Multiple Diffuse Small Angle Scattering of X-Rays*

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The problem of multiple x-ray scattering from spherical particles of radius much larger than the wavelength is treated using the Guinier approximate scattering function. The total scattered intensity is found to be a sum of Gaussians in the polar angle with coefficients dependent on the sample thickness. A method is discussed for determining particle sizes from the variation of the width of the scattering curve with sample thickness. Experimental results are given for two carbon blacks.

INTRODUCTION

MUCH theoretical and experimental work has been done on the subject of small angle x-ray scattering, generally for the purpose of obtaining particle sizes, shapes, and size distributions.[1] Previous work has been based on the assumption that there is negligible multiple scattering so that the angular distribution of the scattered radiation is independent of the sample thickness.[2] In this paper we obtain an expression for the intensity of coherently scattered x-radiation as a function both of angular deviation from the incident beam direction and of sample thickness, especially for thicknesses great enough so that considerable multiple scattering occurs.

THEORETICAL

It is assumed that the incident beam is composed of parallel monochromatic x-rays of wave-length λ, that the Z axis (beam direction) is an axis of cylindrical symmetry, and that the radiation intensity is constant over the cross section of the incident beam. It is also assumed that the scattering material consists of randomly arranged identical spherical particles of radius $a\sim 10^2$ or $10^3\lambda$. No account is taken of refraction within the particles or of interparticle interference.

The calculations are based on Guinier's approximate single scattering function for a sphere,[3] which states

$$I(\theta)=N^2J\frac{r_0^2}{r^2}\exp\left(-\frac{1}{5}\left(\frac{2\pi a}{\lambda}\right)^2\theta^2\right), \tag{1}$$

where $I(\theta)$ is the scattered intensity at a distance r from the particle and at an angle θ with the incident beam, N is the number of electrons in a particle, J the incident beam intensity, and r_0 the classical electron radius.

To simplify the calculation it is assumed that the x-radiation scattered from a particle P_i and intercepted by another particle P_j is a plane wave of intensity constant throughout P_j but proportional to r_{ij}^{-2}, where r_{ij} is the center-to-center distance of the ith and jth particles.

With this assumption the intensity of radiation scattered from P_j which was previously scattered from P_i is

$$I_{ij}=\left\{JN^2\frac{r_0^2}{r_{ij}^2}\exp\left(-\frac{2}{9}\left(\frac{2\pi a}{\lambda}\right)^2\theta_{ij}^2\right)\right\}\frac{N^2r_0^2}{R_j^2}\times\exp\left(-\frac{2}{9}\left(\frac{2\pi a}{\lambda}\right)^2\delta_{ij}^2\right). \tag{2}$$

The coefficient 1/5 has been changed to 2/9 in order to have the area under the Gaussian agree with that under the curve of the exact scattering function. In this expression (see Fig. 1) θ_{ij} is the angle between the polar axis and the line connecting P_i and P_j, R_j is the distance from P_j to the observer, and δ_{ij} is the angle between "the line P_iP_j" and the direction of observation. Now expressing δ_{ij} in terms of θ_{ij}, θ_j (the angle between the direction of observation and the polar axis) and $\varphi_{ij}-\varphi_j$ (the difference between the azimuthal angle of "the line P_iP_j" and that of the direction of observation), one obtains

$$\delta_{ij}^2=\theta_{ij}^2+\theta_j^2+2\theta_{ij}\theta_j\cos(\varphi_{ij}-\varphi_j), \tag{3}$$

where the angles θ_{ij}, θ_j, and δ_{ij} are assumed small. The twice-scattered radiation intensity from P_j is given by the summation of (2) over all particles P_i. Replacing the summation by an integration,

$$I_2(\theta_j)=K_2\int_0^{\pi}\int_{\varphi_i}^{2\pi+\varphi_i}\exp\left(-\frac{2}{9}\left(\frac{2\pi a}{\lambda}\right)^2\theta_{ij}^2\right)\times\exp\left(-\frac{2}{9}\left(\frac{2\pi a}{\lambda}\right)^2[\theta_{ij}^2+\theta_j^2+2\theta_{ij}\theta_j\cos(\varphi_{ij}-\varphi_j)]\right)\theta_{ij}d\theta_{ij}d\varphi_{ij}$$

$$=\frac{9\lambda^2}{16\pi a^2}K_2\exp\left(-\frac{1}{9}\left(\frac{2\pi a}{\lambda}\right)^2\theta_j^2\right), \tag{4}$$

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[1] A. Guinier, Ann. de physique **12**, 161 (1939); R. Hosemann, Zeits. f. Elektrochemie **46**, 535 (1940); B. E. Warren, J. App. Phys. **20**, 96 (1949); Kratky and Porod, Acta Physica Austriaca **II**, 133 (1948). For further references see Shull and Roess, J. App. Phys. **18**, 295 (1947).

[2] A multiple refraction treatment has been carried out by R. von Nardroff, Phys. Rev. **28**, 240 (1926).

[3] A. Guinier, see reference 1.

where K_2 is independent of θ_j. In the evaluation of this integral use has been made of $2\pi a/\lambda \gg 1$. This relation, which ensures that the entire scattering process is concentrated in a very small angle about the forward direction, also enables us to neglect the integration with respect to r_{ij}, as has been done in (4), as long as we are interested only in the angular distribution and not in the intensity of the doubly scattered radiation. Stated in another way, the very small angular deviations in the scattered beam permit us to ignore any limitations on the directions from which P_j can receive once-scattered radiation even for P_j near the edge of the sample. Since all P_j scatter identically the total twice-scattered beam will have the angular distribution (4). An iteration procedure shows that the angular dependence of the kth scattered component is given by

$$I_k(\theta) = K_k \exp\left(-\frac{2}{9k}\left(\frac{2\pi a}{\lambda}\right)^2\theta^2\right). \tag{5}$$

The relative intensities of the various scattered components as a function of sample thickness can be found from a consideration of their growth and decay within the sample. Neglecting edge effects, let I_k now be the integrated (over angle) intensity of the kth scattered component. The unscattered component I_0 decays at a rate determined by absorption and by first scattering; I_1 grows at a rate proportional to the amount of unscattered radiation present and to the mass scattering coefficient, and decays at a rate proportional to I_1 times the sum of the mass absorption and the mass scattering coefficients. Both coefficients are independent of the previous history of the photon. Thus, let μ_a denote the mass absorption coefficient, μ_s the mass scattering coefficient, $\mu = \mu_a + \mu_s$ the total mass coefficient for decay of a given scattered component, and m the number of grams per cm^2 of the sample through which the beam has passed. Then

$$\begin{aligned} dI_0 &= -\mu I_0 dm, \\ dI_1 &= \mu_s I_0 dm - \mu I_1 dm, \\ &\cdots \\ dI_k &= \mu_s I_{k-1} dm - \mu I_k dm. \\ &\cdots \end{aligned} \tag{6}$$

These equations have the solution

$$\begin{aligned} I_k &= J e^{-\mu m} \mu_s{}^k m^k / k!, \\ \sum_{k=0}^{\infty} I_k &= J e^{-\mu_a m} \end{aligned} \tag{7}$$

and, as must be the case, summing over all I_k shows that the total intensity of the radiation in the sample decays at a rate determined only by true absorption.

By integrating the Guinier function over 4π solid angle μ_s can easily be shown to be $9nN^2r_0^2\lambda^2/8\pi a^2$, where n is the number of particles per gram. Let x be defined by

$$x \equiv \mu_s m = 9nN^2r_0^2\lambda^2 m/8\pi a^2. \tag{8}$$

Since I_k in (7) is proportional to the total intensity over all angles in the kth scattered component the proper coefficients for the previously derived angular distributions can now be obtained easily.

$$2\pi C_k \int_0^{\pi} \exp\left(-\frac{2}{9k}\left(\frac{2\pi a}{\lambda}\right)^2\theta^2\right)\theta d\theta = J e^{-\mu m} x^k/k!,$$

$$C_k = \frac{8\pi a^2}{9\lambda^2} J e^{-\mu m} \frac{x^k}{kk!}, \tag{9}$$

for $k \neq 0$, and so the total scattered intensity is proportional to

$$I(\theta, m) = J e^{-\mu m} \frac{8\pi a^2}{9\lambda^2} \sum_1^{\infty} \frac{x^k}{kk!} \exp\left(-\frac{2}{9k}\left(\frac{2\pi a}{\lambda}\right)^2\theta^2\right). \tag{10}$$

For $x \ll 1$ only a small fraction of the incident radiation is scattered at all, and the scattering *versus* angle curve will be complicated at the center by the presence of the unscattered radiation, but as x becomes much larger than 1 the amount of unscattered radiation becomes neligible. For $x \gg 1$ it is clear that $x^k/kk!$ considered as a function of k has a maximum for k of the same order as x. If x is large enough, the important terms in the sum have an index k so large that Stirling's formula is applicable. The most important term, that is, the term with the largest coefficient, can now be obtained by maximizing $x^k/kk!$. It is the term for which $k = x$. The angular width of the kth scattered component at a height $1/e$ of the central maximum is

$$W = 3\lambda(k/2)^{\frac{1}{2}}/\pi a. \tag{11}$$

On the assumption that for sufficiently thick scatterers the scattering curve will be very similar to that of the most intense scattered component we may calculate using $k = x$ and Eq. (8)

$$\alpha \equiv \frac{dW}{d(m)^{\frac{1}{2}}} = \frac{3\lambda}{\pi a\sqrt{2}} \mu_s{}^{\frac{1}{2}} = \frac{9\lambda^2 N r_0 (n)^{\frac{1}{2}}}{4\pi^{\frac{3}{2}} a^2} \tag{12}$$

and for particles of low atomic number, where the atomic weights of the constituent atoms are twice their

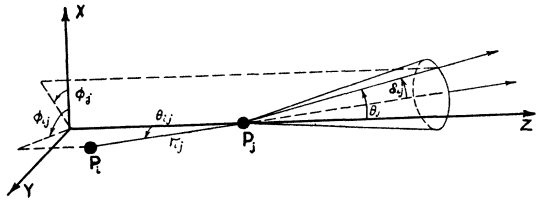

FIG. 1. Geometry of double scattering.

atomic numbers

$$\alpha=\frac{3\lambda^2}{4\pi}r_0L(3\rho/a)^{\frac{1}{2}}, \tag{13}$$

where L is Avogadro's number and ρ is the density within a particle. Thus

$$a=\frac{27}{16\pi^2}\lambda^4\frac{r_0^2L^2}{\alpha^2}\rho, \tag{14}$$

giving the particle radius from the slope of the width *versus* square root of the mass per unit area curve.

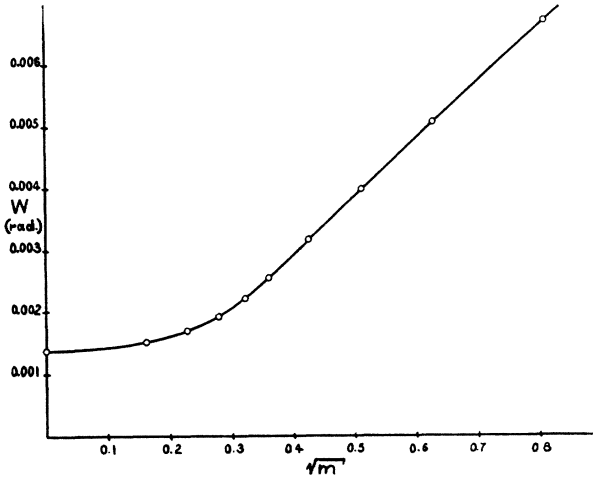

FIG. 2. Theoretical variation of the $1/e$ width of the total scattering curve as a function of the square root of m (in g/cm²) for $\lambda=1.54$A, $a=750$A, and $\rho=2$ g/cm³.

It should be noted that this method of determining particle sizes is not restricted to cylindrically symmetric geometry. With slit system or double-crystal spectrometer geometry the most important term is still that for which $k=x$, and the particle radius is given by the above.

Figure 2 shows the variation with $m^{\frac{1}{2}}$ of the theoretical scattering curve width for $\lambda=1.54$A, $\rho=2$ g/cm³, and $a=750$A. The circles were computed numerically from (10) at values of $x=0$, 1, 2, 3, 4, 5, 7, 10, 15, and 25. It is found that the slope in the vicinity of $x=10$ or $m^{\frac{1}{2}}=0.51$ ($\alpha=9.7\times10^{-3}$) is larger than the slope for x large as computed by means of Stirling's formula ($\alpha=8.6\times10^{-3}$). Thus the w *versus* $m^{\frac{1}{2}}$ curve has an inflection point, becomes slightly concave down and approaches a constant slope for x large. This is a result of the fact that for small x the most important term is that for which $k=x-2$, so that the total scattering curve has a width appreciably less than that of a Gaussian with $k=x$. For x large, however, the total scattering function width is closely equal to that of Gaussian with $k=x$. Thus for small x the index of the most important term increases more rapidly than x and the width consequently increases more rapidly than the square root of m, giving a larger slope at small x than the limiting value. By $x=25$ the slope has decreased to about $\alpha=9.1\times10^{-3}$.

EXPERIMENTAL

Multiple scattering is easily obtained experimentally if the mass absorption coefficient is not so great that absorption has reduced the intensity to an inconveniently low value before appreciable multiple scattering has occurred. Since

$$\mu_s=9nN^2r_0^2\lambda^2/8\pi a^2=1.08\lambda^2a\rho\times10^{22} \tag{15}$$

multiple scattering is feasible experimentally if

$$a_A\gtrsim\mu_a/0.0108\lambda_A^2\rho,$$

where the subscript A denotes that the quantity is expressed in angstrom units. For carbon particles with $a=750$A, $\rho=2$ g/cm³, and $\lambda=1.54$A μ_s is about 8 times greater than μ_a.

Figure 3 shows experimental results obtained with a three-crystal spectrometer[4] for two carbon blacks, Godfrey L. Cabot P-33 and Sterling L, using Fe radiation at 25–32 kv. Comparisons of theory and experiment are complicated by the wide distributions of particle sizes usually encountered in colloidal materials. In particular the measured single scattering width of P-33 is much too small as may be seen from a comparison of Figs. 2 and 3. Since the total scattering coefficient per electron of a particle goes up as the radius of the particle, and the scattered energy is concentrated in an angle inversely proportional to the radius, a few large particles may invalidate any measurement of the single scattering width. In addition the average particle size in our samples is greater than one generally attempts to measure with single scattering techniques and thus the problem of correctly subtracting the unscattered radiation is greatly aggravated.

We have attempted the customary plot of log of scattered intensity *versus* the square of the scattering angle of our single scattering data for P-33. Particle sizes differing by two orders of magnitude could be obtained from different parts of the curve. Most of this difficulty also can be attributed to interference of the unscattered radiation.

Much less equivocal and more reasonable estimates of particle size can be obtained by applying (14) to the linear parts of the curves of Fig. 3. Particle radii were found to be 770 and 480A for P-33 and Sterling L, respectively. The P-33 particle size obtained in this way is larger than that found by earlier workers, who find mean radii of from 370 to 670A. It agrees much better with a weighted average size, $\Sigma f(a)a^3/\Sigma f(a)a^2$ which is obtained naturally from adsorption data, where $f(a)$ is the distribution function of the radii. Values between 715 and 780A have been obtained for this quantity from electron microscope and nitrogen adsorption data.[5]

[4] To be described soon in J. App. Phys.

[5] For a comparison of work on P-33, see R. B. Anderson and P. H. Emmet, J. App. Phys. **19**, 367 (1948).

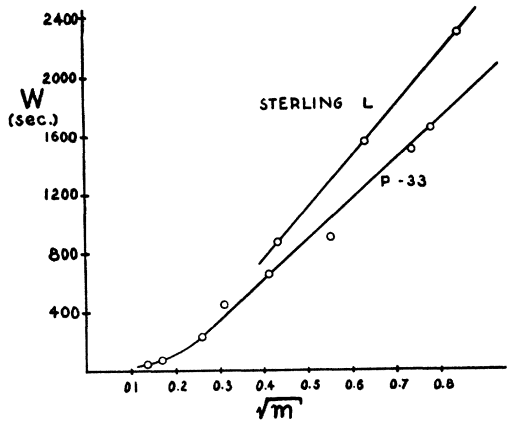

FIG. 3. Experimental curves for carbon blacks with $\lambda=1.93$A showing the variation of the curve width with $m^{\frac{1}{2}}$ (m in g/cm^2).

Electron micrographs were taken of Sterling L by Dr. Paul Kaesberg of the University of Wisconsin. There was a great deal of clustering into large agglomerates but most of the individual particles were of radii 150 to 500A.

For sufficiently thick samples a linear relation between the width of the scattering curve and the square root of the mass per unit area would be expected even for a distribution of particle sizes. To calculate what weighted average is thus obtained seems a formidable problem which we have not attempted. However, our agreement with the careful nitrogen adsorption work of Anderson and Emmet[5] is evidence that the method will be useful for particles too large to be treated by standard single-scattering methods and yet so small that refraction is not appreciable.

For much larger particles ($a\gtrsim 10$ microns) correct particle sizes are expected from von Nardroff's multiple refraction treatment, based on geometric optics,[2] in which is considered only the term corresponding to the most probable number of x-ray-particle interactions. The fact that he obtains a Gaussian for his final multiple refraction formula is a result of statistical analysis, and not of the single-process function, which is the cause of the series of Gaussians obtained here.

According to both multiple process theories α varies directly with $\lambda^2(\rho/a)^{\frac{1}{2}}$ with different proportionality constants in the two cases. Thus varying the experimental parameters does not distinguish between the theories.

Experimental intensity *versus* angle curves were obtained using Godfrey L. Cabot Spheron Grade 6 carbon black with the three-crystal spectrometer and Fe radiation. Six samples were tested with m ranging from 0.0210 to 0.5918 g/cm^2. The thicker specimens show a definite narrow pip at the center, corresponding to the unscattered radiation. This was also observed with the thinner P-33 samples. The thinner specimens of Spheron Grade 6 with $x\lesssim 1$ cannot be unambiguously separated into scattered and unscattered curves as for the thicker samples, but the ratio of unscattered central ordinate to scattered ordinate is in at least good qualitative agreement with the multiple scattering formulas assuming infinite slit geometry. A curve for a sample of intermediate thickness, $m=0.1625$ g/cm^2 is reproduced in Fig. 4. The narrow peak of unscattered radiation merges abruptly into the scattered intensity curve, showing a ratio of peak height to scattered radiation height of between 10 and 14. This is to be compared with the ratio 10.7 as predicted from the multiple scattering equations assuming $a=150$A. For the two thickest samples x is equal to 4.18 and 7.12, and more unscattered central intensity is present than the theory predicts by a factor of about 3 and 8, respectively. This is due to the presence of second order radiation, which, because of its lower total mass coefficient, becomes important for thick samples.

A radius of about 150A for Spheron Grade 6 was obtained by Anderson and Emmet.[5] Our measurements from Eq. (14) give a somewhat larger result (roughly 180A). The reliability of our measurement is doubtful as we were not able to reach high scattering multiplicities with these smaller particles.

The importance of the observation of the pip is, of course, that it is further strong experimental evidence that we are dealing with a low order multiple process where the undeviated incident radiation has still a reasonable probability of getting through. If the cause of the broadening were refraction one would expect a smooth angular distribution (a Gaussian without a pip). This follows from the fact that the cross section for refraction is the geometrical cross section. Even with our thinnest samples a traversing ray must penetrate many particles. Thus if refraction were a correct physical model for particles in this size range it would have to be a highly multiple refraction. According to

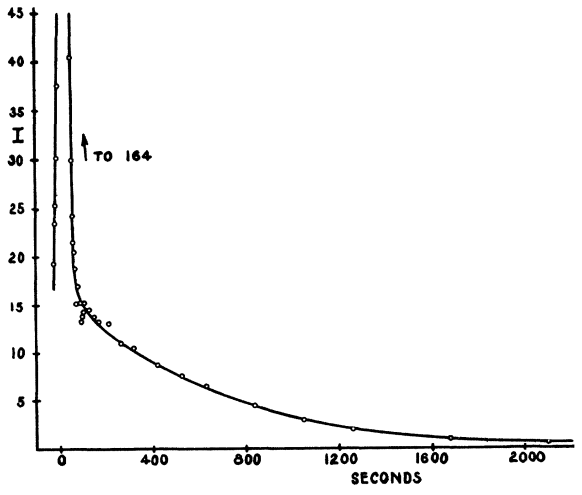

FIG. 4. Scattered intensity from Godfrey L. Cabot Spheron Grade 6 carbon black as a function of angle with $\lambda=1.93$A, $\rho=2$ g/cm^3, $m=0.1625$ g/cm^2, and $a\sim 150$A.

the multiple refraction theory the width of the single Gaussian would be 4530 seconds for the curve shown in Fig. 4.

The theory developed in this paper should be applicable, without serious modification, to the passage of slow neutrons through colloidal materials. Indeed, because of the relatively lesser importance of neutron absorption, higher scattering multiplicities would be experimentally obtainable.

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The Density Effect for Cosmic-Ray Mesons*

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This paper deals with a detailed study of individual pulses produced by fast cosmic-ray mesons in a specimen of silver chloride. A discussion is given of the pulse distributions obtained from the experiment, which was designed to show the increase with energy of the rate of ionization in the relativistic region and the correction to this increase due to the density effect. The measured values are compared with theoretical distributions which take fluctuation and density effect into account. It is concluded that the results agree well with the fluctuation theory developed by Symon and the density effect corrections as given by Halpern and Hall.

1. INTRODUCTION

IN 1945 van Heerden[1] reported the technique of using a crystal of silver chloride as an ionization detector. Such a detector is sufficiently sensitive to measure the ionization produced by a singly charged particle ionizing at the minimum rate. Hofstadter[2] has reported the observation of pulses produced in silver chloride and certain other substances by gamma-rays.

The theoretical treatment of the average ionization produced by fast particles has been given by Bethe and by Bloch. Their results have been summarized by Heitler.[3a] Curves are available in an article by Rossi and Greisen.[3b]

The Bethe-Bloch theory pertains to the case of disperse media. For a condensed medium an additional effect, called the density effect, reduces the rate of ionization for charged particles. The mechanism for the density effect is the polarization of the atoms of the medium with the resulting reduction of the distant electromagnetic interactions. This effect, first suggested by Swann and discussed briefly by Fermi,[4] has been treated in detail by Wick,[5] and Halpern and Hall.[6] The theory of average ionization for an energetic particle ionizing near the minimum rate has been tested experimentally by Corson and Brode[7] and Hazen,[8] who partially verified the rise in the rate of ionization in the relativistic region predicted by the theory. Further tests were performed by Hayward[9] and Hereford[10] to search for the existence of the density effect. Both of these workers report results which agree with the Bethe-Bloch theory of ionization as corrected for the density effect by Halpern and Hall. In each case, however, the experiment is indirect and the results sketchy.

The theory of ionization, including polarization effects, seems to be sound, but has not been tested thoroughly at high energy. In the crystal counter we have an instrument suited for such a study. We cannot directly compare the rate of ionization deduced from the crystal pulse with the *average* rate of ionization given in the above-mentioned theory because the pulses produced in the crystal by monoenergetic particles suffer a large fluctuation due to the fluctuation in energy loss. Landau[11] has investigated this fluctuation in energy lost by a particle in traversing a *thin* thickness of absorber. Similar calculations, carried out in detail by Symon[12] for all thickness of absorber, make it possible to predict the fluctuation in energy loss for mesons. Believing the crystal ionization detector to be ideally suited for the study of ionization at high energy, we have attacked the problem in the following manner.

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