Submitted to Physical Review

LBL-1874
Preprint

c. 1

SMALL ANGLE SCATTERING OF X-RAYS FROM GROUPS OF NON-RANDOMLY ORIENTED ELLIPSOIDS OF REVOLUTION OF LOW CONCENTRATION

F. M. Hamzeh and R. H. Bragg

August 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-1874

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 9 0 7 5 5 7

SMALL ANGLE SCATTERING OF X-RAYS FROM GROUPS OF NON-RANDOMLY ORIENTED ELLIPSOIDS OF REVOLUTION OF LOW CONCENTRATION

F. M. Hamzeh and R. H. Bragg

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, College of Engineering; University of California, Berkeley, California 94720

ABSTRACT

The small angle scattering from oriented ellipsoids of revolution is examined. We consider successively the different cases of a fixed ellipsoid, single ellipsoid with preferred orientation and of a group of widely separated ellipsoids of size distribution. Methods of correction for beam height effects and of interpretation of experimental data are presented.

INTRODUCTION

Since the original work of Guinier[1] and subsequently that of Porod,[2] workers have paid little attention to the case of oriented inhomogeneities (particles) in matter. The experiment by Bragg, et.al.[3] on pyrolitic graphite clearly showed the need for a theoretical basis for interpretation in such cases, and recent developments in materials containing oriented submicroscopic voids, e.g. carbon fibers, have reemphasized this need. This work is not intended to give a complete treatment of scatterings from oriented particles, but to provide a consistent theoretical basis for the interpretation of experiments involving oriented particles in term of well defined geometrical shape parameters. For simplicity, the particle shapes are approximated by ellipsoids of revolution. Furthermore, their concentration is assumed to be low enough for the interparticle interference effect to be negligible. In Section 2 we treat the case of a single ellipsoid of revolution. In section 2.1 and appendix A the structure factor is derived. The Guinier and Porod approximations for a fixed ellipsoid and for an ellipsoid of preferred orientation are derived respectively in sections 2.2 and 2.3. In our notation by ellipsoid of preferred orientation we refer to an ellipsoid whose orientation distribution is described by a general probability function that may or may not have one or several preferred orientations. Thus the random orientation case is a special case where the probability function is a constant. Small angle scattering

from groups of ellipsoids of revolution is the subject for section 3. Two basic assumptions are made:

1) there is complete independence between the orientation of the particles and the distances between their centers
2) the ellipsoids are widely separated so that interparticle interferences are negligible.

Equal ellipsoids, meaning ellipsoids of equal axes but of different orientations, are treated in section 3.1 whereas section 3.2 considers ellipsoids with a size distribution. Methods of correction for beam height effects and of interpretation of experimental data are presented in sections 4 and 5. Ellipsoids of common orientations as for example voids in pyrolitic graphite are treated in section 6 and in more details in an application to this work to be published.

2. Small Angle Scattering from a Single Ellipsoid of Revolution:

Let us fix the particle in a system of three mutually perpendicular axes Oxyz, 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 OXYZ (Fig. 1). The centers of these two systems of axes are made to coincide without any loss of generality, since only relative orientation are of interest. Euler's angles ψ, γ and ϕ mark the orientation of the ellipsoid with respect to OXYZ. Let h be the scattering vector equal to $\frac{2\pi}{\lambda}(\vec{s}-\vec{s}_o)$ where $\vec{s}$ and $\vec{s}_o$ are unit vectors along the scattered and incident beams respectively and let θ be the Bragg's angle, $h = |\vec{h}| = 4\pi/\lambda \sin\theta$. We are interested in the distribution of

scattered radiation along a given line e.g. AB. The corresponding scattering vectors $\vec{h}$ are all contained in the plane fixed by $\vec{s}_o$ and AB. The limiting direction of $\vec{h}$ as the scattering angle 2θ tends to zero is marked by the unit vector $\hat{h}_o$ perpendicular to $\vec{s}_o$. We arbitrary orient $\vec{O}Z$ along $\hat{h}_o$.

2.1 The Structure Factor:

From the symmetry of revolution the dependence of the structure factor of the particle on the angle ϕ drops, the structure factor is a function of the angle between $\vec{h}$ and $\vec{O}z$. In small angle scattering this angle can be approximated by γ the angle between $\hat{h}_o$ and $\vec{O}z$ the error introduced (of the order of $\frac{h\lambda}{4\pi}$) is negligible.

The structure factor $F(h,\gamma)$ is obtained from:

$$F^2(h, \gamma) = (\rho V)^2 \, f(h,\gamma) \, f^*(h,\gamma) \tag{1a}$$

$$f(h,\gamma) = \int_V e^{i\delta} p dV \tag{1b}$$

where pdV is the probability of finding an electron of phase δ in dV and the integration is taken over the volume of the particle. The structure factor for an ellipsoid of revolution was derived by Guinier[1] in 1939. The method he used could only be applied to an ellipsoid of revolution. We integrate (1b) in the reference frame OXYZ. Our method can be generalized to other shapes and has the advantage of giving a simple geometrical interpretation of the final results. For uniform electron density $pdV = \frac{dV}{V} = s(Z,\gamma) \frac{dZ}{V}$. Here

$s(Z,\gamma)$ is the surface area of the intersection of the ellipsoid with the plane at Z parallel to XOY. The determination of $s(Z,\gamma)$ is complicated and is done in Appendix A. For an ellipsoid of axes 2a, 2a, 2b, we get:

$$s(Z,\gamma) = \pi(ab)\,\frac{a}{H}\left(1 - \frac{Z^2}{H^2}\right) \tag{A9b}$$

where

$$H = [a^2 \sin^2\gamma + b^2\cos^2\gamma]^{1/2} \tag{A9c}$$

Note that at $Z = H$, $s(H,\gamma) = 0$, thus H represents the maximum variation in Z. In the system OXYZ, δ is approximately equal to hZ, therefore:

$$f(h,\gamma) = \int_{-H}^{+H} \frac{3}{4\pi}\left(1 - \frac{Z^2}{H^2}\right) e^{ihZ}\, dZ \equiv \phi(hH) \tag{2a}$$

where

$$\phi(hH) = 3\,\frac{\sin hH - hH\cos hH}{(hH)^3} \tag{2b}$$

The lines of constant intensity are the lines of constant hH; these are contours similar to the ellipsoid projection on the observation plane and are rotated relative to it 90° about the incident beam direction.

2.2 The Coherent Scattering Intensity:

The coherent scattering intensity from a fixed ellipsoid of revolution is given by

$$I = I_e\,(\rho V)^2\,\phi^2(hH) \tag{3}$$

where I_e is the scattering intensity by a single electron and is essentially constant for the angles to be considered, ρ the electron density difference of the ellipsoid with respect to the matrix and V is the volume of the ellipsoid.

In the small angle region (Guinier region) we expand $\phi(hH)$ with respect to h. Following Guinier, we approximate the first two terms in the series by an exponential to get:

$$I_G = I_e \, (\rho V)^2 \exp\left[-\frac{h^2R^2}{3}\right] \tag{4}$$

where $R = \sqrt{3/5}\, H$. Equation (4) is the law of Guinier for a fixed ellipsoid where R plays the role of a radius of gyration. It is straight forward to show that the average of R^2 over all, equally probable orientation is equal to $R_o^{\,2} = \frac{2a^2 + b^2}{5}$ where R_o is the radius of gyration of the randomly oriented ellipsoid 2a, 2a, 2b.

In general, the structure factor for a centrosymmetric particle in the small angle region is given by an exponential law:[5]

$$F^2(h) = (\rho V)^2 \exp[-h^2D^2] \tag{5a}$$

where

$$D^2 = \frac{\Sigma_k f_k d_k^{\,2}}{\Sigma_k f_k}, \tag{5b}$$

f_k is the scattering factor at the point M_k and d_k is the projection of the point M_k on the plane XOY. D^2, thus represents the square average of inertial distances of the particle with respect to the plane XOY. The generalization of Eq. (5b) to include particles with

continuous distributions of scattering points is given by:

$$D^2 = \frac{\int_V Z^2 \rho(M)\,dV}{\int_V \rho(M)\,dV} \tag{5c}$$

For an ellipsoid of revolution we get:

$$D^2 = \frac{\rho}{V\rho} \int_{-H}^{+H} Z^2 s(Z,\gamma)\,dZ = \frac{H^2}{5} \equiv \frac{R^2}{3}$$

thus making the connection between Eqs. (4) and (5a,b).

In the large angle region (Porod region) the expression for the structure factor can be approximated by $9(\rho V)^2 \cos^2 hH/(hH)^4$. The cosine term oscillates rapidily and can be replaced by its average value 1/2, therefore:

$$I_p = I_e \frac{2\pi\rho^2}{h^4} \left(\frac{9V^2}{4\pi H^4} \right) \tag{6}$$

The quantity in parenthesis has the dimension of a surface area with no obvious connection to the surface area of the ellipsoid. We define $S_\perp$ by $4S_\perp = 9V^2/4\pi H^4$. If we let $V(H) = 4\pi/3\ H^3$ then

$$S_\perp = \frac{V}{V(H)}\ s(o,\gamma) \quad .$$

If we let a = b, for a sphere of radius a, $S_\perp = \pi a^2$ which is the projection of the surface area of the sphere on the plane XOY.

Unfortunately, this sort of simple interpretation of $S_\perp$ is correct only for the spherically symmetric case. In Appendix B we have shown that the average over all, equally probable, orientation of 4 $S_\perp$ is equal to the surface area of the ellipsoid. Actually, $S_\perp$ may be defined for a general particle as a surface whose average over all random orientations will give the surface area of the particle divided by 4. With this definition of $S_\perp$ formula (6) becomes: $I_p = I_e \frac{2\pi\rho^2}{h^4} 4S_\perp$; true for all particles.

2.3. Ellipsoid of Revolution with Preferred Orientation:

By particle with preferred orientation we mean a particle with a distribution in orientation expressed by a probability density. The structure factor for an ellipsoid of revolution is a function of h and the angle γ. Therefore, a general form for the probability density function need only to depend on the angle γ with an implicit dependence on the particular choice of OZ. Let $P(\hat{h}_o,\gamma)$ be that function normalized to one. The average scattering intensity is therefore equal to:

$$I(\hat{h}_o,h) = I_e F^2(\hat{h}_o,h) \tag{8a}$$

where

$$F^2(\hat{h}_o,h) = \frac{1}{2} \int_o^\pi F^2(hH)\, P(\hat{h}_o,\gamma)\sin\gamma d\gamma \tag{8b}$$

In the Guinier region:

$$F_G{}^2(\hat{h}_o,h) = (\rho V)^2 \exp[- h^2\overline{D^2}(\hat{h}_o)] \tag{9a}$$

where

$$\bar{D}^2(\hat{h}_o) = \frac{\overline{H^2}(\hat{h}_o)}{5} = \frac{1}{5}\,\frac{1}{2}\int_o^{\pi} H^2\, P(\hat{h}_o,\gamma)\,\sin\gamma d\gamma \tag{9b}$$

we refer to $\overline{D^2}\,(\hat{h}_o)$ as the average inertial distance.

In the Porod region we get:

$$F_p^2\,(\hat{h}_o,h) = \frac{2\pi\rho^2}{h^4}\;4\,\bar{S}_\perp\,(\hat{h}_o) \tag{9c}$$

where

$$4\,\bar{S}_\perp\,(\hat{h}_o) = \frac{9V^2}{4\pi}\,\frac{1}{2}\int_o^{\pi}\frac{P(\hat{h}_o,\gamma)\,\sin\gamma d\gamma}{H^4}\quad . \tag{9d}$$

For randomly oriented ellipsoid $P(\hat{h}_o,\gamma) \equiv 1$ and therefore $4\overline{S_\perp}$ is equal to the surface area of the ellipsoid, see appendix B. For the sake of generality let us introduce $\bar{H}(\hat{h}_o)$ to be the observable dimension of the ellipsoid, $\bar{H}$ is a function of a, b and $\hat{h}_o$. In the Guinier region $\bar{H}^2$ is the average of H^2 and is related to $D^2(\hat{h}_o)$ by: $\bar{H}(\hat{h}_o) = \sqrt{5\,D^2(\hat{h}_o)}$. In the Porod region $(\bar{H})^{-4}$ is equal to the average of H^{-4} and is related to $\bar{S}_\perp\,(\hat{h}_o)$ by $\bar{H}^4 = \dfrac{9V^2}{16\pi\,\bar{S}_\perp\,(\hat{h}_o)}$. In general $\bar{H}(\hat{h}_o)$ can be constructed, in different interval of h to satisfy

$$F^2[h\,\bar{H}(\hat{h}_o)] = F^2(\hat{h}_o,h)\quad .$$

With this definition of $\bar{H}$ the average scattering intensity for an ellipsoid of revolution with preferred orientation is given by:

$$I(\hat{h}_o,h) = I_e F^2[h\,\bar{H}(\hat{h}_o)] \equiv I(h\,\bar{H}(\hat{h}_o)] \tag{8c}$$

Thus for each $\hat{h}_o$ there corresponds a small angle scattering curve with no explicit dependence on $\hat{h}_o$. See also section 4.

3. Scattering from a Group of Ellipsoids of Revolution:

It is of practical importance to determine the intensity scattered by a group of particles. We treat only the case of widely separated ellipsoids of revolution.

The reference frame OXYZ can be defined as in section 2 except for the center O which is chosen to be the center of symmetry of the volume irradiated by the X-rays. Let us assume that there is complete independence between the orientations of the particles and the distances between their centers. Since only relative orientations are of importance one can think of the center O to coincide with the center of symmetry of each particle without any loss of generality.

3.1 Equal Ellipsoids:

For simplicity we assume at first that all the ellipsoids are equal. That is, the same a and same b but of different orientations. Let N be the total number of scatterers and $NP(\hat{h}_o,\gamma)$ be their distribution as a function of orientation. $P(\hat{h}_o,\gamma)$, (normalized to one) can be thought of as a probability density function for a single particle with preferred orientations. Let L_o represent an average dimension of the irradiated volume, for all scattering angles satisfying the

criterion $h > 2\pi/Lo$, the coherent scattering intensity for widely separated particles is idential, on a relative scale, to the mean intensity scattered by one isolated particle with preferred orientation where the probability density function is equal to $P(\hat{h}_o,\gamma)$. Call $I(\hat{h}_o,h)$ the total coherent scattering intensity then:

$$I(\hat{h}_o,h) = NI_e F^2(\hat{h}_o,h) \tag{10}$$

It was Guinier[1] who first noticed that the structure factor of a fixed ellipsoid of revolution is the same as that of a sphere of radius H. Actually this is true only if the sphere has an average electronic density difference with respect to the matrix equal to $\rho_s = \frac{V}{V(H)}\rho$. Physically speaking, the X-ray beam sees the total electronic charge difference of the ellipsoid and the matrix, therefore when a correspondence principle is invoked it must conserve this total charge difference, namely: $\rho_s V(H) = \rho V$. In the following we call the Guinier sphere a sphere of radius H and charge density difference equal to ρ_s. Because of the spherical symmetry, the scattering from fixed or a randomly oriented sphere must be the same. This suggests that formula 6 should take on the form of a Porod formula with a surface quantity equal to the surface area of the Guinier sphere. In fact $9V^2\rho^2/4\pi H^4 = \rho_s^2 \; 4\pi H^2 = \rho_s^2 \; S_s$, where $S_s = 4\pi H^2$ is the surface area of the Guinier sphere, and:

$$I_p = I_e \frac{2\pi\rho_s^2 S_s}{h^4} \; ; \tag{6a}$$

Q.E.D.

From this equivalence principle we will demonstrate that the small angle scattering from a group of equal ellipsoids of revolution of orientation distribution $NP(\hat{h}_o,\gamma)$ and low concentration is equivalent to the small angle scattering from a group of widely separated Guinier spheres of size distribution $P'(\hat{h}_o,H)$ where H varies between a and b. (See Fig. 2) In fact consider the total scattering intensity from formulae (10) and (8b):

$$I(\hat{h}_o,h) = \frac{NI_e}{2} \int_o^{\pi} F^2(hH)\ P(\hat{h}_o,\gamma)\ \sin\gamma d\gamma \tag{11a}$$

where $H^2 = a^2 \sin^2\gamma + b^2 \cos^2\gamma$. In Equation (11a) we divide the interval between 0 and π into two intervals from 0 to $\pi/2$ and $\pi/2$ to π. The contribution from 0 to $\pi/2$ is the first integral on the right hand side of Equation (11b) below. For the contribution from $\pi/2$ to π we make a change of variable to $\gamma' = \gamma-\pi/2$ and obtain the second integral on the right hand side of Eq. (11b) where $H'^2 = a^2\cos^2\gamma' + b^2 \sin^2\gamma'$:

$$I(\hat{h}_o,h) = \frac{NI_e}{2} \left\{ \int_b^a \frac{F^2(hH)P[\hat{h}_o,\gamma(H)]HdH}{[(a^2-b^2)(a^2-H^2)]^{1/2}} + \int_b^a \frac{F^2(hH')P[\hat{h}_o,(\gamma'+\pi/2)(H)]H'dH'}{[(a^2-b^2)(a^2-H'^2)]^{1/2}} \right\} . \tag{11b}$$

Let

$$p(\hat{h}_o,H) = \frac{1}{2}\ P[\hat{h}_o,\gamma(H)] + P[\hat{h}_o,(\gamma+\pi/2)(H)] \tag{12a}$$

Since

$$H(\gamma) = H(\gamma'+\pi/2) \equiv H'(\gamma'),$$

then:

$$I(\hat{h}_o,h) = NI_e \int_b^a F^2(hH)\ P'\ (\hat{h}_o,H)dH \tag{12b}$$

where

$$P'(\hat{h}_o,H) = \frac{H}{\sqrt{(a^2-b^2)(a^2-H^2)}} \; p(\hat{h}_o,H) \tag{12c}$$

In Equations (12b and c) a is taken to be larger than b. These equations can be easily modified to the case of elongated ellipsoid ($a < b$). For distributions $p(\hat{h}_o,H)$ that are not null at $H = a$(or $\gamma=\pi/2$) the corresponding distributions $P'(\hat{h}_o,H)$ are singular at $H = a$. In fact this singularity is only apparent because dH is null at $H = a$ and therefore it is helpful to make a change of variable

$$d\xi = - HdH/\sqrt{a^2-H^2} \quad \text{or} \quad \xi = \sqrt{a^2-H^2} \; .$$

The problem of widely separated spheres with size distribution have been extensively studied in the literature. To mention a few references: Schull and Ross[6] studied the cases of gaussian, maxwellian and rectangular distributions; Rothwell[7] studied the gaussian and lambda-shaped distributions and Paul Schmidt[8] the $R^n \exp(-\alpha R)$ type of distributions for polydispersed solutions of ellipsoidal particles (in particular spheres). The purpose of our derivation of Eqs. (12a, b and c) is to utilize the results in the literature without having to embark on new unnecessary computations.

3.2 Ellipsoids with Size Distributions:

Let us now consider a group of widely separated ellipsoids of revolution with size distribution. For ellipsoids of revolution there is the possibility of distribution functions for the equatorial radius

a and the semi-axes of revolution b. To be more specific we write:

$$F^2(\hat{h}_o,h) = \rho^2 V^2[\bar{H}(\hat{h}_o),b]\ \phi[h\bar{H}(\hat{h}_o)] \tag{13}$$

where we have taken the same uniform charge density for all the particles (e.g. average density). $\bar{H}$, being the observable dimension of the ellipsoid defined in section 2.3. In the Guinier approximation $\bar{H}^2$ is the average of H^2 and is related to the radius of gyration, R_o, only in the case of random orientation where $\bar{H} = \sqrt{5/3}\ R_o$. In the Porod approximation $(\bar{H})^{-4}$ is equal to the average of H^{-4} where in the case of random orientation $V^2(\bar{H},b)/\bar{H}^4$ is related to the surface area of the particle.

Equation (13) makes it mathematically more convenient to consider distribution functions of $\bar{H}$ and b instead of a and b. One exception is when $\hat{h}_o$ is chosen such that $\bar{H} = b$, for example, in the case of totally oriented ellipsoids of revolution with $\gamma = 0$, in which case one must consider distribution functions of a and b. Let $N(\bar{H})dH$ be the total number of particles having sizes in the range $\bar{H}$, $\bar{H} + d\bar{H}$ and $g(b)db$ be the probability function for a particle to have its semi-axes of revolution in the range b, b + db. The quantity $N(\bar{H})g(b)d\bar{H}db$ represents the total number of particles having sizes in the range $\bar{H}$, $\bar{H} + d\bar{H}$ and b, b + db, thus:

$$\overline{I(\hat{h}_o,h)} = I_e\rho^2 \int_0^\infty d\bar{H}\ N(\bar{H})\ \overline{V^2(\bar{H})}\ \phi(h\bar{H}) \tag{14a}$$

where

$$\overline{V^2(\bar{H})} = \int_0^\infty db\ g(b)\ V^2(\bar{H},b) \quad . \tag{14b}$$

Equation (14a) can be put into a somewhat more usable form by introduction of a mass distribution function $M(\bar{H})d\bar{H}$ representing the total mass of the particles in the range $\bar{H}$, $\bar{H} + d\bar{H}$, therefore:

$$\overline{I(\hat{h}_o,h)} = KI_e\rho^2 \int_0^\infty d\bar{H}\ M(\bar{H})\ \overline{V^2(\bar{H})}\ \phi(h\bar{H}) \tag{15}$$

where $V^2(\bar{H})$ should be expressed explicity in terms of $\bar{H}$ and K being a constant proportional to the total mass.

In order to avoid confusion, we attribute the inertial distance $\bar{D}(\hat{h}_o)$ to the Guinier region where $\bar{H}(\hat{h}_o)$, given from the relation $\bar{H}^4(\hat{h}_o) = 9V^2/16\pi\bar{S}_\perp(\hat{h}_o)$, is attributed to the Porod region. This notation will also be adopted throughout sections 5 and 6.

If we introduce the normalized distribution function:

$$g(\bar{D}) = \frac{M(\bar{D})\ \overline{V^2(\bar{D})}}{\int_0^\infty M(\bar{D})\ \overline{V^2(\bar{D})}\ d\bar{D}} \tag{16}$$

in the Guinier region the observable dimension is

$$\langle \bar{D} \rangle (\hat{h}_o) = \left[\int_0^\infty g(\bar{D})\ \bar{D}^2\ d\bar{D}\right]^{1/2} , \tag{17}$$

which favors values of $\bar{D}$ that falls between the largest $\bar{D}$ and the value of $\bar{D}$ maximizing $g(\bar{D})$.

The observable dimension in the Porod region is

$$\langle \bar{H} \rangle (\hat{h}_o) = \left[\int_o^\infty \frac{g(\bar{H})d\bar{H}}{\bar{H}^4} \right]^{-1/4} \tag{18}$$

which favors values that fall between the smallest $\bar{H}$ and the value of $\bar{H}$ maximizing $g(\bar{H})$. From the experimental point of view, by changing $\hat{h}_o$ and measuring $\langle \bar{D} \rangle$ or $\langle \bar{H} \rangle$ one should be able to tell about the shape of the inhomogeneities while measuring $\langle \bar{D} \rangle$ and $\langle \bar{H} \rangle$ between the Guinier and Porod approximations should give information about the size distribution of the inhomogeneities. In the remaining of this paper the effect of size distribution will be ignored for simplicity.

4. Correction for the Effect of Beam Height:

The methods of correction for beam height effects are valid only if the intensity of scattered radiations depends solely on the scattering angle 2θ. Thus in the general case of oriented particles, Guinier and Fournet[9] suggested the use of a beam with very small height at the price of very great loss in intensity. For oriented ellipsoids of revolution the theoretical plane $(I(\hat{h}_o,h)$-vs-$h)$ will contain a family of small angle scattering curves each corresponding to a given direction of $\hat{h}_o$ with no explicit dependence on $\hat{h}_o$. For each of these curves the scattered radiations depends only on the scattering angle 2θ where $\hat{h}_o$ is a parameter that takes us from one curve to the other.

Thus for each experimental set up $\hat{h}_o$ is given and therefore the methods of correction for beam height are applicable without any limitation on the beam height. This result for a group of widely separated ellipsoids of revolution is true for all particle shapes.

For randomly oriented particles the methods of correction for beam height are well treated in the literature: Guinier and Fournet[10] summarized these methods for the case of uniform intensity distribution along the slit height. Recently P. W. Schmidt[11] treated the case where the distribution of intensity along the slit height is approximated by a Gaussian and W. S. Rothwell[12] did some useful calculations for slits of small but non zero widths and of finite heights. As stated above these methods apply also for particles of preferred orientation. However, for the random orientation case there is only one scattering curve in the theoretical plane (I-vs-h) that is corrected to one curve in the experimental plane (J-vs-h) where I and J correspond to the point collimation and slit collimation cases respectively. For oriented particles we mentioned above that the plane (I-vs-h) contains a family of small angle scattering curves each corresponding to a given direction of $\hat{h}_o$. At h = o all these curves will come to a common intersection ($I(\hat{h}_o,o) = NI_e\rho^2v^2 \equiv I(o)$ independent of $\hat{h}_o$). In the experimental plane (J-vs-h) by varying $\hat{h}_o$ a similar family of curves as in the theoretical plane is generated. At h = o these curves do not come to a common intersection but are dispersed between the two values $c\sqrt{5\pi}/b \quad I(o)$, corresponding to $\hat{h}_o$ along the direction of the polar axis of the ellipsoid and $c\sqrt{5\pi}/a \quad I(o)$ corresponding to

$\hat{h}_o$ along the direction of the equatorial axis of the ellipsoid of revolution.

$$(J(\hat{h}_o,o) = \frac{c\sqrt{5\pi}}{\bar{D}(\hat{h}_o)} I(o)$$

dependent of $\hat{h}_o$). Note that all particles are assumed to be equal. Here as in previous sections the axes of the ellipsoid of revolution are taken equal to 2a, 2a, 2b, and c is a constant equal to the intensity of the beam along the slit height.

5. Methods of Interpretation of Experimental Results

In this section we discuss the use of the Guinier and Porod approximations strictly for widely separated particles. More on the use of the Porod approximation will be discussed elsewhere.

For low enough concentrations, interference effects which are generally pronounced at low angles are negligible. One way of obtaining $\bar{D}(\hat{h}_o)$ from the Guinier approximation is by plotting lnI-vs-h^2. From Eqs. (9a) and (10) it is apparent that:

$$\frac{d \ln I}{dh^2} = -\bar{D}^2 \tag{19}$$

where the dependence on $\hat{h}_o$ is understood.

For equal ellipsoids another method is to plot h^3I-vs-h. This will give a maximum at $d(h^3 I)/dh = 0$ which occurs when

$$\bar{D}^2 = 3/(2h^2) \tag{20}$$

From our model of Guinier spheres discussed in section 3.1, it is important to note that this peak represents a continuous size distribution of spheres of radii between a and b, and therefore, is expected to be dispersed between values of h corresponding to a and b and in some extreme cases it may become too dispersed to be observable. From the shape of the peak information about the distribution $P'(\hat{h}_o,\bar{D})$ and therefore the preferred orientation distribution can be obtained.

In the Porod region the geometrical interpretation of the quantity $\bar{S}_\perp(\hat{h}_o)$ is not clear to us. We, therefore, choose a related quantity $\bar{H}(\hat{h}_o)$ defined by $\bar{H}^4(\hat{h}_o) = 9V^2/16\pi\bar{S}_\perp(\hat{h}_o)$ and of geometrical significance closely related to that of H. For large values of h the fundamental equation is obtained from Eqs. (9c,d) and (10):

$$I[h\bar{H}(\hat{h}_o)] = NI_e \frac{9V^2}{4\pi} \frac{2\pi\rho^2}{h^4\bar{H}^4(\hat{h}_o)} \tag{21}$$

Equation (21) shows that for large values of h, $h^4 I[h\bar{H}(\hat{h}_o)]$ remains constant over a reasonable interval which defines the Porod region.* If the cross section of the beam is not pointlike but rather has a large height, then it is the product $h^3 J[h,\bar{H}(\hat{h}_o)]$ which should be constant at large value of h.

The determination of $\bar{H}(\hat{h}_o)$ from (21) requires absolute intensity measurement. A method that avoids the measurement of the direct beam intensity by making use of normalization relation will be discussed

*If the electronic density in the interior of the particles is not rigorously constant, high-angle scattering pattern such as that for amorphous body will occur. The product $h^4 I[h\bar{H}(h_o)$ thus will begin to increase when h becomes too large. This is also due to compton scattering, thermal scattering by crystals and various parasitic scatterings.

elsewhere. However, much information about size and preferred orientation distribution are obtained by taking ratios of $\bar{H}$ for different $\hat{h}_o$ from the Porod region and comparing them to ratios of $\bar{D}$ from the Guinier region.

6. Equal Ellipsoids of Common Orientations:

An important case is when all the particles have a difinite common orientation. In this case the direction of the axis of revolution can be determined experimentally by verification of the symmetry of revolution. If photographic plates are used when the direction of the incident X-ray beam is oriented along the axis of revolution the small angle spot will be circular. If photographic plates are not used, it is possible to check the symmetry of revolution by plotting, for given h, the intensity versus an angle of rotation of the sample in a plane normal to the beam direction. The symmetry of revolution is obtained if the observed intensity is independent of the angle of rotation. Due to experimental errors the experimental points actually will oscillate about a constant average. When this is obtained the incident beam direction defines the direction of the axis of revolution. Good intuitive guesses to the direction of the axis of revolution can enormously simplify the experimental procedure. Such guesses are guided by the structure of the material, the nature of its bonds and its method of preparation. For example, in pyrolitic graphite the axis of revolution is normal to the deposition plane.

In the common orientation case it is advantageous to direct the incident beam normal to the axis of revolution. The small angle spot will then have the form of an ellipse. For equal particles and slit collimation the variation of intensity with angle in the Guinier region is proportional to

$$\frac{V^2}{b} \exp\left(\frac{-h^2b^2}{5}\right)$$

in the direction parallel to the axis of revolution and

$$\frac{V^2}{a} \exp\left(\frac{-h^2a^2}{5}\right)$$

in the perpendicular direction. Two experimental measurements thus determined the parameters a and b which define the ellipsoid; true only if size variation of the ellipsoids are negligible.

In the Porod region, from Eq. (21), the variation of the intensity with angle is proportional to

$$\frac{V^2}{h^3b^4}$$

in the direction parallel to the axis of revolution and

$$\frac{V^2}{h^3a^4}$$

in the perpendicular direction. By using Eq. (21), b and a can be determined from absolute intensity measurement. However, it is possible to determine the ratio a/b without having to measure the intensity of the direct beam. This ratio measured from the Porod region should be compared to the same ratio evaluated in the Guinier

0 0 0 0 3 9 0 7 5 6 7

region. If all the particles are equal the two ratios must be the same.

ACKNOWLEDGEMENTS

This work was supported in part by the U. S. Atomic Energy Commission.

APPENDIX A

Evaluation of $s(Z,\gamma)$:

In the following we evaluate the expression of $s(Z,\gamma)$, the surface intersection of the ellipsoid and the plane $Z = Z$. We let M represent Euler's matrix:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = M \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \tag{A1}$$

(We don't give the explicit expression of M. It can be found in many references, for example Ref. 13.) The equation of the ellipsoidal surface is:

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2} = 1 \tag{A2}$$

And in terms of X, Y, Z:

$$(X,\ Y,\ Z)\ A \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = 1 \tag{A3}$$

where A is a 3 by 3 matrix:

$$A_{XX} = \frac{\cos^2\psi + \cos^2\gamma\ \sin^2\psi}{a^2} + \frac{\sin^2\gamma\ \sin^2\psi}{b^2} \tag{A4)a}$$

$$A_{YY} = \frac{\sin^2\psi + \cos^2\gamma\ \cos^2\psi}{a^2} + \frac{\sin^2\gamma\ \cos^2\psi}{b^2} \tag{A4)b}$$

$$A_{ZZ} = \frac{\sin^2\gamma}{a^2} + \frac{\cos^2\gamma}{b^2} \qquad \text{(A4)c}$$

$$A_{XY} = A_{YX} = \sin^2\gamma \cos\psi \sin\psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) \qquad \text{(A4)d}$$

$$A_{XZ} = A_{ZX} = -\sin\gamma \cos\gamma \cos\psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) \qquad \text{(A4)e}$$

$$A_{YZ} = A_{ZY} = \sin\gamma \cos\gamma \cos\psi \left(\frac{1}{a^2} - \frac{1}{b^2}\right) \qquad \text{(A4)f}$$

If we make the following changes of variables:

$$\begin{pmatrix} X' \\ Y' \end{pmatrix} = \begin{pmatrix} \cos\psi & \sin\psi \\ -\sin\psi & \cos\psi \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \qquad \text{(A5)a}$$

$$\eta = Y' + \frac{\sin\gamma \cos\gamma \,(b^2 - a^2)}{a^2\sin^2\gamma + b^2\cos^2\gamma} Z. \qquad \text{(A5)b}$$

Eq. (A3) becomes:

$$\frac{X'^2}{a^2} + \frac{\eta^2}{\dfrac{a^2b^2}{a^2\sin^2\gamma + b^2\cos^2\gamma}} + \frac{Z^2}{a^2\sin^2\gamma + b^2\cos^2\gamma} = 1 \qquad \text{(A6)}$$

Equation (A6) represents the equation of the ellipse intersection of the ellipsoidal surface and the plane Z = Z where Z (on the right hand side) is a parameter. To clarify, we call:

$$K = 1 - \frac{Z^2}{a^2\sin^2\gamma + b^2\cos^2\gamma} , \tag{A7}$$

thus the equation of the ellipse (intersection) becomes:

$$\frac{X'^2}{Ka^2} + \frac{\eta^2}{\dfrac{Ka^2b^2}{a^2\sin^2\gamma + b^2\cos^2\gamma}} = 1 \tag{A8}$$

From Eq. (A8) we get $s(Z,\gamma)$:

$$s(Z,\gamma) = \pi K \frac{a^2b}{(a^2\sin^2\gamma + b^2\cos^2\gamma)} \tag{A9)a}$$

or, from Eqs. (A7):

$$s(Z,\gamma) = (\pi ab)\frac{a}{H}\left(1 - \frac{Z^2}{H^2}\right) \tag{A9)b}$$

where,

$$H = (a^2\sin^2\gamma + b^2\cos^2\gamma)^{1/2} \tag{A9)c}$$

It is obvious that $s(Z = H,\gamma) = 0$, thus H represents the maximum variation in Z. (As a verification of Eq. (A9)b one can evaluate the expression of the volume of the ellipsoid by integrating $s(Z,\gamma)dZ$ over [-H, +H]).

APPENDIX B

The Average of $4S_\perp$ over all Equally Probable Orientations:

For randomly oriented ellipsoid of revolution

$$4\bar{S}_\perp = \frac{9}{4\pi} V^2 \overline{1/H^4} \tag{B1}$$

consider:

$$\overline{1/H^4} = \int_0^{\pi/2} \frac{-d\cos\gamma}{[a^2 \sin^2\gamma + b^2\cos^2\gamma]^2}$$

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

$$\overline{1/H^4} = \frac{1}{(b^2 - a^2)^2} \int_0^1 \frac{dx}{\left[x^2 + \frac{a^2}{b^2 - a^2}\right]^2}$$

$$= \frac{1}{4\pi a^4 b^2} \left(2\pi a^2 + \frac{2\pi ab}{e} \tan^{-1}\frac{b}{a} e\right) \tag{B2}$$

Where $e = \sqrt{(b^2-a^2)/b^2}$ is the eccentricity of the ellipsoid 2a, 2a, 2b. By examining Fig. 3 one can easily show that:

$$\sin^{-1} e = \zeta = \tan^{-1}\frac{b}{a} e \tag{B3}$$

From Eqs. (B1), (B2) and (B3) we get:

$$4\bar{S}_\perp = \frac{9}{4\pi} V^2 \overline{1/H^4} = S \tag{B4}$$

where $S = 2\pi a^2 + 2\pi(a\ b/e) \sin^{-1} e$ is the surface area of the ellipsoid.

REFERENCES

1. A. Guinier, Ann. de Physique 12, 161, (1939).
2. G. Porod, Acta Phys. Austriaca 2, 255, (1948).
3. R. H. Bragg, M. L. Hammond, J. C. Robinson and P. L. Anderson, Nature 200, 557 (1963).
4. A. Guinier and G. Fournet, "Small Angle Scattering of X-rays" University Microfilm, Ann Arbor, Michigan, pp. 28-30.
5. Reference 4, pp. 29.
6. C. G. Shull and L. C. Roess, J. Appl. Phys. 18, 295, (1947).
7. W. S. Rothwell, J. Appl. Phys. 41, 4459, (1970).
8. P. W. Schmidt, Acta Cryst. 11, 674, (1958).
9. Reference 4, pp. 134
10. Reference 4, pp. 111-121
11. P. W. Schmidt, Acta Cryst. 19, 938, (1965).
12. W. S. Rothwell, J. Appl. Phys. 39, 1840, (1968).
13. Corben and Steble, "Classical Mechanics" Wiley 1950, pp 177.

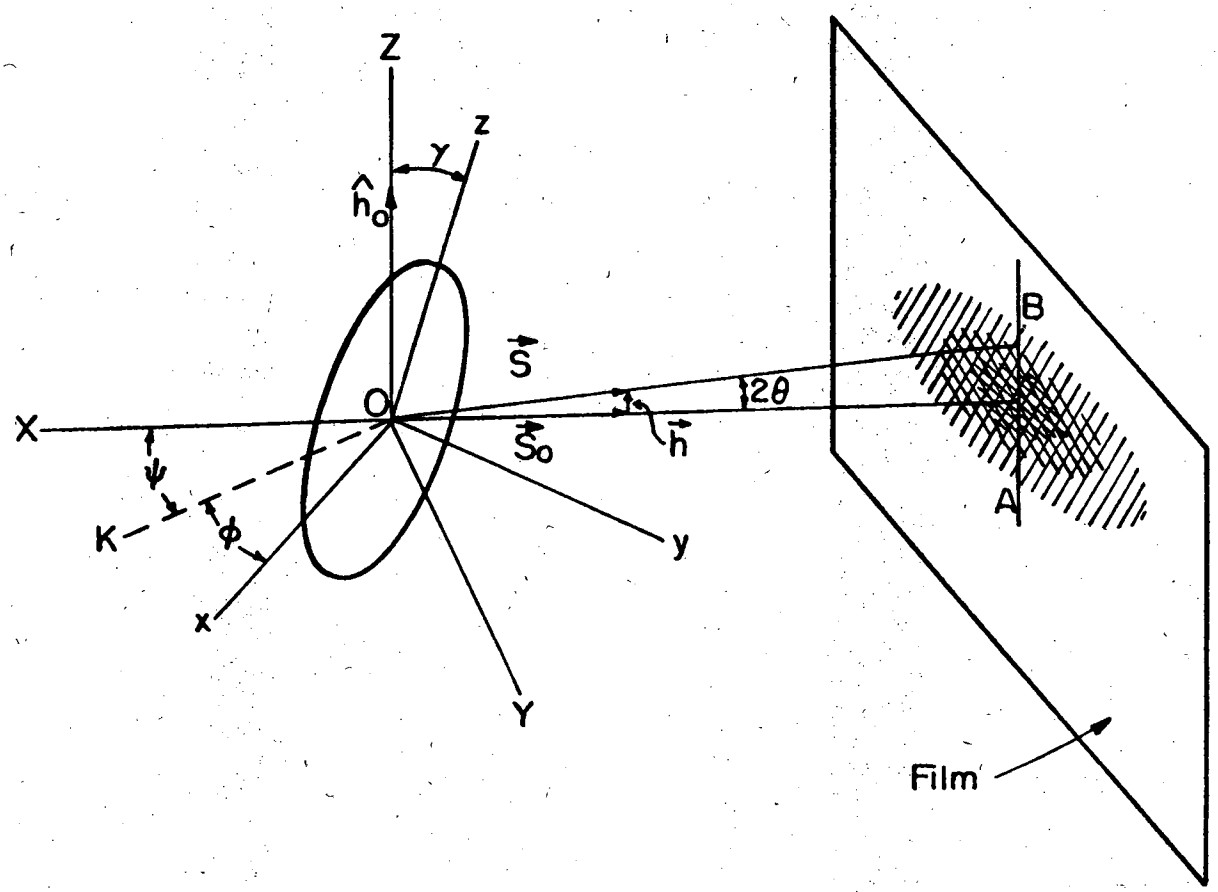
FIGURE CAPTIONS

Fig. 1. Definition of a fixed reference frame: $\vec{OZ}$ parallel to $\vec{AB}$, $\vec{XO}$ parallel to incident x-ray beam. OK is the line of nodes.

Fig. 2. The small angle scattering from a group of equal ellipsoids of revolution of orientation distribution and low concentration is equivalent to the small angle scattering from a group of widely separated Guinier spheres of radius distribution. The plane π is normal to $\hat{h}_o$ and tangent to E_3.

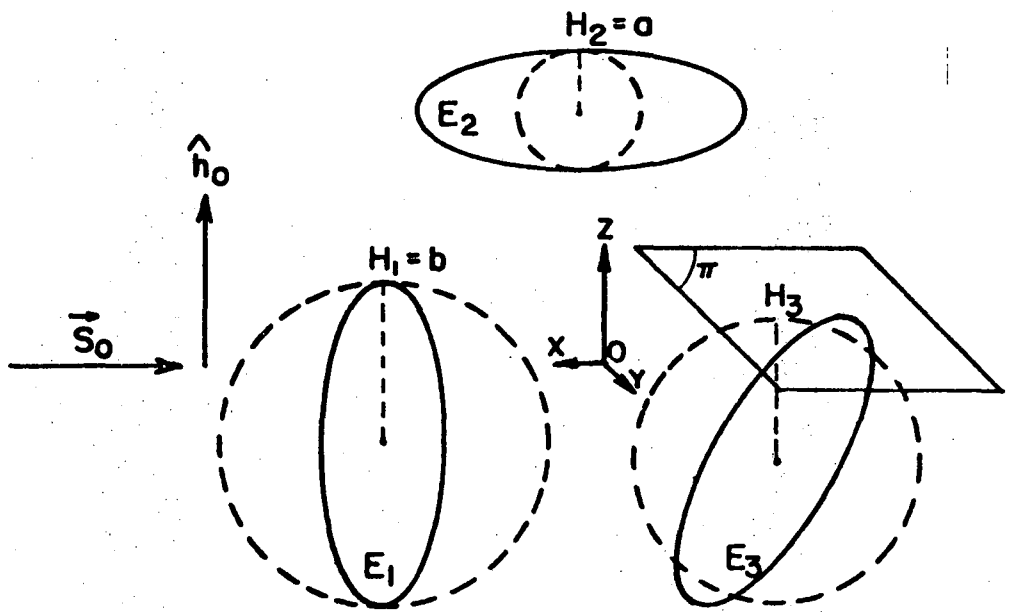
Fig. 3. A geometrical demonstration of the relation $\sin^{-1} e = \tan^{-1} \frac{b}{a} e$

$$e = \sqrt{\frac{b^2 - a^2}{b^2}} \quad .$$



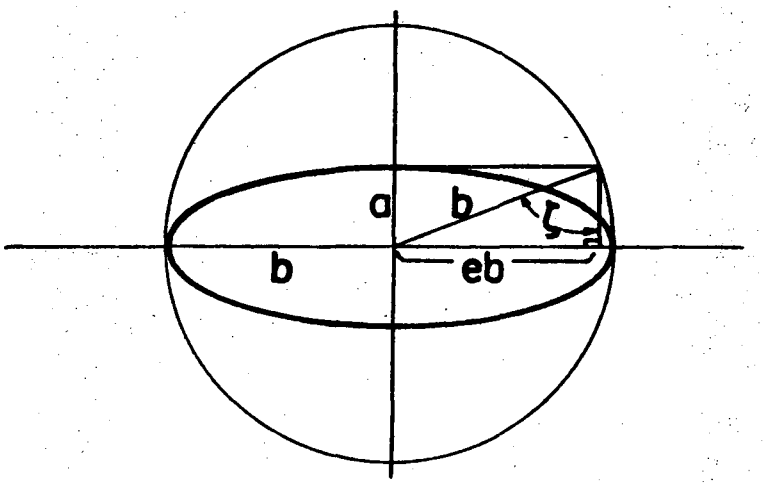
XBL738-1628

Fig. 1



XBL 738-1713

Fig. 2



XBL 7210-7065

Fig. 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720