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SMALL ANGLE SCATTERING OF X-RAYS FROM ORIENTED ELLIPSOIDS OF REVOLUTION

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ABSTRACT

We examine the dependence on orientation of the Guinier and the asympototic approximations for ellipsoids of revolution. By introducing the assumption of random orientation into our results the known Guinier and Porod formulae are easily derived.

1. INTRODUCTION

In this note we consider the small angle scattering (SAS) from oriented ellipsoids of revolution of uniform size and shape and with low enough concentration to scatter independently of one another. We assume that a large number of particles are irradiated by the incident X-rays beam yet the beam can be likened to a single ray on the macroscale. In Section 2 we derive the electronic structure factor and the coherent scattering intensity, and Section 3 and 4 study the Guinier and asymptotic approximations respectively. All involved calculations are done in Appendices A, B and C.

2. COHERENT SCATTERING INTENSITY

Let us fix the particle in a system of three mutually perpendicular axes Ox, Oy, Oz, where O is the center of symmetry and Oz the axis of revolution. The space in which the particle is found is described by a second set of three mutually perpendicular axes, OX, OY, OZ (Fig. 1a). The centers of these two systems of axes can be made to coincide without loss of generality, since only relative orientations are of interest. Euler's angles ψ, γ and ϕ mark the orientation of the ellipsoid with respect to XYZ. Let $\vec{h}$ be the scattering vector and 2θ the scattering angle. We arbitarily orient OZ along $\vec{h}$. For an ellipsoid of axes 2a, 2a, 2b the electronic structure factor is derived in Appendix A:

$$F(h,\gamma) = 3\,\frac{\sin\beta - \beta\cos\beta}{\beta^3} = \Phi(\beta) \qquad (1)a$$

where

$$\beta = h\,(a^2 \sin^2\gamma + b^2 \cos^2\gamma)^{1/2} \qquad (1)b$$

and h is the modulus of $\vec{h}$. By varying θ the axis OZ changes direction. In SAS this variation of OZ is small enough for one to consider γ and h as independent variables. (The error involved is of the order of few per thousand, $O(\frac{1}{4\pi} h\lambda)$).

We call I_e the intensity scattered by one electron, ρ the electron density difference between the inhomogeneities and the medium and V the volume of one inhomogeneity. If N is the total number of scatterers and $P(\gamma)$ their distribution as a function of orientation, the coherent scattering intensity is

$$I(h) = I_e N \rho^2 V^2 \frac{1}{2} \int_0^{\pi} P(\gamma)\, F^2\, (h,\gamma) \sin\gamma\, d\gamma \qquad (2)a$$

where

$$\frac{1}{2} \int_0^{\pi} P(\gamma) \sin\gamma\, d\gamma = 1\ . \qquad (2)b$$

A geometrical interpretation of $\frac{\beta}{h}$ is that $Z = \frac{\beta}{h}$ is the equation of the plane tangent to the ellipsoid and parallel to XOY. In the case of common orientation, the lines of constant intensity are the lines of constant β. These are ellipses similar to the ellipse intersection of the ellipsoidal surface with the plane (zOZ) but rotated at 90° to the latter.

3. THE GUINIER APPROXIMATION

In the Guinier region we expand $F(h,\gamma)$ with respect to h. Following Guinier we approximate the first two terms in the series by an exponential to get $F(h,\gamma) = \exp(-\beta^2/10)$, and

$$F^2(h \text{ small}, \gamma) = e^{-\beta^2/5} \qquad (3)$$

For a single ellipsoid (of a given orientation, γ) or many ellipsoids of common orientation γ, the integration in equation (1) reduces to a single term and the average structure factor is proportional to $\exp(-\beta^2/5)$ where β is known. If we let $R = \sqrt{\frac{3}{5}}\,\beta/h$:

$$F^2(h \text{ small}, \gamma) = e^{\frac{-h^2R^2}{3}} \tag{4}$$

Formula (4) is the same as for a sphere of radius β/h. For the two experimental situations described in Figs. 1b and 1c we get $R = \sqrt{\frac{3}{5}}\,b;\ \sqrt{\frac{3}{5}}\,a$ respectively.

For the random distribution case $P(\gamma) \equiv 1$, we substitute (3) into (1) and integrate (this is done in Appendix B) and obtain

$$I\ (h \text{ small}) = I_e N\rho^2V^2 e^{\frac{-h^2R_o^2}{3}} \tag{5)a}$$

where

$$R_o = \frac{2a^2 + b^2}{5} \tag{5)b}$$

is the formula for the radius of gyration.

4. THE ASYMPTOTIC APPROXIMATION

In the asymptotic region:

$$F^2\ (h \text{ large}, \gamma) = \frac{9}{4}\cos^2\beta \tag{6)a}$$

In Eq. (6)a the cosine term oscillates rapidly with h and can be replaced by its average 1/2. Thus approximately

$$F^2\ (h \text{ large}, \gamma) = \frac{9}{2}\,\frac{1}{\beta^4}\ . \tag{6)b}$$

If we fix γ for the case of single oriented particle or for many particles of common orientation we get:

$$I\ (h \text{ large}) = (I_e N)\ \frac{2\pi\rho_{ef}^2 S(\gamma)}{h^4} \tag{7)a}$$

where $S(\gamma) = 4\pi(\beta/h)^2$ and

$$\rho_{ef} = \frac{V}{V(\gamma)}\rho \; ; \; V(\gamma) = \frac{4\pi}{3}\left(\frac{\beta}{h}\right)^3 \qquad (7)b$$

The effective electronic density ρ_{ef} is obtained by uniformly distributing the total electronic charge of the ellipsoid over the volume of a sphere of radius β/h. Equation (7)a thus contains the Porod formula and the conservation of the total electronic charge of the ellipsoid.

It was shown by Bragg, et al.[1] that SAS from pyrolitic graphite is caused by ellipsoidal voids. By applying formula (7)a to the two experimental situations described in our Fig. 1b and 1c and comparing with their results in their Figs. 1a and 1b for graphite we conclude that these voids are elongated ellipsoids oriented in the direction perpendicular to the deposition plane.

For the random distribution case we substitute (6)b into (2) and derive the Porod formula; this is done in Appendix C.

In conclusion this work should be considered as an introduction into the SAS of oriented particles. It is important to study cases involving different sizes and shapes of particles. Also, Eq. (2)a should be calculated for physically meaningful distributions. This will require the use of numerical analysis.

ACKNOWLEDGEMENT

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[1] Bragg, et al., Nature 200, 557 (1963).

APPENDIX A: THE ELECTRONIC STRUCTURE FACTOR OF AN ORIENTED ELLIPSOID OF REVOLUTION

The axes of the ellipsoid are: 2a, 2a, 2b. In Fig. 1a, we let ψ, γ and ϕ represent the Euler's angles defined by the following three rotations: ψ about the axis OZ, γ about the new axis OX(OK), and ϕ about the new axis OZ(oz). The structure factor $F(h,\gamma)$ is obtained from

$$F^2(h,\gamma) = f(h,\gamma)\, f^*(h,\gamma) \qquad \text{(A-1)a}$$

$$f(h,\gamma) = \int_V e^{i\delta}\, p dV \qquad \text{(A-b)b}$$

where pdV is the probability of finding an electron (with a phase δ) in dV, and the integration is taken over the volume of the particle.

Rothwell[A.1] integrated Eq. (A-1)b in the reference frame Oxyz, using an incorrect expression for δ. The correct expression for δ is:

$$\delta = hz = h[(\sin\psi \sin\gamma)x + (\cos\psi \sin\gamma)y + (\cos\gamma)z]. \qquad \text{(A-2)a}$$

And by using cylindrical coordinates r, α, z: $x = r\cos\alpha$, $y = r\sin\alpha$:

$$\delta = h[r \sin\gamma \sin(\psi + \alpha) + z\cos\gamma] \qquad \text{(A-2)b}$$

Taking Eq. (A-2)b for δ the derivation of $f(h,\gamma)$ is identical to Rothwell's because:

$$\int_{\psi}^{2\pi+\psi} d\alpha' e^{i\xi\sin\alpha'} = \int_{o}^{2\pi} d\alpha' e^{i\xi\sin\alpha'} \equiv 2\pi J_o(\xi) \quad . \qquad \text{(A-3)}$$

This also explains why Rothwell obtained the correct answer for $f(h,\gamma)$. The first part of Eq. (A-3) is a consequence of the periodicity (of period 2π) of the function $\exp[i\, \xi \sin\alpha']$ with respect to α'.

In the following we integrate Eq. (A-1)b in the frame OXYZ. The method is complicated but will give a simple geometrical interpretation of the final results. In OXYZ: $\delta = hZ$. Assuming a uniform electron density $\rho dV = (dV)/V = (s(Z,\gamma)/V)dZ$. Here $s(Z,\gamma)$ is the surface of the ellipse intersection of the ellipsoidal surface and the plane Z = Z. We need to determine $s(Z,\gamma)$. We let M represent Euler's matrix:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = M \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \quad . \tag{A-4}$$

(We don't give the explicit expression of M. It can be found in many references, for example Ref. A.2.) The equation of the ellipsoidal surface is:

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2} = 1 \quad . \tag{A-5}$$

And in terms of X, Y, Z:

$$(X, Y, Z)\, A \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = 1 \quad , \tag{A-6}$$

where A is a 3 by 3 matrix:

$$A_{XX} = \frac{\cos^2 \psi + \text{cox}^2 \gamma \sin^2 \psi}{a^2} + \frac{\sin^2 \gamma \sin^2 \psi}{b^2} \qquad \text{(A-7)a}$$

$$A_{YY} = \frac{\sin^2 \psi + \cos^2 \gamma \cos^2 \psi}{a^2} + \frac{\sin^2 \gamma \cos^2 \psi}{b^2} \qquad \text{(A-7)b}$$

$$A_{ZZ} = \frac{\sin^2 \gamma}{a^2} + \frac{\cos^2 \gamma}{b^2} \qquad \text{(A-7)c}$$

$$A_{XY} = A_{YX} = \sin^2 \gamma \cos \psi \sin \psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) \tag{A-7)d}$$

$$A_{XZ} = A_{ZX} = - \sin \gamma \cos \gamma \sin \psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) \tag{A-7)e}$$

$$A_{YZ} = A_{ZY} = \sin \gamma \cos \gamma \cos \psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) . \tag{A-7)f}$$

If we make the following changes of variables:

$$\begin{pmatrix} X' \\ Y' \end{pmatrix} = \begin{pmatrix} \cos \psi & \sin \psi \\ -\sin \psi & \cos \psi \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \tag{A-8)a}$$

$$\eta = Y' + \frac{\sin \gamma \cos \gamma \, (b^2 - a^2)}{a^2 \sin^2 \gamma + b^2 \cos^2 \gamma} Z , \tag{A-8)b}$$

Eq. (A-6) becomes:

$$\frac{X'^2}{a^2} + \frac{\eta^2}{\dfrac{a^2 b^2}{a^2 \sin^2 \gamma + b^2 \cos^2 \gamma}} + \frac{Z^2}{a^2 \sin^2 \gamma + b^2 \cos^2 \gamma} = 1 . \tag{A-9}$$

Equation (A-9) represents the equation of the ellipse intersection of the ellipsoidal surface and the plane Z = Z where Z is a parameter. To clarify, we call:

$$K = 1 - \frac{Z^2}{a^2 \sin^2 \gamma + b^2 \cos^2 \gamma} , \tag{A-10}$$

thus the equation of the ellipse (intersection) becomes:

$$\frac{X'^2}{Ka^2} + \frac{\eta^2}{\dfrac{Ka^2 b^2}{a^2 \sin^2 \gamma + b^2 \cos^2 \gamma}} = 1 \tag{A-11}$$

From Eq. (A-11) we get $s(Z,\gamma)$:

$$s(Z,\gamma) = \pi K \frac{a^2 b}{\sqrt{(a^2 \sin^2 \gamma + b^2 \cos^2 \gamma)}} , \qquad \text{(A-12)a}$$

or, from Eqs. (A-10) and (A-12)a:

$$s(Z,\gamma) = (\pi ab) \frac{a}{H}\left(1 - \frac{Z^2}{H^2}\right) \qquad \text{(A-12)b}$$

where,

$$H = (a^2 \sin^2 \gamma + b^2 \cos^2 \gamma)^{1/2} . \qquad \text{(A-13)}$$

It is obvious that $s(Z = H,\gamma) = 0$, thus H represents the maximum variation in Z. (As a verification of Eq. (A-12)b one can evaluate the expression of the volume of the ellipsoid by integrating $s(Z,\gamma)dZ$ over $[-H, +H]$). The electronic structure factor, from Eq. (A-1) and (A-12)b, equals:

$$f(\gamma) = \int_{-H}^{+H} \frac{3}{4H} \left(1 - \frac{Z^2}{H^2}\right) e^{ihZ}\, dZ \equiv \Phi(hH) \qquad \text{(A-14)}$$

Beside the structure factor, the above derivation gives a simple interpretation of $\beta = hH = h(a^2 \sin^2 \gamma + b^2 \cos^2 \gamma)^{1/2}$.

References to Appendix A:

A.1. Rothwell, J. of Math. Phys. 4, 1334 (1963).

A.2. Corben and Stehle, Classical Mechanics, (Wiley, 1950) p. 177.

APPENDIX B: THE GUINIER APPROXIMATION FOR RANDOMLY ORIENTED ELLIPSOIDS OF REVOLUTION

Letting $P(\gamma) = 1$, from (2) and (3) we get:

$$I(h \text{ small}) = I_e N\rho^2 V^2 \left\{ 1 + \frac{h^2}{5} \int_0^{\pi/2} (a^2 \sin^2\gamma + b^2 \cos^2\gamma) d \cos\gamma + \ldots \right\} \tag{B-1}$$

By letting $\cos\gamma = x$, $\sin^2\gamma = 1 - x^2$

$$[\text{the integral in Eq. (B-1)}] = a^2 + (b^2 - a^2) \int_0^1 x^2 dx$$

Thus

$$I(h \text{ small}) = I_e N\rho^2 V^2 \left\{ 1 - \frac{h^2 R_o^2}{3} + \ldots \right\} \tag{B-2}$$

where

$$R_o^2 = \frac{2a^2 + b^2}{5} \tag{B-3}$$

Following Guinier we write Eq. (B-2) as

$$I(h \text{ small}) = (I_e N\rho^2 V^2)\, e^{-\frac{h^2 R_o^2}{3}}, \tag{B-4}$$

This is the Guinier formula where R_o given in Eq. (B-3) is the expression for the radius of gyration for an ellipsoid of revolution 2a, 2a, 2b.

APPENDIX C: THE POROD FORMULA FOR RANDOMLY ORIENTED ELLIPSOIDS OF REVOLUTION

By letting $P(\gamma) = 1$ in Eq. (2) and substituting for the electronic structure factor from Eq. (6) we get:

$$I(h\ \text{large}) = I_e N \rho^2 \gamma^2 \frac{9}{2h^4} \int_0^{\pi/2} \frac{-d\cos\gamma}{[a^2 \sin^2\gamma + b^2 \cos^2\gamma]^2} \tag{C-1}$$

Let $\cos\gamma = x$, $\sin^2\gamma = 1 - x^2$

$$[\text{the integral in (C-1)}] = \frac{1}{(b^2 - a^2)^2} \int_0^1 \frac{dx}{\left[x^2 + \dfrac{a^2}{b^2 - a^2}\right]^2}$$

$$= \frac{1}{4\pi a^4 b^2} \left(2\pi a^2 + \frac{2\pi ab}{e} \tan^{-1} \frac{b}{a} e\right), \tag{C-2}$$

Where $e = \sqrt{\dfrac{b^2 - a^2}{b^2}}$ is the eccentricity of the ellipsoid 2a, 2a, 2b. By examining Fig. 2, one can easily show that:

$$\sin^{-1} e = \zeta = \tan^{-1} \frac{b}{a} e \tag{C-3}$$

From Eqs. (C-3) and (C-2):

$$[\text{the integral in Eq. (C-1)}] = \frac{4\pi S}{9V^2} \tag{C-4}$$

where $V = \frac{4\pi}{3} a^2 b$ is the volume of the ellipsoid and $S = 2\pi a^2 + 2\pi(a\,b/e)\sin^{-1} e$ its surface area. From Eqs. (C-4) and (C-1) we get the Porod formula:

$$I(h\ \text{large}) = (I_e N) \frac{2\pi\rho^2 S}{h^4} \tag{C-5}$$

FIGURE CAPTIONS

Fig. 1. Oriented ellipsoid in fixed frame of reference.

Fig. 2. A geometrical demonstration of the relation: $\sin^{-1} e = \tan^{-1} \frac{b}{a} e$.

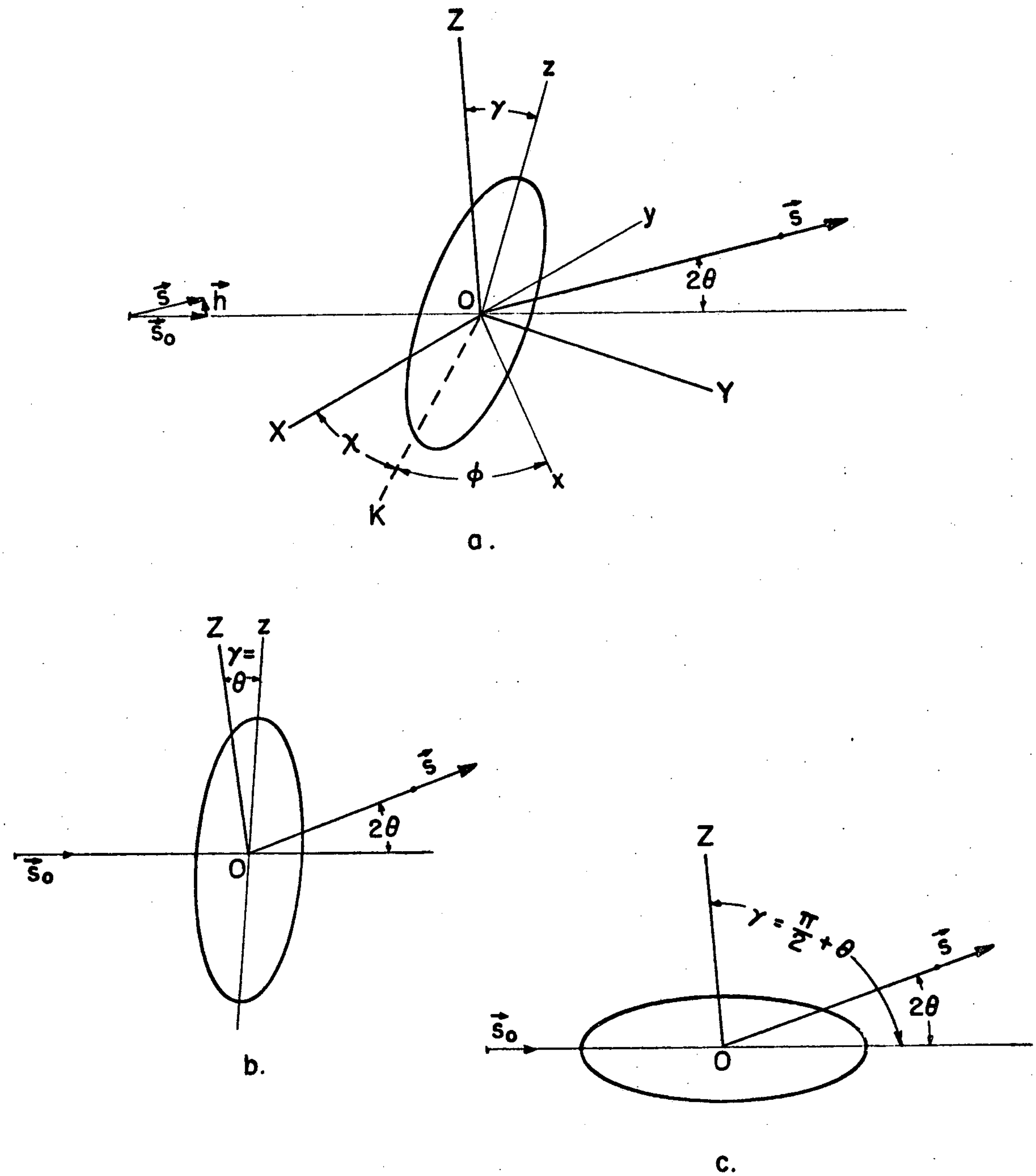

Fig. 1

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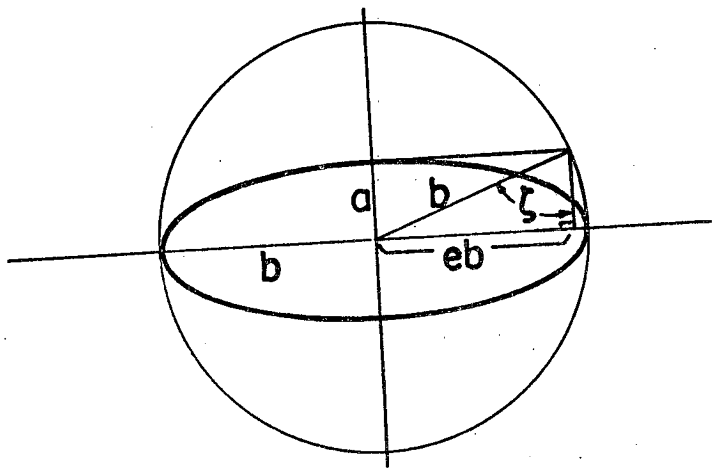

Fig. 2

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