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The Small Angle X-ray Scattering from Polydisperse Solutions of Ellipsoidal Particles*

BY PAUL W. SCHMIDT

Department of Physics, University of Missouri, Columbia, Missouri, U. S. A.

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Calculations are made of the predicted intensity of the small angle X-ray scattering from polydisperse solutions of ellipsoidal particles. By the proper choice of a distribution function for the particle radius the intensity can be expressed in terms of simple functions. Estimates suggest that the scattering is relatively insensitive to the form of the distribution function. Some possible applications of the calculations to analysis of scattering data from systems containing flattened and elongated particles are discussed.

Introduction

In the determination of the size and shape of colloidal particles by small angle X-ray scattering, one method of analyzing the experimental results consists of comparing the data with calculations of the scattered intensity predicted for different particle shapes. Suggestions about which shapes may be involved can often come from electron micrographs, chemical behavior, or other information which is known about the sample. Although except for the simplest shapes the calculation of the predicted intensity is not easy, the intensities have been tabulated for many common particle shapes. A review of some of the methods and results is given by Guinier *et al.* (1955). Recently calculations of the intensity scattered by ellipsoidal and cylindrical particles have been made (Malmon, 1957; Hight & Schmidt, 1957).

Since in most of the work mentioned above only the scattering from a single particle is considered, the results can be applied directly only to dilute, monodisperse solutions. In order to consider the scattering from polydisperse solutions, the scattering functions for a single particle must be averaged over different particle sizes, and possibly over different particle shapes. Most of the treatments of polydisperse samples consider only spherical particles. The calculations that have been made for polydisperse assemblies of ellipsoidal particles (Roess & Shull, 1947) extend over only a few shapes and are not carried out to angles as large as those for which data often can be obtained.

Further calculations of the scattering from polydisperse solutions of ellipsoidal particles should be useful in analysis of the data from a wide range of colloidal samples, since by adjustment of parameters an ellipsoid of revolution can be made to approximate a wide range of non-spherical particles, from platelets to rods.

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Calculations

The scattered intensity will be calculated for a dilute, polydisperse solution of ellipsoids of revolution, neglecting interparticle interferences. The particles will be assumed to have uniform charge density. For all ellipsoids in a given sample, the axial ratio, that is, the ratio of semi-axes of revolution to equatorial radius, will be the same. Errors produced by the collimating system will be neglected.

Calculation of the scattering from a polydisperse system of this type involves a distribution function for the equatorial radius of the particles. In the calculations below, the distribution function $N_n(R)$ of the equatorial radius R will be taken to be

$$N_n(R) = a^{n+7}R^n \exp(-aR)/(n+6)!$$

where a is a constant. The distribution function is normalized so that the zero angle scattering will have the value 1. The choice of this particular distribution function was dictated largely by the fact that it was easy to handle mathematically.

For an ellipsoidal particle of equatorial radius R and axial ratio v, the scattered intensity $R^6I(hR)$ is given by (Guinier *et al.*, 1955, p. 19)

$$R^6I(hR) = R^6\int_0^1 F(tR)\,dy \qquad (1)$$

where λ is the X-ray wavelength, φ is the scattering angle, and

$$h = 4\pi \sin \tfrac{1}{2}\varphi/\lambda\,.$$
$$t = h[1+(v^2-1)y^2]^{\frac{1}{2}}\,.$$
$$F(z) = (9\pi/2)z^{-3}[J_{3/2}(z)]^2\,.$$

The factor R^6 occurs in (1) because the scattered intensity is proportional to the square of the particle volume. The scattered intensity $P_n(h, v)$ for a polydisperse solution of ellipsoids is given by

$$P_n(h, v) = \int_0^\infty N_n(R) R^6 I(hR)\, dR$$
$$= a^{n+7}(-1)^n/(\eta+6)! \times \frac{\partial^n}{\partial a^n}[Q_0(h, v)]$$

where

$$Q_0(h, v) = \int_0^\infty \exp(-aR) R^6 I(hR)\, dR \,.$$

The order of integration over R and y can be interchanged to give

$$Q_0(h, v) = \int_0^1 Q(t)\, dy \,,$$

where

$$Q(h) = \int_0^\infty R^6 F(hR) \exp(-aR)\, dR \,. \quad (2)$$

Evaluation of (2) gives (Magnus & Oberhettinger, 1954)

$$Q(h) = 720 a^{-7}[1 + (1/5)x^2](1+x^2)^{-3} \,,$$

where

$$x = 2h/a \,.$$

Thus

$$P_0(h, v) = (1/5)(1+x^2)^{-1}[(1+v^2x^2)^{-2} + A(x)T(v, x)] \,, \quad (3)$$

where

$$A(x) = (1+x^2)^{-1}[2 + (\tfrac{1}{2})x^2] \,,$$
$$T(v, x) = (1+v^2x^2)^{-1} + (1+x^2)^{-1}D^{-1} \tan^{-1} D \,,$$
$$D = x(v^2-1)^{\frac{1}{2}}(1+x^2)^{-\frac{1}{2}}$$

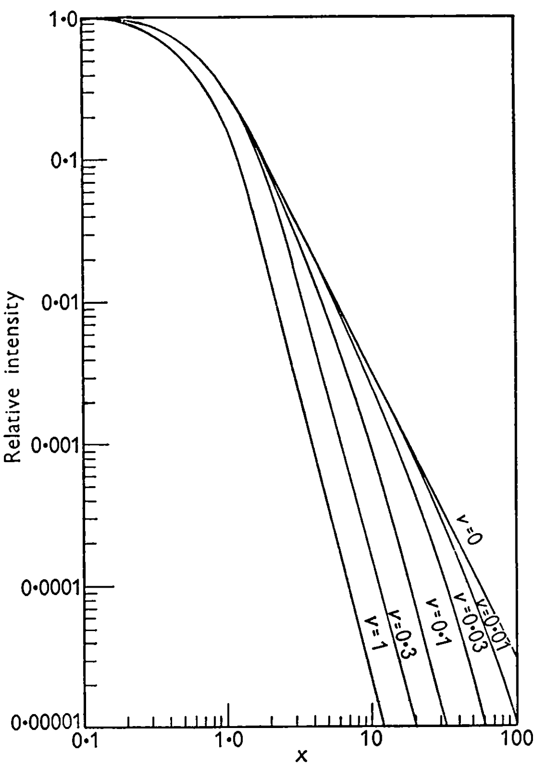

Fig. 1. The relative scattered intensity calculated for oblate ellipsoids of axial ratio v, plotted as a function of reduced angle x.

for $v > 1$. For $v < 1$, $T(v, x)$ is given by

$$T(v, x) = (1+v^2x^2)^{-1} + (1+x^2)^{-1}D^{-1} \tanh^{-1} D \,.$$
$$D = x(1-v^2)^{\frac{1}{2}}(1+x^2)^{-\frac{1}{2}} \,.$$

Figs. 1 and 2 show plots of $P_0(v, x)$ for both prolate and oblate ellipsoids.

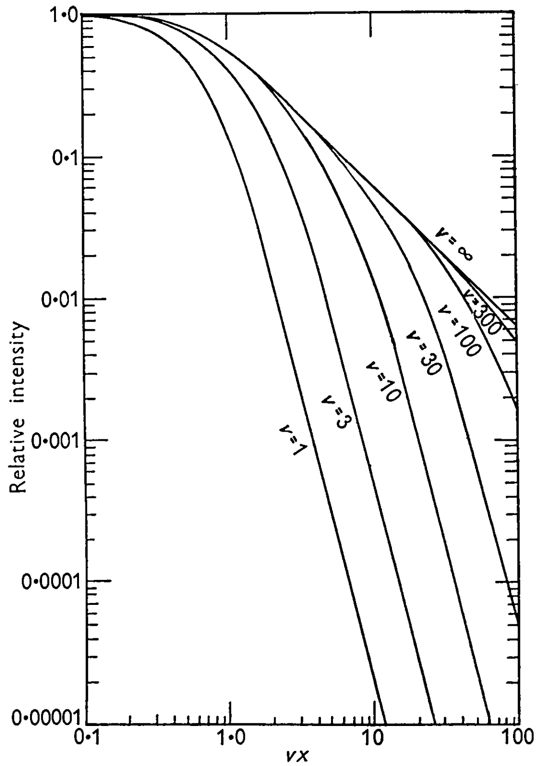

Fig. 2. The relative scattered intensity for prolate ellipsoids, plotted as a function of vx, where x is the reduced angle and v is the axial ratio.

When polydisperse systems are considered, the question of which parameter to use as the average radius arises. The X-rays are scattered most strongly by the larger particles, since the scattered intensity is proportional to the sixth power of the particle radius. Thus the average radius of the distribution function is not the average radius measured by the scattered X-rays. The effective average radius for scattering was taken to be the average of $R^6 N_n(R)$, instead of the average of $N_n(R)$. Then for $n = 0$ the effective average radius is 7 times as large as the average of $N_n(R)$. In interpretation of experimental data the effective average radius is probably the more meaningful parameter, since it represents the distribution function that actually governs the scattering process, which very nearly neglects the smaller particles. The small particles could have quite a different distribution from the one given by $N_n(R)$ without greatly affecting the scattered intensity. The ordinary average radius thus is not as good a measure of what is actually observed as is the effective average radius.

The effect of the form of the distribution function has been investigated by calculating $P_1(h, v)$ and $P_3(h, v)$ for $v = 0, 0{\cdot}1, 1$. Although the curves for different n do not have exactly the same shape on the log–log plots, they can almost be made to coincide by adjusting the horizontal scale. The adjustment necessary is very nearly proportional to the change in effective average radius. Thus, if scattered intensity is plotted as a function of a quantity proportional to h times the effective average radius, the curves for different n very nearly coincide, and the differences are small compared to experimental inaccuracies. The fact that the scattering curves almost coincide when plotted in this way is another indication that the effective average radius is to be preferred in the analysis of data.

Because of the similarity in the scattering curves for different n, only the simplest function, $P_0(v, x)$, will be discussed further. The relative insensitivity of the scattered intensity to changes in n suggests that a similar scattered intensity would be obtained for any broad distribution of ellipsoidal equatorial radii.

Comparison with results calculated from the exact expression indicates than an error of no more than a few per cent is made for $v < 0{\cdot}1$ and $x > 1$ with the approximation

$$P_0(h, v) = 0{\cdot}1x^{-2}[(1+v^2x^2)^{-1}+2(1+v^2x^2)^{-2}] .$$

Similarly, for $vx > 2$ errors of at most a few per cent are made using

$$P_0(h, v)=(\pi/20)(v^2-1)^{-1/2}x^{-1}(1+x^2)^{-3/2}[1+3(1+x^2)^{-1}] .$$

Applications

The scattered intensity for very large and very small axial ratios is seen to follow the general behavior pointed out by Porod (1948) for highly flattened or elongated particles. For thin platelets of any shape, at moderately large scattering angles, the intensity is proportional to h^{-2}, while at larger angles the dependence changes to h^{-4}. For rods with small cross section, the scattering is proportional to $1/h$ at moderately large angles and to h^{-4} at very large angles. Since the scattered intensity for polydisperse ellipsoidal samples follows the behavior predicted for all highly elongated or flattened particles, the scattering functions for ellipsoids can be used for approximate evaluation of data from other systems containing highly flattened or elongated particles of other than ellipsoidal shape. The approximation is made better because the polydispersity tends to smear out any characteristics of a particular shape.

The scattering functions for polydisperse ellipsoidal systems have been applied to small angle X-ray scattering data from aluminum hydroxide gels (Bale & Schmidt, 1958). The interpretation of the data was made difficult by the fact that the scattering did not indicate the sample was a simple platelet or rod, for which the scattered intensity would vary with the inverse first or second power of the angle. Neither did the sample scatter like many polydisperse materials in which the scattering at large angles decreased with the inverse fourth power of the angle. Since the plots of the logarithm of the scattered intensity as a function of the scattering angle had no straight line portions, the scattering was not proportional to a power of h. Chemical data suggested a platelet structure for aluminum hydroxide, and fitting the data with the $P_0(h, v)$ curves for $v < 1$ was tried and found successful. Similar methods could be used for any system suspected of consisting of non-spherical particles.

Calculations like those used by M'Ewen & Pratt (1957) for light scattering show that from the absolute magnitude of the intensity of the small angle X-ray scattering from a solution containing a known concentration of platelet particles, the thickness of the platelets can be determined. However, measurements of the absolute magnitude of the scattered intensity are quite subject to error. The platelet thickness could be determined without measuring the absolute intensity if one could obtain data in the angular region in which the angular dependence changes from h^{-2} to h^{-4}. This transition region is determined by the platelet thickness, since, from (3), the transition begins when vx becomes appreciable. As vx is proportional to the thickness of the platelet, the curves of $P_0(v, x)$ will give an estimate of the thickness. The order of magnitude of the thickness would be expected to be the same for shapes other than ellipsoidal, and so the ellipsoidal scattering functions could be applied to systems which are not composed of ellipsoidal particles. The thickness of long rod-like particles could be found by analogous techniques.

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