{-(2d+1-\alpha)} \), the fact that this dimension distribution leads to a scattered intensity proportional to \( h^{-2} \) can be useful in the analysis of the small-angle scattering from polydisperse systems.

I would like to express my gratitude to D. F. R. Mildner and H. Brumberger for their advice and assistance in the preparation of this manuscript.

References


