SMALL-ANGLE

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PREFACE

X-ray diffraction was first utilized in establishing the atomic structure of crystals. Later the technique of X-ray diffraction found other applications, however, and branched off from pure crystallography, extending to studies of imperfections in crystals, sizes of crystallites, and even to studies of the atomic structure of amorphous bodies. These fields of application of X-rays were made possible by further developments in the theory of the diffraction of X-rays by matter and also by improvements in experimental methods.

The small-angle scattering of X-rays is one of these fields that has been rather recently opened. Although the first observations were made in 1930 [295] particular attention has been given to this field only since the late 1930's. At the present time a large, ever-increasing number of laboratories are interested in small-angle scattering, as is shown by the number of references compiled in the bibliography of this book.

For these reasons it seemed worth while to us to devote a monograph to this specific branch of X-ray diffraction. In fact, the theories that are used in this field are generally not discussed in textbooks on X-rays. They are quite distinct from the concepts that are customarily associated with X-ray diffraction; almost no use of Bragg's law will be made in this book, except to point out that the habit, so natural to crystallographers, of interpreting every detail in a diffraction pattern in terms of lattice distances should be discarded. The experimental aspect also is different; small-angle scattering in general cannot be studied with the usual apparatus of a crystallography laboratory; special cameras and sometimes special tubes are required.

Since the late 1930's many theoretical works have appeared in this field; starting from different points of view, these have occasionally arrived at different, but non-contradictory, results. In a parallel manner, apparatus based on quite varied principles have been used in experimental methods. We believed that it was now time to collect and evaluate the results that have been obtained from the different approaches. Our object has been to make the new research in this field more rapid and more efficient. Finally, we have also tried to evaluate the different attempts at applications in order to specify those which are the most fruitful.

The plan of this book is as follows: in a first, short chapter we present the phenomenon of small-angle scattering and investigate its physical significance.

The second chapter is devoted to a discussion of the progress realized in the theoretical study of small-angle scattering. We have tried to show the problems that have actually been solved and the limitations that now appear to us as difficult to overcome.

In a third chapter we discuss the experimental methods that have been employed, trying not to treat all the details but giving the general principles that should be satisfied in a small-angle scattering system. Evidently these techniques will be similar whether the objective is the study of continuous scattering or the study of crystalline diffraction patterns. Thus it will be seen that problems are mentioned in this section which are not considered from a theoretical point of view in the second chapter.

The fourth chapter is devoted to the problem of the interpretation of the experimental results and includes several examples which demonstrate the validity of the theoretical results.

In a fifth chapter we compare the results of small-angle X-ray scattering with the results of other physical methods for measuring particle sizes, such as interpretations of Debye-Scherrer line widths and measurements with the electron microscope.

The sixth and last chapter is devoted to a discussion of the applications of small-angle X-ray scattering. These are found in a number of diverse fields, such as chemistry, biology, and metallurgy. Some applications are of technical interest, as, for example, the study and testing of catalysts. Others are of interest to theoretical physics, as, for example, the structure of liquid helium below the λ-point.

Although the object of the first chapters of this book is to present all the theoretical and experimental data necessary to the specialist in X-ray diffraction, the last chapter has been written without use of mathematics and without details of X-ray techniques so that it can be read without difficulty by a non-specialist. Our object has been to present the different types of problems that can be studied by small-angle scattering and the results that have actually been obtained up to the present. Thus a chemist, biologist, or metallurgist should be able to decide from this whether or not any given problem can be approached effectively by means of X-rays.

In this monograph we have tried more to give a logical, ordered presentation of this subject than to give a complete compilation of all the published papers. Any gaps can be filled by the reader by referring to the bibliography. Let us point out that several general articles on small-angle scattering have now appeared: the article by Hosemann [84] and

another by Porod [137] are particularly noted. As a result we have been able to shorten our discussion on several points, since the reader can find the complete development of these ideas in the works cited.

When reference is made in the text to a formula in the same chapter, the formula is denoted by a single number, as, for example, 36. When the formula has been developed in a different chapter, it is denoted by a double number, such as 2.36 (equation 36 of Chapter 2).

If a bibliographic reference appears as numbers within brackets, [ ], the reference will be found in the general bibliography at the end of the book. References appearing as "Author (year)" are tabulated in a special bibliography at the end of each chapter.

Our sincere thanks are extended to Dr. R. S. Bear, Dr. W. W. Beeman, Dr. J. W. M. DuMond, Dr. A. N. J. Heyn, Dr. R. A. Van Nordstrand, and Dr. C. B. Walker for having made available to us papers which are as yet unpublished and drawings or original photographs which they have authorized us to reproduce here. Permission has been given to reproduce a number of illustrations from technical journals, for which we wish to thank both the authors and the publishers.

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CONTENTS

1. ORIGIN AND CHARACTERISTICS OF SMALL-ANGLE X-RAY SCATTERING

The fundamental relation describing the diffraction of X-rays by crystalline matter, $\lambda = 2d \sin \theta$, shows that the angle of diffraction, θ, varies inversely with the separation of the diffracting lattice planes. In ordinary crystals, particularly those of inorganic matter, the majority of the observed lattice spacings are of the same order of magnitude as the X-ray wavelengths generally employed, so that the angles θ are usually rather large. This advantageous condition has had important consequences, both in the discovery of the phenomenon of X-ray diffraction and in its employment in studies of crystal structures.

The study of small-angle X-ray diffraction was introduced when it became desirable to detect large lattice spacings, of the order of tens or hundreds of interatomic distances. These spacings are found in some particular minerals and in certain complex molecules, such as the high polymers or proteins. In studies of the structures of macromolecular crystals the X-ray diffraction patterns must be extended to include very small angles. For example, with Cu $K\alpha$ radiation and a spacing of 100 A the diffraction angle θ is equal to 0.45°, and, with a period of 1000 A, θ equals 0.045° or 2'. This illustrates the importance of small-angle scattering techniques in such fields as biochemistry, for example.

One might consider using longer-wavelength X-rays to obtain larger diffraction angles for a given lattice spacing. This is not generally feasible, however, since the long-wavelength X-rays are absorbed to a very great extent in matter, which not only complicates the necessary diffraction apparatus and the means of detection of the X-rays but also considerably diminishes the intensity of the diffracted beam. For these practical reasons we must recognize a gap in the spectrum of useful electromagnetic radiation extending from wavelengths of the order of 2 A up to those of the remote ultraviolet.

In studying crystals with large periodicities only the operational technique is different, since the interpretation of the patterns is based on the same principles as the usual structure determinations. The difficulties encountered are greater, however, as a result of the complexity of the unit cell and the imperfection of the crystals. One can intuitively picture "perfect" crystals as being formed only by the grouping of small numbers

1

of atoms bound by strong forces. In molecular and macromolecular crystals the degree of perfection is much less; only rarely is the theory of diffraction by perfect crystals a good approximation in small-angle diffraction phenomena. In this domain the theory of diffraction by imperfect crystals assumes particular importance, as is illustrated by the correlation of small-angle diffraction and the diffraction by imperfect crystals in an X-ray study of high polymers by Hosemann [84]. Since diffraction by imperfect crystals is a theoretical problem not confined to small-angle scattering and one that has been well discussed elsewhere, we shall not examine it further in this monograph.

If a sample has a non-periodic structure or if its lattice has been sufficiently perturbed, the diffraction patterns are not limited to spots or lines but contain more or less extended regions of scattering. Let us examine schematically the origin of this scattering at small angles.

It is well known that the diffraction pattern of a sample can be simply described in terms of a reciprocal, or Fourier, space. If we designate by $\rho(\mathbf{x})$ the electronic density of the diffracting body at a point defined by the vector $\mathbf{x}$, then $A(\mathbf{h})$, the transform of $\rho(\mathbf{x})$ at the point defined by the vector $\mathbf{h}$ in reciprocal space, is given by

$$A(\mathbf{h}) = \int \rho(\mathbf{x}) e^{-i\mathbf{h}\cdot\mathbf{x}} \, d\mathbf{x} \tag{1}$$

The theory of X-ray diffraction is based on the fact that $A(\mathbf{h})$ represents the amplitude of the diffracted radiation when $\mathbf{h}$ is defined as

$$\mathbf{h} = (2\pi/\lambda)(\mathbf{s} - \mathbf{s}_0)$$

where λ is the wavelength of the radiation and $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors in the direction of the incident and diffracted rays, respectively. The magnitude of $\mathbf{h}$ is then equal to $(4\pi \sin \theta)/\lambda$, where 2θ is the scattering angle (the angle between the incident and scattered rays). Thus scattering at very small angles corresponds to small values of h.

Equation 1 can be interpreted as follows: the scattered intensity observed for conditions corresponding to a certain value of $\mathbf{h}$ is equal to the square of the value of $A(\mathbf{h})$, where $A(\mathbf{h})$ is the component corresponding to $\mathbf{h}$ in the development of $\rho(\mathbf{x})$ in a Fourier series. For small values of $\mathbf{h}$, that is, at very small angles, the terms in $\rho(\mathbf{x})$ that primarily control the magnitude of $A(\mathbf{h})$ are those that show a periodicity of $x = 2\pi/h$, a periodicity large with respect to the X-ray wavelength. These general considerations show again that diffraction at very small angles (less than a few degrees) gives information concerning the structure of matter on a scale that is large compared to the X-ray wavelength.

It has been experimentally observed that certain samples cause an intense, *continuous* scattering below angles of the order of 2° without

producing the usual type of diffraction effects found on ordinary X-ray patterns. This was first observed by Krishnamurti [295] and Warren [171] for certain varieties of finely divided carbons, carbon blacks, and various other substances, all having in common the characteristic of being present as fine particles of submicroscopic size. Actually it was later recognized that the continuous scattering in the neighborhood of the direct beam is related to the existence of matter in the form of *small particles*, or, more generally, to the existence of *heterogeneities in the matter*, these heterogeneities having *dimensions from several tens to several hundred times the X-ray wavelength*. This offers another example of the general relation previously cited.

It is relatively easy to describe qualitatively the central scattering due to the presence of small particles. This is analogous to the well-known phenomenon of optical diffraction, where a halo is produced by the passage of a light ray in a powder whose grain dimensions are of the order of a hundred times the wavelength of the light.

Let us consider a particle bathed in a beam of X-rays; all the electrons are then sources of scattered waves. When the scattering direction is the same as that of the incident ray, these scattered rays are all in phase, and, as the scattering angle increases, the difference in phase between the various scattered waves also increases. The amplitude of the resultant scattered wave then decreases with increasing angle because of increasing destructive interference; it becomes zero when there are as many waves with phases between 0 and π as there are between π and 2π. This will occur for a scattering angle of the order of $2\theta = \lambda/D$, D being the "average dimension" of the particle, demonstrating how the study of the continuous central scattering offers a method for obtaining particle dimensions.

This method is applicable only for particles whose sizes lie within certain limits. If D is too large the scattering is limited to angles so small as to be inaccessible to experiment, and if D is too small, of the order of several wavelengths, the scattering is widely spread but too weak to be observable.

These rough qualitative considerations can be made more precise. To show exactly on which factors the small-angle scattering depends, let us consider a small particle that has been cut from a section of matter of electronic density $\rho(x)$. Let us define a "form factor" of this particle, $s(x)$ (Ewald (1940)), that has the value 1 when the vector x lies within the particle and the value 0 when x lies outside the particle. The amplitude of radiation scattered by this particle, as found from equation 1, is then

$$A_1(h) = \int \rho(x)\, s(x) e^{-ih\cdot x}\, dx \tag{2}$$

There is a general theorem related to the operation of "folding" in the theory of Fourier transformations stating that, if $A(h)$ and $S(h)$ are respectively the Fourier transforms of $\rho(x)$ and $s(x)$, then

$$A_1(h) = \int A(y) S(h - y)\, dy \tag{3}$$

where y is a variable of integration.

Given the dimensions of the region in which $s(x)$ is different from zero, its transform, $S(h)$, is fully determined, and, if the particle has dimensions of several tens to several hundreds of atomic diameters, $S(h)$ will be different from zero only for very small values of h.

Let us consider now the function $A(h)$. If we first assume that the sample is of constant electronic density, $\rho(x) = k$, the transform $A(h)$ acts as a Dirac delta-function,[1] being zero everywhere except at $h = 0$, where it is infinite. For the more general case of a homogeneous body whose electronic density shows periodicities only on an atomic or molecular scale, the transform $A(h)$ shows a large number of peaks. However, all these peaks except the one for $h = 0$ are produced for values of h well outside the domain in which $S(h)$ has a non-zero value.

Then, since $A(y)$ is essentially a Dirac delta-function about $y = 0$, it may be predicted that around the origin of the reciprocal space the amplitude $A_1(h)$ is simply proportional to $S(h)$, the function $\rho(x)$ not intervening. *The scattering around the center is thus practically independent of the "short-range order" of the atoms, depending only on the exterior form and dimensions of the particle.*

Small-angle scattering thus appears as a means of studying the dimensions of colloidal particles, and it is in this direction that the technique has been generally exploited. It was quickly realized, however, that the assumptions adopted in the first theoretical approaches (widely separated, identical particles) were not being satisfied in the constitution of real samples. Interpretation of the scattering then demanded that the theory be generalized to take into account the diversity of particles sizes and the effect of the closer packing of the particles. Also, without speaking of particles, the possibility should be considered of obtaining an expression for the intensity scattered near the center in terms of the electronic density at all points of the sample. The theoretical approaches to these and other problems are discussed in the following chapter.

REFERENCE FOR CHAPTER 1

Ewald, P. P. (1940), *Proc. Phys. Soc. (London)*, *52*, 167.

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[1] The Dirac delta-function $\delta(x)$ is zero for $x \neq 0$, infinite for $x = 0$, and $\int \delta(x)\, dx = 1$.

2. GENERAL THEORY

In this study we shall consider only coherent scattering, neglecting Compton scattering which is always small at small angles. We shall discuss only the single-scattering process, disregarding the phenomenon of multiple scattering [31], [33].
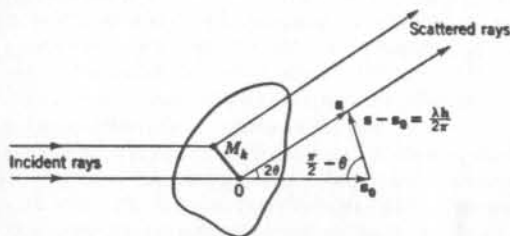
Fig. 1. Diffraction by a single particle.

We shall assume always that the transverse dimensions of the X-ray beam are large enough so that a large number of particles are irradiated, yet sufficiently small compared to the sample-receiver distances so that the beam can be likened to a single ray in the macrogeometry of the experimental apparatus.

2.1. SCATTERING PRODUCED BY A SINGLE PARTICLE
2.1.1. FIXED PARTICLE

The classical formula in the theory of X-ray diffraction gives the amplitude of radiation scattered by the point M_k (Fig. 1) (of scattering factor f_k) in the direction defined by the unit vector s as

$$A_k = A_e f_k e^{-i\frac{2\pi}{\lambda}(s-s_0)\cdot OM_k} \tag{1}$$

where A_e designates the amplitude scattered by one electron for the same conditions; O, an arbitrary origin serving to describe the path differences between different rays; and s_0, the unit vector defining the direction of the incident radiation. Let us designate by h the vector $(2\pi/\lambda)(s - s_0)$. If 2θ represents the angle of scattering, $\angle ss_0$, the magnitude of h is $h = (4\pi \sin \theta)/\lambda$.

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The total amplitude of radiation scattered by a particle is then

$$A(h) = \sum_k A_k = A_e(h)\sum_k f_k e^{-(h\cdot OM_k)} \tag{2}$$

and the scattered intensity, the product of the amplitude A and its complex conjugate A^*, is

$$I(h) = A_e^2(h)\sum_k\sum_j f_k f_j \cos(h\cdot M_kM_j) \tag{3}$$

The intensity scattered by one electron

$$I_e(h) = A_e^2(h) = 7.90 \times 10^{-26} I_0 p^{-2} \times \frac{1 + \cos^2 2\theta}{2} \tag{4}$$

is a function only of θ, that is, of the magnitude of h; I_0 represents the intensity of the incident beam, and p is the distance between the particle and receiver, expressed in centimeters.

2.1.1.1. Centrosymmetric Particle

If the particle possesses a center of symmetry, the expression for the diffracted amplitude can be simplified, for, if the origin is taken at the center of symmetry, then to each vector OM_k there corresponds another vector $-OM_k$. Therefore

$$A(h) = \sum_k A_k = A_e(h)\sum_k f_k \cos(h\cdot OM_k)$$

We shall define the structure factor of the particle as the ratio of the total scattered amplitude to the amplitude of radiation scattered by one electron under the same conditions:

$$F(h) = \frac{\sum_k A_k(h)}{A_e(h)} = \sum_k f_k \cos(h\cdot OM_k) \tag{5}$$

The scattered intensity is then

$$I(h) = I_e(h)[\sum_k f_k \cos(h\cdot OM_k)]^2 = I_e(h)F^2(h) \tag{6}$$

The term "point M_k" has been used to refer to and define the structure of a particle. In considering a large particle the basic element in its description is the atom; the point M_k then refers to the "center of the kth atom," and the scattering factor f_k is the scattering factor of this kth atom. As f_k varies with the scattering angle, it should be denoted by $f_k(h)$. However, in the angular range where the structure factor of a large particle is different from zero, $f_k(h)$ can be effectively considered as a constant, equal to $f_k(0)$. For example, the structure factor of a molecule of human hemoglobin is effectively zero for all angles such that $h > 0.15$, and in this range the variation of the scattering factor of a carbon atom is less than 0.4 per cent.

When a small particle (an atom, for example) is being considered, the point M_k will refer to a volume element, small even on the angstrom scale, surrounding the point M_k. The scattering factor f_k then equals $\rho_k dv_k$, where ρ_k is the electronic density of the particle in the neighborhood of the point M_k, and dv_k is the volume element considered.

In general we will find it convenient to describe the structure of a particle in terms of elements which are small enough so that the scattering factors of these elements can be considered as constants, independent of the angle of scattering, over the range in which the structure factor of the particle under consideration is different from zero.

2.1.2. MOVING PARTICLE

In the majority of low-angle scattering investigations, such as examinations of solutions, suspensions, and emulsions, the particles are capable of motion. This motion can always be described as the sum of a translation and a rotation. A translation, defined by a vector $\mathbf{V}$, introduces the multiplicative factor $e^{-i\mathbf{h}\cdot\mathbf{V}}$ in the expression for the scattered amplitude, but this has no effect on the scattered intensity. Only rotations intervene in the calculation of an average intensity.

When the probabilities of different orientations are defined, we can obtain from equations 3 or 6 the expression for the observed average intensity

$$\overline{I(\mathbf{h})} = I_e(\mathbf{h})\overline{F^2(\mathbf{h})}$$

this relation defining the average of the square of the structure factor. There would be a temptation to describe $\overline{F^2(\mathbf{h})}$ as equal to $\overline{F(\mathbf{h})}^2$, the square of the average of the structure factor. However, in order that the average of a product, ab, be equal to the product of the averages of a and b, it is necessary that the variables be completely independent, that is, that knowledge of the value of a in no way modifies the probabilities of the different values of b. This limitation is not met by the structure factors, since $a = b = F(\mathbf{h})$. The only general case in which $\overline{F^2}$ and $\overline{F}^2$ are equal is that pertaining to spherically symmetric particles, for then a rotation of the particle around its center does not modify the distribution of scattering centers and consequently leaves $F(\mathbf{h})$ unchanged. For this case one finds

$$\overline{F^2} = \overline{F}^2 = F^2$$

In this section, the discussion is restricted almost entirely to considering all particle orientations as equally probable; a treatment of the more general case will be found at the end of the chapter. When this assumption is made, the only mathematical problem is one of calculating the

average of the function, $\cos(\mathbf{h}\cdot\mathbf{r})$, as the vector $\mathbf{r}$, of magnitude r, takes all orientations with equal probability. To calculate this average, let us define the angle between the vectors $\mathbf{h}$ and $\mathbf{r}$ as the angle φ, a variable with limits of 0 and π radians. The probability that this angle is contained between the values φ and $\varphi + d\varphi$ is equal to $\frac{1}{2}\sin\varphi\,d\varphi$. The average of the phase function, $\cos(\mathbf{h}\cdot\mathbf{r})$, is then

$$\int_0^\pi \cos(hr\cos\varphi)\frac{\sin\varphi}{2}\,d\varphi$$

$$= \int_0^{\pi/2} \cos(hr\cos\varphi)\sin\varphi\,d\varphi$$

$$= -\frac{1}{hr}\int_0^{\pi/2} \cos(hr\cos\varphi)\,d(hr\cos\varphi)$$

$$= -\frac{1}{hr}\int_{hr}^0 \cos u\,du$$

leading to the classic result

$$\overline{\cos(\mathbf{h}\cdot\mathbf{r})} = \frac{\sin hr}{hr} \tag{7}$$

The result depends only on the magnitude of $\mathbf{h}$; the distribution of scattered intensity thus contains an axis of revolution coinciding with the incident beam.

Equation 3 then resolves into the expression for $\overline{F^2(h)}$ [1] expressed by Debye (1915),

$$\overline{F^2(h)} = \sum_k \sum_j f_k f_j \frac{\sin(h\,|\mathbf{M}_k\mathbf{M}_j|)}{h\,|\mathbf{M}_k\mathbf{M}_j|} \tag{8}$$

2.1.2.1. Centrosymmetric Particle

When a center of symmetry exists, application of equation 7 to equation 5 results in a simple expression for the average of the structure factor:

$$\overline{F(h)} = \sum_k f_k \frac{\sin(h\,|\mathbf{OM}_k|)}{h\,|\mathbf{OM}_k|} \tag{9}$$

Generalization of this equation to include particles with a continuous distribution of scattering points leads to the following expression:

$$\overline{F(h)} = \int_V \rho(M_k) \frac{\sin(h\,|\mathbf{OM}_k|)}{h\,|\mathbf{OM}_k|}\,dv_k$$

[1] The notation $f(h)$ will be used when the function depends only on the magnitude of $\mathbf{h}$; the notation $f(\mathbf{h})$ will demonstrate dependence of the function on both magnitude and direction of $\mathbf{h}$.

The coefficient of the term $\sin hr/hr$ in this integral, obtained by considering the ensemble of points defined by $|\mathbf{OM}_k| = r$, is

$$\int_r^{r+dr} \rho(M_k)\, dv_k = \bar\rho(r) 4\pi r^2\, dr$$

this defining the function $\bar\rho(r)$. The generalization of equation 9 then takes the form

$$\overline{F(h)} = \int_0^\infty \bar\rho(r) \frac{\sin hr}{hr} 4\pi r^2\, dr \tag{10}$$

We see thus that the average of the structure factor is uniquely determined by the distribution of scattering centers as a function of their distance from the center of the particle.

Equation 3 shows that the parameters possessing physical significance in the expression for the intensity are the distances $|\mathbf{M}_k\mathbf{M}_j|$ between each of the pairs of scattering centers. Nevertheless, for convenience of calculation one might on occasion prefer an expression for the intensity in which the distances $|\mathbf{OM}_k|$ and $|\mathbf{OM}_j|$ are the essential parameters, where O designates the center of symmetry of the particle. Fournet [48] has shown this to be

$$\overline{F^2(h)} =$$
$$\sum_k \sum_j \left\{ f_k f_j \sum_{p=0}^\infty \pi(2p + \tfrac{1}{2}) \frac{J_{2p+1/2}(h|\mathbf{OM}_k|) J_{2p+1/2}(h|\mathbf{OM}_j|)}{h\sqrt{|\mathbf{OM}_k||\mathbf{OM}_j|}} P_{2p}(\cos \Phi_{kj}) \right\} \tag{11}$$

where P_m represents the Legendre polynomial of order m, and Φ_{kj}, the angle $\angle M_k O M_j$. [The Legendre polynomial of order m, $P_m(x)$, can be described as the coefficient of the term y^m in the expansion of the function $(1 - 2yx + y^2)^{-1/2}$.] In certain cases this equation can be employed more simply than equation 8 (Fournet [48]).

Fournet has employed equation 11 to illustrate the difference between $\overline{F^2(h)}$ and $\overline{F(h)}^2$. If we evaluate the sum of terms for $p = 0$,

$$\sum_k \sum_j f_k f_j \frac{\pi}{2} \frac{J_{1/2}(h|\mathbf{OM}_k|) J_{1/2}(h|\mathbf{OM}_j|)}{\sqrt{h|\mathbf{OM}_k|}\sqrt{h|\mathbf{OM}_j|}} = \left[\sum_k f_k \sqrt{\frac{\pi}{2}} \frac{J_{1/2}(h|\mathbf{OM}_k|)}{\sqrt{h|\mathbf{OM}_k|}} \right]^2$$

then, on transforming the Bessel functions into sine functions with the relation $J_{1/2}(x) = \sqrt{(2/\pi x)} \sin x$, we find that the sum of these terms is equal to

$$\left[\sum_k f_k \frac{\sin h|\mathbf{OM}_k|}{h|\mathbf{OM}_k|} \right]^2$$

which is the square of the average of the structure factor. Thus we can write

$$\overline{F^2(h)} = \overline{F(h)}^2$$
$$+ \sum_k \sum_j \left\{ f_k f_j \sum_{p=1}^\infty \pi(2p + \tfrac{1}{2}) \frac{J_{2p+1/2}(h|\mathbf{OM}_k|) J_{2p+1/2}(h|\mathbf{OM}_j|)}{h\sqrt{|\mathbf{OM}_k||\mathbf{OM}_j|}} P_{2p}(\cos \Phi_{kj}) \right\} \tag{12}$$

2.1.2.2. Spherically Symmetric Particle

A particularly important case to be considered is that of the spherically symmetric particle. The electronic density at any point depends only on the distance r of this point from the center of the particle and can thus be denoted by $\rho(r)$.

The structure factor is then obtained from equation 10, replacing $\bar\rho(r)$ by $\rho(r)$:

$$F(h) = \int_0^\infty \rho(r) \frac{\sin hr}{hr} 4\pi r^2\, dr \tag{13}$$

For this particular case, rotation of the particle does not modify the amplitude of scattered radiation, leading to the relation

$$\overline{F^2(h)} = \overline{F(h)}^2 = F^2(h) \tag{14}$$

2.1.2.3. Calculation of the Average Intensity

The calculation of the average intensity can be made by several methods.

(a) *Analytical Method*: The intensity scattered by the particle in an arbitrary position is calculated (see equation 3). Then the expression is averaged, taking into account the different orientations, in a manner similar to that employed by Guinier ([65], p. 195) and Fournet ([48], p. 45). This method is particularly simple when applied to a spherically symmetric particle; equations 13 and 14 can then be used directly.

(b) *Geometrical Method*: Kratky and Porod [108]. Equation 8 can be generalized intuitively to allow the consideration of a particle of volume V, defined by an electronic density $\rho(M_k)$; the resulting expression is

$$\overline{F^2(h)} = \int_V \int_V \rho(M_k)\rho(M_j) \frac{\sin (h|\mathbf{M}_k\mathbf{M}_j|)}{h|\mathbf{M}_k\mathbf{M}_j|} dv_k\, dv_j \tag{15}$$

Let us consider the coefficient of $\sin hr/hr$ in the integral, assuming for the moment that ρ is a constant. This coefficient is obtained by considering the ensemble of terms where $|\mathbf{M}_k\mathbf{M}_j| = r$. The number of electrons at distances between r and $r + dr$ from a volume element dv_k of the particle is simply $\rho\{V_k(r + dr) - V_k(r)\}$, in which $V_k(r)$ designates

the part of the volume of the particle situated at a distance smaller than or equal to r from dv_k. When we now consider all possible positions of dv_k, we can introduce a function, $p(r)$, defined by the relation

$$\int_V \rho\{V_k(r + dr) - V_k(r)\}\rho\, dv_k = \rho^2 p(r)\, dr \qquad (16)$$

The average of the square of the structure factor can then be expressed as

$$\overline{F^2(h)} = \rho^2 \int_0^\infty p(r) \frac{\sin hr}{hr}\, dr \qquad (17)$$

In order to determine the physical significance of $p(r)$, let us describe the volume element dv_j of equation 15 in a system of spherical coordinates centered on the point M_k, for which $dv_j = r^2\, d\omega\, dr$. Equation 15 then becomes

$$\overline{F^2(h)} = \int_V \left\{ \rho(M_k) \int_V \rho(M_j) \frac{\sin hr}{hr} r^2\, d\omega\, dr \right\} dv_k \qquad (18)$$

The point M_j in the integral with respect to $d\omega\, dr$ is any point in the particle situated at a distance r from the point M_k, where

$$\mathbf{OM}_j - \mathbf{OM}_k = \mathbf{r} \quad \text{with} \quad |\mathbf{r}| = r$$

and the integral extends only over the volume V of the particle. This integral can be extended over all space by writing

$$\overline{F^2(h)} = \int_V \left\{ \rho(\mathbf{OM}_k) \int_0^\infty \int_0^{4\pi} \rho(\mathbf{OM}_k + \mathbf{r}) \frac{\sin hr}{hr} r^2\, d\omega\, dr \right\} dv_k \qquad (19)$$

on condition that $\rho(\mathbf{OM}_k + \mathbf{r})$ is taken equal to the density of the particle ρ if the point $\mathbf{OM}_k + \mathbf{r}$ is inside the particle, and to zero if the point is outside.

We can now write that the partial integral

$$\int_V \rho(\mathbf{OM}_k)\rho(\mathbf{OM}_k + \mathbf{r})\, dv_k$$

is equal to the product of ρ^2 times the volume $V(\mathbf{r})$ of the solid common to the particle and to the "ghost" of the particle translated by the vector $\mathbf{r}$ (Wilson (1949)) (Fig. 2). $V(\mathbf{r})$ is evidently a function of the direction of the vector $\mathbf{r}$. If we introduce the average value, as defined by the relation

$$\int_0^{4\pi} V(\mathbf{r})\, d\omega = 4\pi\, \overline{V(r)}$$

equation 19 becomes

$$\overline{F^2(h)} = \rho^2 \int_0^\infty \overline{V(r)} \frac{\sin hr}{hr} 4\pi r^2\, dr$$

Let us now introduce a function $\gamma_0(r)$, defined as

$$\gamma_0(r) = \frac{\overline{V(r)}}{V(o)} = \frac{\overline{V(r)}}{V} \qquad (20)$$

Our last equation then becomes

$$\overline{F^2(h)} = V\rho^2 \int_0^\infty \gamma_0(r) \frac{\sin hr}{hr} 4\pi r^2\, dr \qquad (21)$$
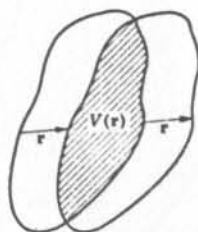
Fig. 2. A representation of the function $V(\mathbf{r})$.

A comparison of equations 17 and 21 shows that the functions $p(r)$ and $\gamma_0(r)$ are related by the following expression:

$$p(r) = 4\pi r^2 V \gamma_0(r) \qquad (22)$$

2.1.2.4. The Characteristic Function of the Particle $\gamma_0(r)$

The characteristic function $\gamma_0(r)$ was introduced by Porod [137]. It has no intuitive connection with the form of the particle.

$\gamma_0(r)$ represents the probability that a point at a distance r in an arbitrary direction from a given point in the particle will itself also be in the particle.

Let us consider an arbitrary line in the particle, terminating on its boundaries to form a segment of length M, and let us further consider an arbitrary point on this segment. The probability that a second point on the line at a distance r from the first is also inside the segment M is: $\gamma_M(r) = 1 - (r/M)$ if $r < M$ and is zero if $r > M$ (Fig. 3). If $g(M)$[1] is

[1] A precise definition of $g(M)$ is as follows: Through a point $\mathbf{r}$ in the particle there will pass an infinite set of randomly oriented lines. If $g_\mathbf{r}(M)$ is the distribution function for the lengths M of these lines, then $g(M)$ is the average of this function as the point $\mathbf{r}$ takes all positions in the particle, i.e.,

$$g(M) = \frac{1}{V} \int g_\mathbf{r}(M)\, dv_\mathbf{r}$$

the distribution function for the group of such lines in the particle, then

$$\gamma_0(r) = \int_{M-r}^{\infty} \left(1 - \frac{r}{M}\right) g(M)\, dM \qquad (23)$$

It can be shown from equation 23 that

$$g(M) = M \left(\frac{d^2\gamma_0}{dr^2}\right)_{r=M}$$
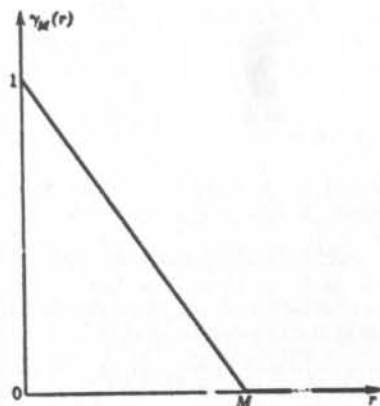
Fig. 3   The function $\gamma_M(r)$ for a single segment of length M.

The function $\gamma_0(r)$ possesses the following general properties:

1. At $r = 0$, $\gamma_0(r)$ has the value unity; as r increases, $\gamma_0(r)$ decreases, always staying positive, and becomes zero beyond the value $r = R_1$ corresponding to the line of maximum length through the particle.

2. An integration from zero to infinity of the two sides of equation 16 gives

$$\rho^2 \int_0^{\infty} p(r)\, dr = \int_V \rho V \rho\, dv_k = \rho^2 V^2$$

which, when combined with equation 22, leads to the relation

$$\int_0^{\infty} 4\pi r^2 \gamma_0(r)\, dr = V$$

3. *The initial slope of $\gamma_0(r)$ is a function of the external surface of the particle, S.* Let us trace around the particle the shell of thickness r (Fig. 4), where r is small with respect to the dimensions of the particle.

We can now calculate $\gamma_0(r)$ by means of equation 16, neglecting the terms smaller than r^3.

$$\int_V \rho[V_k(r + dr) - V_k(r)]\rho\, dv_k = 4\pi\rho^2 V r^2 \gamma_0(r)\, dr$$
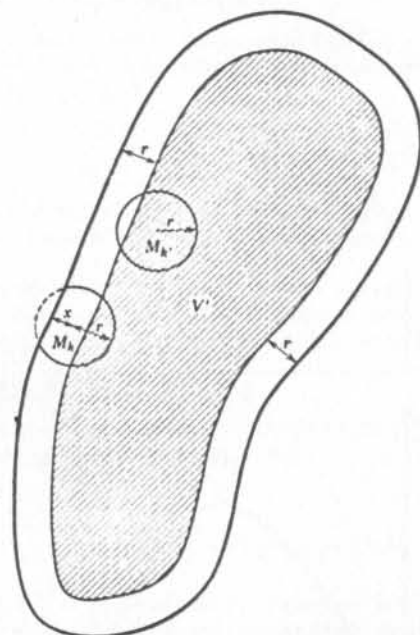
Fig. 4.   Calculation of the initial slope of the characteristic function $\gamma_0(r)$.

For a point $M_{k'}$ in the inner volume $V' = V - Sr$

$$V_k(r + dr) - V_k(r) = 4\pi r^2\, dr$$

and therefore

$$\int_{V'} \rho[V_k(r + dr) - V_k(r)]\rho\, dv_k = 4\pi\rho^2 r^2(V - Sr)\, dr$$

For a point M_k in the shell at a depth x from the surface (Fig. 4),

$$V_k(r + dr) - V_k(r) = 2\pi r(r + x)\, dr$$

and therefore

$$\int_{shell=Sr} \rho[V_k(r + dr) - V_k(r)]\rho\, dv_k = \int_{x=0}^{x=r} 2\pi\rho^2 r(r + x)S\, dx\, dr = 3\pi r^2\rho^2 S\, dr$$

Thus as a first approximation

$$4\pi\rho^2 r^2 V \gamma_0(r)\, dr = 4\pi\rho^2 r^2 \left(V - \frac{Sr}{4}\right) dr$$

or

$$\gamma_0(r) = 1 - (S/4V)r + \cdots \tag{24}$$
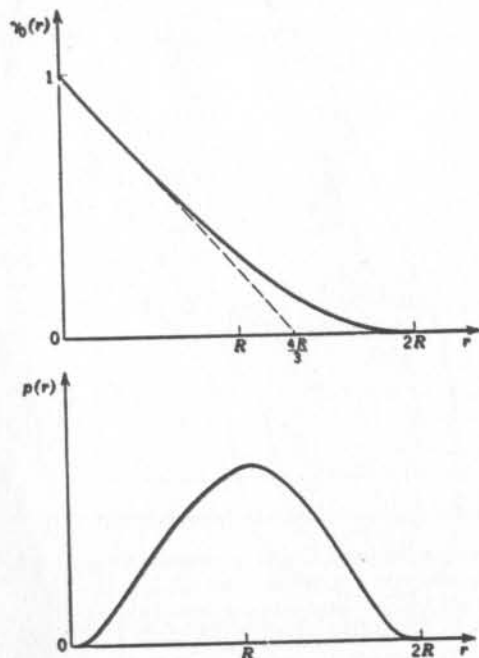
Fig. 5. The functions $p(r)$ and $\gamma_0(r)$ for the sphere of radius R.

As an example, let us consider a *spherical* particle of radius R. The volume $V(r) = \overline{V(r)}$ common to two spheres of radius R whose centers are separated by the distance r is given by a simple geometrical calculation as

$$\overline{V(r)} = (\pi/12)(2R - r)^2(4R + r)$$

Consequently,

$$\gamma_0(r) = 1 - \frac{3r}{4R} + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

Equation 24 gives a similar result when V is replaced by $(4/3)\pi R^3$ and S by $4\pi R^2$ (Fig. 5).

Figure 3 shows that, for the line in the particle of length M, $\int \gamma_M(r)\, dr = M/2$. The integral of the characteristic function of the particle is thus

$$\int_0^\infty \gamma_0(r)\, dr = \int_0^\infty \frac{M}{2} g(M)\, dM = \frac{l}{2} \tag{25}$$

The integral of the characteristic function is therefore equal to one-half of an average length of all the lines contained in the particles.

Thus for a spherical particle

$$l = 2\int_0^{2R}\left[1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3\right] dr = \frac{3}{2} R$$

It can be verified that $(3/2)R$ is the average length of the lines passing through all the points in a sphere in all directions and terminating on its boundaries.

We see therefore that this function shows properties analogous to those of the Fourier transform of the profiles of Debye-Scherrer lines broadened by the effect of the small size of a crystal (Bertaut (1950)).

2.1.2.5. General Properties of $\overline{F^2(h)}$

From these general properties of the function $\gamma_0(r)$ we can deduce the following consequences for the function $\overline{F^2(h)}$:

1. The value of $\overline{F^2(h)}$ at $h = 0$, $F^2(0)$, is

$$F^2(0) = V\rho^2 \int_0^\infty 4\pi r^2 \gamma_0(r)\, dr = V^2 \rho^2$$

This is the square of the total number of electrons in the particle. All the scattered waves are in phase and the amplitudes are added.

2. The value of $F^2(h)$ at small values of h is found from equation 21 by making the expansion

$$\frac{\sin hr}{hr} = 1 - \frac{h^2 r^2}{6} + \frac{h^4 r^4}{120} + \cdots$$

Then, by introducing the factor $F^2(0)$, this equation becomes

$$\overline{F^2(h)} = F^2(0)\left\{1 - \frac{h^2}{6}\frac{1}{V}\int_0^\infty 4\pi r^4 \gamma_0(r)\, dr \right.$$

$$\left. + \frac{h^4}{120}\frac{1}{V}\int_0^\infty 4\pi r^6 \gamma_0(r)\, dr + \cdots\right\} \tag{21a}$$

Thus, as h increases from zero, $\overline{F^2(h)}$ decreases following a parabolic curve. The curvature of this curve is determined by an integral in which the values of $\gamma_0(r)$ for large r play a predominant part because of the factor r^4. In §2.1.3.1 we shall see a simple and much more important expression for the curvature of $\overline{F^2(h)}$ at small angles.

3. A useful representation of the value of $\overline{F^2(h)}$ for large values of h can also be obtained from the function $\gamma_0(r)$. This comes from the fact that, since $h\overline{F^2(h)}$ and $r\gamma_0(r)$ are related by a Fourier transform, the high-angle part of the curve of $\overline{F^2(h)}$ corresponds to the part of the curve of $\gamma_0(r)$ at small values of r, and an approximate expression for this part of $\gamma_0(r)$ is known.

$\gamma_0(r)$ can be expressed as a polynomial in r, of which the first two terms are known:

$$\gamma_0(r) = 1 - (S/4V)r + \cdots$$

We also know that $\gamma_0(r)$ becomes zero beyond $r = R_1$. Therefore, by making the substitutions $hr = y$ and $hR_1 = u$, equation 21 becomes

$$\overline{F^2(h)} = \frac{4\pi V\rho^2}{h^3} \int_0^u \left(y - \frac{S}{4Vh} y^2 + \frac{\alpha y^3}{h^2} + \cdots \right) \sin y \, dy$$

By integrating by parts the following formulas can be established:

$$\int_0^u y \sin y \, dy = -u \cos u + \sin u$$

$$\int_0^u y^2 \sin y \, dy = -u^2 \cos u + 2u \sin u + 2 \cos u - 2$$

$$\int_0^u y^n \sin y \, dy = -u^n \cos u + nu^{n-1} \sin u - \int_0^u n(n-1)y^{n-2} \sin y \, dy$$

Therefore

$$\overline{F^2(h)} = \frac{2\pi\rho^2 S}{h^4} + \frac{A}{h^6} + \cdots + \frac{f_1(u,h)\cos u}{h^3} + \frac{f_2(u,h)\sin u}{h^3}$$

At large values of h the principal term in $\overline{F^2(h)}$ is $2\pi\rho^2 S/h^4$, to which are added damped oscillations of pseudoperiod $hR_1/2\pi$. The average curve of the continuous decrease of $\overline{F^2(h)}$ is therefore given as

$$\overline{F^2(h)} \approx \frac{2\pi\rho^2 S}{h^4} \tag{26}$$

This depends uniquely on the external surface of the particle.

4. A Fourier inversion of equation 21 gives

$$r\gamma_0(r) = \frac{2}{\pi} \int_0^\infty \frac{h\overline{F^2(h)}}{4\pi\rho^2 V} \sin hr \, dh$$

or

$$\gamma_0(r) = \frac{1}{2\pi^2\rho^2 V} \int_0^\infty h^2\overline{F^2(h)} \frac{\sin hr}{hr} \, dh \tag{27}$$

Evaluated at $r = 0$, this becomes

$$\int_0^\infty h^2\overline{F^2(h)} \, dh = 2\pi^2\rho^2 V \tag{28}$$

The integral of $h^2\overline{F^2(h)}$ depends only on the *volume of the particle* and not on its form. This is a particular illustration of a general theorem regarding the integral in reciprocal space of the intensity scattered by an arbitrary object, which relates this integral to the total number of scattering electrons in the object.

5. Let us calculate an average value l of the length of all the lines contained in a particle by evaluating the integral $\int_0^\infty \gamma_0(r) \, dr$. By making the substitution $y = hr$, the integral of equation 27 becomes

$$l = 2 \int_0^\infty \gamma_0(r) \, dr = \frac{1}{\pi^2\rho^2 V} \int_0^\infty \int_0^\infty h\overline{F^2(h)} \frac{\sin hr}{r} \, dh \, dr$$

$$= \frac{1}{\pi^2\rho^2 V} \int_0^\infty \frac{\sin y}{y} \, dy \int_0^\infty h\overline{F^2(h)} \, dh$$

or

$$l = \frac{1}{2\pi\rho^2 V} \int_0^\infty h\overline{F^2(h)} \, dh \tag{29}$$

This integral can be expressed in terms of the total energy E scattered in all the low-angle scattering region. On a film placed at a distance p from the sample, the area that receives the rays scattered through the small angles contained between 2θ and $2\theta + d(2\theta)$ can be written to a first approximation as

$$d\sigma \simeq 2\pi p^2 2\theta \, d(2\theta)$$

or

$$d\sigma \simeq (\lambda^2/2\pi) \, p^2 h \, dh$$

Equations 4 and 6 then give

$$E = I_e(h) \int \overline{F^2(h)} \, d\sigma = \frac{\lambda^2}{2\pi} I_0 \times 7.90 \times 10^{-26} \int \overline{F^2(h)} h \, dh$$

$$= 7.90 \times 10^{-26} \lambda^2 I_0 \rho^2 V l \tag{30}$$

All the results of the preceding discussion are still valid if the electronic density of the particle is not a constant but shows fluctuations around an average value $\bar{\rho}$, if these fluctuations are such that statistically the surroundings of all the atoms in the particle are the same.

If, on the other hand, $\bar{\rho}$ varies from one part to another of the particle (for example, a hollow particle, etc.), equation 16 can be generalized by introducing the function $n_k(r)$, which represents the number of electrons situated at distances smaller than or equal to r from the volume element dv_k enclosing the point M_k. In order to modify our notation as little as possible, we redefine $p(r)$ by the relation

$$\int_V [n_k(r + dr) - n_k(r)]\rho(M_k)\,dv_k = \bar{\rho}^2 p(r)\,dr$$

where $\bar{\rho}$ is the average electronic density. $\overline{F^2(h)}$ can now be obtained by replacing ρ by $\bar{\rho}$ in equation 17, but it is necessary to note carefully that $p(r)$ is no longer uniquely determined by the *geometry* of the particle.

2.1.2.6. A Tabulation of the Average Intensity Distributions for Particles of Different Shapes

We list below the average intensity distributions for particles of different shapes which take all orientations with equal probability. The intensity distribution function tabulated is $i(h)$, rather than $\overline{F^2(h)}$, which is defined by the relation

$$\overline{F^2(h)} = n^2 i(h) = V^2 \rho^2 i(h)$$

where $n = V\rho$ is the total number of electrons in the particle; $i(0)$ is then always equal to unity.

(a) Sphere of radius R (Rayleigh (1914)) (Fig. 6),

$$i(h) = \Phi^2(hR) = \left[3\frac{\sin hR - hR\cos hR}{h^3 R^3}\right]^2 = \frac{9\pi}{2}\left[\frac{J_{3/2}(hR)}{(hR)^{3/2}}\right]^2 \quad (31)$$

(b) Ellipsoid of revolution, axes $2a$, $2a$, $2\nu a$ (Guinier [65]) (Fig. 7),

$$i(h) = \int_0^{\pi/2} \Phi^2(ha\sqrt{\cos^2\theta + \nu^2\sin^2\theta})\cos\theta\,d\theta \quad (32)$$

Another equation has been developed for this case by Schull and Roess [155], employing hypergeometric functions.

(c) Cylinders of revolution of diameter $2R$ and height $2H$ (Fournet [48])

$$i(h) = \int_0^{\pi/2} \frac{\sin^2(hH\cos\theta)}{h^2 H^2 \cos^2\theta} \times \frac{4J_1^2(hR\sin\theta)}{h^2 R^2 \sin^2\theta}\sin\theta\,d\theta \quad (33)$$
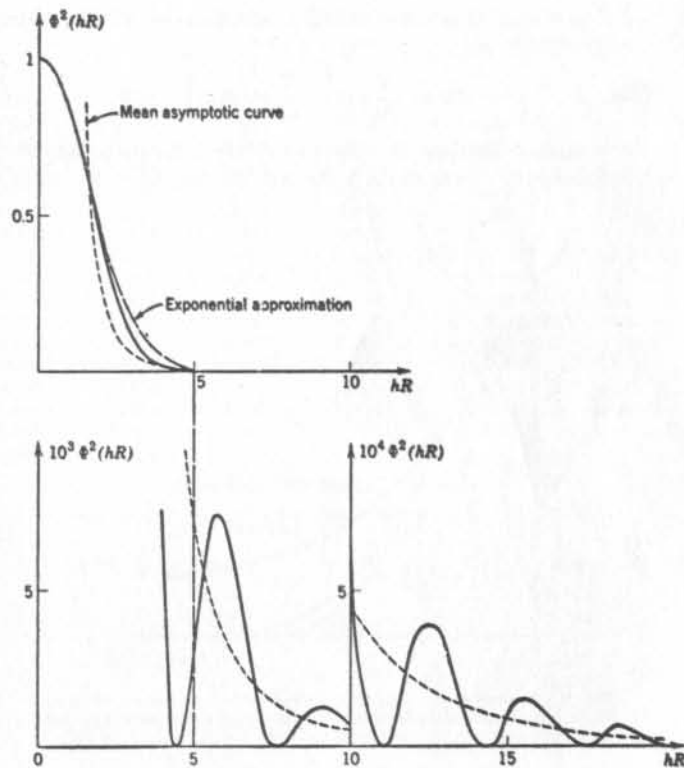
Fig. 6. Scattered intensity from a sphere of radius R, $\Phi^2(hR)$. The curve is drawn with different scales for the various ranges of hR ($\times 1000$ for $4 < hR < 10$; $\times 10,000$ for $hR > 10$).

Exponential approximation: $e^{-\frac{h^2 R^2}{5}}$ (equation 39); mean asymptotic curve: $\frac{9}{2}\frac{1}{(hR)^4}$ (equation 26).

(d) Rod of infinitesimal transverse dimensions and length $2H$ (Neugebauer (1943)) (Fig. 8a)

$$i(h) = \frac{Si(2hH)}{hH} - \frac{\sin^2(hH)}{h^2 H^2} \quad (34)$$

where

$$Si(x) = \int_0^x \frac{\sin t}{t}\,dt$$

(e) Flat disc of infinitesimal thickness and diameter $2R$ (Kratky and Porod [108]) (Fig. 8b)

$$i(h) = \frac{2}{h^2 R^2}\left[1 - \frac{1}{hR}J_1(2hR)\right] \qquad (35)$$

These various functions $i(h)$ behave according to the predictions of the general study: at $h = 0$, $i(h)$ is unity and the tangent to the curve is
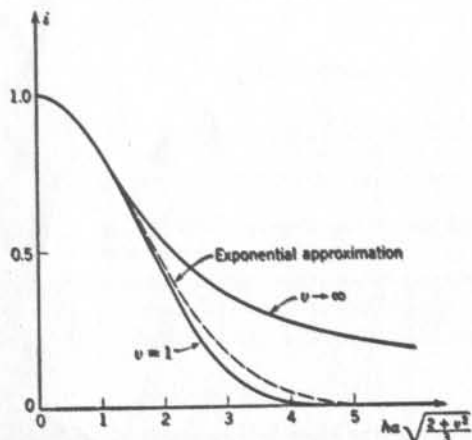
Fig. 7. Scattered intensity from ellipsoids of revolution of axes $2a, 2a, 2\nu a$. The abscissae have been chosen so that the radius of gyration of each ellipsoid corresponds to the same length (§2.1.3.1, p. 26).

Exponential approximation: $e^{-\frac{h^2 a^2}{5}\cdot\frac{2+\nu^2}{3}}$.

horizontal, and, as h increases, $i(h)$ decreases parabolically, tending finally towards zero along a curve which oscillates somewhat about a curve varying as h^{-4}. For narrow cylinders or thin discs whose small dimension is ϵ, this asymptotic law is valid only if $h \gg (1/\epsilon)$. If in these cases h is large with respect to $1/H$ or $1/R$ but small with respect to $1/\epsilon$, equations 34 and 35 show that the curves decrease respectively as h^{-1} (cylinder) and h^{-2} (disc).

An examination of Figs. 6, 7, and 8 shows that particles of very different forms can have nearly the same scattering curves.

Tables 1–3 will facilitate numerical calculations of equations 31 through 35.

Table 1

$$\Phi(x) = 3\,\frac{\sin x - x\cos x}{x^3} \quad \text{and} \quad \Phi^2(x)$$

x	$\Phi(x)$	$\Phi^2(x)$	x	$\Phi(x)$	$\Phi^2(x)$
0.000	1.000	1.000	2.100	0.622	0.388
0.100	0.999	0.998	2.250	0.575	0.330
0.200	0.996	0.992	2.500	0.499	0.248
0.300	0.991	0.982	3.000	0.346	0.119
0.400	0.983	0.968	3.200	0.288	0.083
0.500	0.975	0.951	3.500	0.205	0.042
0.600	0.964	0.930	4.000	0.0875	0.0076
0.700	0.952	0.906	4.493	0.0000	0.0000
0.800	0.937	0.879	5.000	−0.057 0	0.003 25
0.900	0.921	0.849	5.600	−0.085 0	0.007 22
1.000	0.903	0.816	5.760	−0.086 3	0.007 45
1.200	0.863	0.745	5.800	−0.086 0	0.007 40
1.400	0.816	0.668	6.000	−0.084 3	0.007 10
1.600	0.766	0.587	7.300	−0.023 0	0.000 53
1.800	0.702	0.502	7.720	−0.000	0.000 00
2.000	0.654	0.427			

Table 2

$$i(x) = \frac{Si(2x)}{x} - \frac{\sin^2 x}{x^2}$$

x	$i(x)$	x	$i(x)$
0.0	1.000	1.6	0.768
0.2	0.996	1.8	0.719
0.4	0.984	2.0	0.673
0.6	0.961	2.2	0.627
0.8	0.931	2.4	0.583
1.0	0.898	3.0	0.473
1.2	0.858	3.5	0.406
1.4	0.813	4.0	0.357

Table 3

x	$J_1(x)$	x	$J_1(x)$
0.0	0.0000	2.6	0.4708
0.2	0.0995	2.8	0.4097
0.4	0.1960	3.0	0.3391
0.6	0.2867	3.2	0.2613
0.8	0.3688	3.4	0.1792
1.0	0.4401	3.6	0.0955
1.2	0.4983	3.8	0.0128
1.4	0.5419	4.0	−0.0660
1.6	0.5699	4.2	−0.1386
1.8	0.5815	4.4	−0.2028
2.0	0.5767	4.6	−0.2566
2.2	0.5560	4.8	−0.2984
2.4	0.5202	5.0	−0.3276

Fig. 8. (a) Scattered intensity from rods of length $2H$. Asymptotic curve: $\pi/(2hH)$ (equation 34). (b) Scattered intensity from flat circular discs of radius R. Asymptotic curve: $2/(h^2 R^2)$ (equation 35).

2.1.2.7. Particle with Preferred Orientations

For simplicity we shall consider only particles with a center of symmetry; the structure factor is then given by equation 5. Let us fix the particle in a system of three mu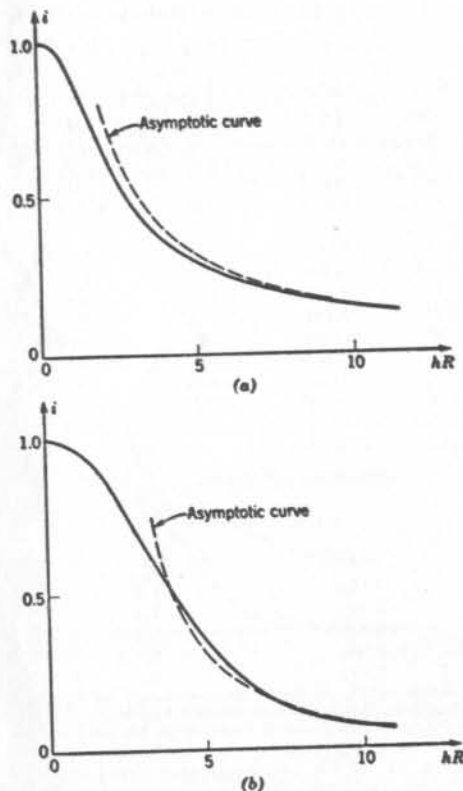tually perpendicular axes, Ox, Oy, Oz. The space in which the particle is found is described by a second set of three mutually perpendicular axes, OX, OY, OZ. The centers of these two systems of axes can be made to coincide without loss of generality, since only relative orientations are of interest. Euler's angles, χ, θ, and φ,

will be employed to mark the orientation of the particle system with respect to the spatial system. (In this paragraph θ will designate only the Euler angle, the scattering angle appearing only in terms of h.) We arbitrarily orient the spatial axes so that h is directed along the axis OZ. The amplitude scattered by a particle of orientation, θ, φ, can be denoted as: $A_r(h)F(h, \theta, \varphi)$. Then, by designating by $P_1(h, \theta)$ and $P_2(h, \varphi)$ the probability density functions of θ and φ (where the notation $P_1(h, \theta)$ is to recall the particular choice of OZ), the average intensity is found as

$$\overline{F^2(h)} = \iint F^2(h, \theta, \varphi) P_1(h, \theta) P_2(h, \varphi) \, d\theta \, d\varphi \qquad (36)$$

This approach will be useful whenever exterior physical conditions impose a preferred orientation as, for example, when molecules are oriented by the flow of a solution.

2.1.3. CONCEPT OF A RADIUS OF GYRATION OF A PARTICLE
2.1.3.1. Moving Particle

We shall consider primarily particles for which all orientations are equally probable.

Let us rewrite equation 8, expanding the trigonometric function in a power series:

$$\overline{F^2(h)} = \sum_k \sum_j f_k f_j \left\{ 1 - \frac{h^2}{6} |\mathbf{M}_k \mathbf{M}_j|^2 + \cdots \right\}$$

$$= \sum_k \sum_j f_k f_j - \frac{h^2}{6} \sum_k \sum_j f_k f_j |\mathbf{M}_k \mathbf{M}_j|^2 + \cdots \qquad (37)$$

The first term of the expansion is equal to $(\sum_k f_k)^2$, that is, $F^2(0)$.

To describe the second term, let us consider a point, O, chosen so that $\sum_k f_k \mathbf{OM}_k = 0$. The point O then defines the electronic center of mass of the particle. Employing this point as an origin, we can write

$$|\mathbf{M}_k \mathbf{M}_j|^2 = |\mathbf{OM}_k|^2 + |\mathbf{OM}_j|^2 - 2 |\mathbf{OM}_k| \, |\mathbf{OM}_j| \cos \Phi_{kj}$$

In the second term of our expansion in equation 37 the contribution of the factor $|\mathbf{OM}_k|^2$ is

$$-\frac{h^2}{6} \sum_k \sum_j f_k f_j |\mathbf{OM}_k|^2 = -\frac{h^2}{6} \sum_j f_j \sum_k f_k |\mathbf{OM}_k|^2$$

The contribution of the factor $|OM_j|^2$ is the same. The contribution of the angularly dependent term is zero, since

$$2\sum_k\sum_j f_k f_j |OM_k||OM_j|\cos\Phi_{kj} = 2\sum_j f_j |OM_j| \left\{\sum_k f_k |OM_k|\cos\Phi_{kj}\right\}$$

and the sum over k can be recognized as being the projection of $\sum_k f_k OM_k$ on the vector OM_j. Thus equation 37 reduces to the following:

$$\overline{F^2(h)} = \left\{(\sum_k f_k)^2 - \frac{2h^2}{6}\sum_j f_j \sum_k f_k |OM_k|^2 + \cdots\right\}$$

or

$$\overline{F^2(h)} = (\sum_k f_k)^2 \left\{1 - \frac{h^2}{3}\frac{\sum_k f_k |OM_k|^2}{\sum_k f_k} + \cdots\right\}$$

We can now introduce the parameter R_0, defined by the relation

$$R_0^2 = \frac{\sum_k f_k |OM_k|^2}{\sum_k f_k} \tag{38}$$

By analogy with classical mechanics, R_0 can be considered as the electronic radius of gyration of the particle about its electronic center of mass. We can thus hope to have a good approximation by writing (Guinier [65])

$$\overline{F^2(h)} = n^2 e^{-\frac{h^2 R_0^2}{3}} \tag{39}$$

where $n = \sum_k f_k$, the total number of electrons in the particle. This relation, the law of Guinier, coincides with the exact expression for terms up to the 4th power of h and, like the exact expression, vanishes with increasing h.

Equation 39 can be derived from the general relation, equation 12, in which $\overline{F^2(h)}$ and $\overline{F(h)}^2$ were expressed in an explicit manner. For simplicity we shall limit the derivation to the case of particles possessing a center of symmetry.

The principal part of the double summation over indices k and j involves terms in h^4 or still higher powers. *Thus any constant term and the term in h^2 in the expression for the average intensity must arise from the square of the average amplitude and consequently must depend only on the distribution of scattering centers as a function of their distance from the center of the particle* (see equation 9). The ratio of the coefficient of the

term involving h^2 to the constant term should then be a universal function of this distribution. A calculation

$$\frac{\overline{F(h)^2}}{F^2(0)} = \left[\frac{\sum_k f_k - \frac{h^2}{6}\sum_k f_k r_k^2}{\sum_k f_k} + \cdots\right]^2 = 1 - \frac{h^2}{3}\frac{\sum_k f_k r_k^2}{\sum_k f_k} + \cdots$$

shows that this function is simply

$$\frac{1}{3}\frac{\sum_k f_k r_k^2}{\sum_k f_k} = \frac{1}{3}R_0^2$$

confirming the results of the preceding paragraph.

The curves of the scattering by two particles having the same radius of gyration then coincide at very small angles, and it is only the tails of the curves, due to terms in h^4, h^6, etc., which show the influence of the forms of the particles. When the scattering curves of particles of two different forms are to be compared, it is thus *essential* to choose two particles having the same radius of gyration (see Fig. 7). For example, to a sphere of radius R, one should compare an ellipsoid of revolution of axes

$$2\sqrt{\frac{3}{2+v^2}}\,R \qquad 2\sqrt{\frac{3}{2+v^2}}\,R \qquad 2v\sqrt{\frac{3}{2+v^2}}\,R$$

v being the ratio of the unequal axes. Certain authors (Kratky and Porod [108]) have compared reduced curves (curves of the function $i(h)$, chosen so that the abscissae for both are the same for the ordinate $i(h) = 1/2$, but this arbitrary choice does not permit *the separation of the influences of the dimensions and of the forms of the particles.*

In order to eliminate any possible confusion, we want now to emphasize separately two points:

1. *The validity of the concept of a radius of gyration.* We must re-emphasize that the concept of a radius of gyration is sound, whatever the form of the particle (viz., Guinier [65], p. 191, or the discussion of equation 12), since it seems that some authors have recognized this concept only for spherical particles. The magnitude of the slope of the curve of $\log I(h)$ vs. h^2 at the origin is always equal to one-third of the square of the radius of gyration. The influence of the form of the particle manifests itself particularly at larger values of h in the form of deviations of the curve of $\log I(h)$ from the extrapolation of its tangent at the origin.

2. *The validity of the approximate law of Guinier.* To illustrate this, let us consider a family of ellipsoids of revolution of the same radius of

gyration, R_0, and of half axes R, R, and vR; v and R are thus variables. The first terms in the power series describing the intensity are given by

$$\overline{F^2(h)} = F(0)^2 \left[1 - \frac{h^2 R_0^2}{3} + \cdots \right]$$

In this family of ellipsoids there are two for which the expression for the scattered intensity coincides with the law of Guinier (equation 39) up to terms of the 6th power of h; these are the flat ellipsoid defined by $v = 0.24$ and the elongated ellipsoid, where $v = 1.88$.

Again, in a family of cylinders of revolution of diameter $2R$ and height $2H$ there is a cylinder for which the same precision of agreement is found; this is the cylinder for which $H/R = \sqrt{30/11} = 1.65$.

These examples show that the particles that obey the approximate law of Guinier closely are those that are nearly isodiametric (see Fig. 6 for the case of a sphere).

On the other hand, rather wide differences will be found for the curves of very elongated ellipsoids, thin discs, and narrow cylinders.

Finally, let us call attention to the fact that experiments have verified that the exponential law, equation 39, is a *very good* approximation for a large number of scattering curves, a surprisingly large number in view of the approximations involved in the derivation.

The precision with which a radius of gyration can be measured in an experiment depends to a certain extent on the form of the particles. The determination of the radius of gyration to the same degree of precision for a series of particles having the same radius of gyration but different forms requires information on the scattering at smaller and smaller angles, the further the particle departs from a spherical form.

Kratky and Porod [108] have given an approximate formula for particles in the form of narrow cylinders or thin discs which is valid for values of h large with respect to the reciprocal of the large particle dimension but small with respect to the reciprocal of the small dimension. In its dependence on the small dimension of the particle this scattering function behaves as though the low-angle region of the curve (the exponential approximation) were involved, whereas in its dependence on the large dimension the scattering behaves as though the tail of the curve (the curves in h^{-1} and h^{-2}, respectively, for cylinders and discs) were involved.

An accurate calculation based on equation 33 gives as the relation for narrow cylinders of diameter $2R$ and length $2H$, containing n electrons each,

$$\overline{F^2(h)} \simeq n^2 \frac{\pi}{2hH} \cdot \frac{4 J_1^2(hR)}{(hR)^2} \simeq \frac{n^2 \pi}{2hH} e^{-\frac{h^2 R^2}{4}} \tag{40}$$

and for thin discs of diameter $2R$ and thickness $2H$

$$\overline{F^2(h)} \simeq n^2 \frac{2}{h^2 R^2} \cdot \frac{\sin^2(hH)}{(hH)^2} \simeq \frac{2n^2}{h^2 R^2} e^{-\frac{h^2 H^2}{3}} \tag{41}$$

Let us also recall the equation relating the radius of gyration of a particle and its characteristic function $\gamma_0(r)$. By comparing the expansion of $\overline{F^2(h)}$, equation 21a, p. 16, with equation 39, this is found to be

$$R_0^2 = \frac{1}{2V} \int_0^\infty 4\pi r^4 \gamma_0(r)\, dr = \frac{\int_0^\infty r^4 \gamma_0(r)\, dr}{2 \int_0^\infty r^2 \gamma_0(r)\, dr} \tag{42}$$

We note that the radius of gyration can then be defined either by equation 39, where, following the method of Guinier, it is determined from a trace of the curve of $\log I$ vs. h^2, or by equation 42, in which case it is convenient to determine the function $\gamma_0(r)$ with the aid of equation 27 and then R_0^2 with equation 42.

2.1.4. SPHERICALLY SYMMETRIC PARTICLE

The calculation of the average intensity is considerably simplified when the particle possesses spherical symmetry. The electronic density function $\rho(r)$ is then sufficient to determine $A(h)$ and, consequently, $F^2(h)$. Conversely, a Fourier transformation of equation 13 gives

$$\rho(r) = \frac{1}{2\pi^2 r} \int_0^\infty h F(h) \sin hr\, dh \tag{43}$$

and the radius of gyration, from its definition, is determined by the relation

$$R_0^2 = \frac{\int_0^\infty r^4 \rho(r)\, dr}{\int_0^\infty r^2 \rho(r)\, dr}$$

2.1.5. THE DISTRIBUTION OF SCATTERING FROM A FIXED PARTICLE

Figure 9 shows the geometrical relations between the film, the orientation of the particle, and the distribution of scattered intensity on the film. We are interested primarily in the distribution of scattered radiation along the line AB. The corresponding scattering vectors $\mathbf{h}$ are all contained in the plane fixed by $\mathbf{s}_0$ and AB. The limiting direction of $\mathbf{h}$ as the scattering angle 2θ tends to zero is marked by the unit vector $\mathbf{l}_0$ perpendicular to $\mathbf{s}_0$ (since $\angle \mathbf{h}\mathbf{s}_0 = (\pi/2) - \theta$; see Fig. 1).

Let us consider how the concept of a radius of gyration appears under these circumstances by studying the series expansion of equation 3. An analogous case has already been considered in §2.1.3, giving immediately the result

$$F^2(\mathbf{h}) = \frac{I(\mathbf{h})}{A_e{}^2(\mathbf{h})} = (\sum_k f_k)^2 - \sum_j f_j \sum_k f_k (\mathbf{h} \cdot \mathbf{OM}_k)^2 + \cdots$$

where the point O is defined by the relation
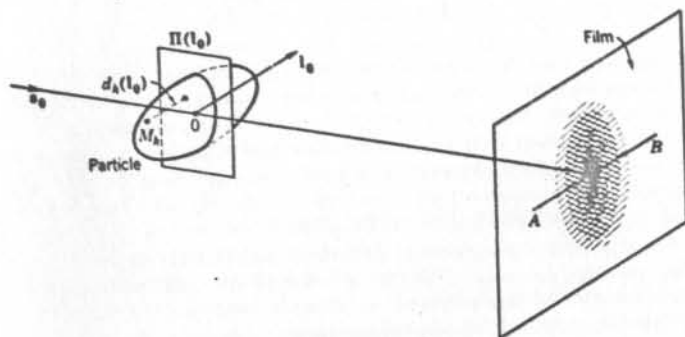
$$\sum_k f_k \mathbf{OM}_k = 0$$

Fig. 9. The relation between the orientation of a particle and the distribution of scattered intensity in the plane of observation.

Then

$$\frac{F^2(\mathbf{h})}{F^2(0)} = 1 - \frac{\sum_k f_k (\mathbf{h} \cdot \mathbf{OM}_k)^2}{\sum_k f_k} + \cdots$$

As a first approximation, the scalar product $\mathbf{h} \cdot \mathbf{OM}_k$ for small values of 2θ is equal to the product of the magnitude h and the scalar product $\mathbf{l}_0 \cdot \mathbf{OM}_k$. This scalar product, $\mathbf{l}_0 \cdot \mathbf{OM}_k$, is equal in magnitude to the distance $d_k(\mathbf{l}_0)$ of the point M_k from the plane $\Pi(\mathbf{l}_0)$ through O perpendicular to $\mathbf{l}_0$. The notation $d_k(\mathbf{l}_0)$ serves to recall the dependence on the orientation of $\mathbf{l}_0$. We can now write the expansion of $F^2(\mathbf{h})$ as

$$\frac{F^2(\mathbf{h})}{F^2(0)} = 1 - h^2 \frac{\sum_k f_k d_k{}^2(\mathbf{l}_0)}{\sum_k f_k} + \cdots$$

The coefficient of the term in h^2 can be designated as the square of an

average *inertial distance*, $D(\mathbf{l}_0)$, of the particle with respect to the particular plane $\Pi(\mathbf{l}_0)$. Then, as in the law of Guinier, this expression can be written to a good approximation as

$$F^2(\mathbf{h}) = F^2(0)e^{-h^2 D^2(\mathbf{l}_0)} \tag{44}$$

Equation 44 explains the distribution of scattered radiation found on the film of Fig. 9. The particle is presenting its largest dimension in the direction parallel to AB. The average inertial distance, the factor of primary importance in determining the scattered intensity, is thus also a maximum for this particular direction. Equation 44 then shows that it is along this line AB that the decrease in intensity with increasing h will be the most rapid.

2.2. SCATTERING PRODUCED BY A GROUP OF IDENTICAL PARTICLES
2.2.1. GENERAL RESULTS FOR FLUIDS[1]
2.2.1.1. Basic Hypotheses

Scattering experiments are rarely conducted with a single particle as the scatterer; thus it is of more practical importance to calculate the intensity scattered by a group of particles. In this section we shall consider the simplest such case, that of a group of identical particles.

We shall also restrict our study by requiring that the structure of the ensemble of particles satisfy two hypotheses. To simplify later references, these hypotheses will be denoted as H_1 and H_2.

Hypothesis H_1. We shall assume that:

1. *All particles, each possessing a center of symmetry, can with equal probability take all possible orientations.*

2. *The knowledge of the relative positions of two particles in no way modifies the probabilities of their different orientations.*

The second part of hypothesis H_1 is always realized for spherically symmetric particles. For the more general case it would seem that, if the particles are not too densely packed and if their shapes are not too anisotropic, this hypothesis should be good at least as a first approximation.

Hypothesis H_2. We shall assume that the group of particles is isotropic and without order at long distances.

In order to clarify hypothesis H_2, let us define $\mathbf{R}_k$ as the vector from an arbitrary origin to the center of the kth particle. The vector joining the centers of the kth and jth particles is then $(\mathbf{R}_k - \mathbf{R}_j)$. Hypothesis H_2 then requires that all vectors $(\mathbf{R}_k - \mathbf{R}_j)$ of the same magnitude have an equal probability of orientation in all directions (isotropic) and that for long distances (viz., 1000 A) the probability of finding vectors $(\mathbf{R}_k - \mathbf{R}_j)$

[1] We include in the term "fluids" gases, liquids, solutions, and suspensions. Thus the word fluid refers to all matter satisfying hypotheses H_1 and H_2.

of a given magnitude, r, is a continuous function of r and is nearly constant. This hypothesis is well justified for fluids.

2.2.1.2. Consequences of Hypothesis H_1

Let us consider a group of particles, each possessing a center of symmetry. We shall designate by r_{kl} the vector extending from the center of the kth particle to a point l of scattering factor f_{kl} in the same particle.

The amplitude of radiation scattered by this group of particles is then given as (cf. equation 2)

$$A(\mathbf{h}) = A_e(h) \sum_k \{ \sum_l f_{kl} e^{-i\mathbf{h}\cdot(\mathbf{R}_k + \mathbf{r}_{kl})} \}$$

since the position of the scattering point, l, is defined by the vector sum $\mathbf{R}_k + \mathbf{r}_{kl}$.

By virtue of the center of symmetry of each particle, this can be written as

$$A(\mathbf{h}) = A_e(h) \sum_k e^{-i\mathbf{h}\cdot\mathbf{R}_k} \sum_l f_{kl} \cos(\mathbf{h}\cdot\mathbf{r}_{kl}) \qquad (45)$$

The sum $\sum_l f_{kl} \cos(\mathbf{h}\cdot\mathbf{r}_{kl})$ corresponds to the structure factor $F_k(\mathbf{h})$ of the kth particle (see equation 5); since the particles are identical, the index k serves only to mark the kth particle.

The mathematical formulations of equation 45 and equation 2 are identical, with the sum over the index l playing the role of the quantity f_k, so the scattered intensity can be found easily by analogy with equation 3:

$$I(\mathbf{h}) = I_e(h) \sum_k \sum_j [\sum_l f_{kl} \cos(\mathbf{h}\cdot\mathbf{r}_{kl})][\sum_m f_{jm} \cos(\mathbf{h}\cdot\mathbf{r}_{jm})] \cos[\mathbf{h}\cdot(\mathbf{R}_k - \mathbf{R}_j)] \qquad (46)$$

In equation 46 indices k and j refer to particles, and indices l and m refer to the different scattering points in particles k and j, respectively.

The intensity calculated above is that furnished by one certain configuration of the ensemble of particles. In the course of time this configuration changes, the particles shifting and changing orientation. Thus we can observe only average intensities. We shall discuss here only the general method of calculating the average intensity; for details, see Fournet [48].

First we separate the terms where $k = j$ in equation 46. These terms represent the intensity scattered by one particle multiplied by the average number of particles being examined (see §2.2.1.3). For the calculation of the other terms, use is made of the second part of hypothesis H_1, which enables us to separate the calculation of the averaging of the

orientations of the particles from the averaging of the positions of the particles. The final result is:

$$\overline{I(\mathbf{h})} = I_e(h)\{\overline{N\,F^2(\mathbf{h})} + \overline{F(\mathbf{h})^2 \sum_k \sum_{j \neq k} \cos[\mathbf{h}\cdot(\mathbf{R}_k - \mathbf{R}_j)]}\} \qquad (47)$$

where $\overline{F^2(\mathbf{h})}$ and $\overline{F(\mathbf{h})^2}$ are the quantities defined earlier (p. 7). The problem that remains is the calculation of the average of the double sum of terms.

2.2.1.3. Consequences of Hypothesis H_2

Let us consider two very small volume elements, Δv_k and Δv_j, located by vectors $\mathbf{R}_k$ and $\mathbf{R}_j$, which are contained in the volume V irradiated by the X-rays. The contribution of this elementary pair, Δv_k, Δv_j, to the desired average is $n_{kj} \cos[\mathbf{h}\cdot(\mathbf{R}_k - \mathbf{R}_j)]$, where n_{kj} is the number of pairs of particles found in these volume elements, one particle being in Δv_k and the other in Δv_j. Now, letting the elementary volumes Δv_k and Δv_j approach the volume elements dv_k and dv_j, small even on an atomic scale, we introduce a probability function p_{kj}, in terms of which the probability of finding a particle in dv_k and at the same time a *different* particle in dv_j is: $p_2 = p_{kj}\, dv_k\, dv_j$. It is essential to consider that the particle in dv_j is different from that in dv_k, since we have excluded the case of $k = j$ in the double sum above. The sum of the cosine terms is now found as the integral (see equation 7)

$$\int_V \int_V \frac{\sin(h|\mathbf{R}_k - \mathbf{R}_j|)}{h|\mathbf{R}_k - \mathbf{R}_j|} p_{kj}\, dv_k\, dv_j$$

The volume element dv_k being infinitesimal, we shall describe a particle as being in dv_k if the center of the particle is found there.

Before calculating p_{kj}, let us carefully define the experimental conditions. We shall designate by V_0 the total volume offered to the particles. This volume contains a well-defined number of particles, N_0. The volume V_0 must be distinguished from the volume V actually irradiated by the X-rays.

1. If V_0 is smaller than or equal to V, then it follows that $N = N_0$, where N is the number of particles in V.

2. If V_0 is larger than V, the case generally met experimentally, then N cannot be known exactly, as previous authors have implicitly assumed. Only statistical information, such as an average value of N, can be known.

We shall assume that V_0 is large as compared with V, as is true of most experiments, and in any event a situation which is easily realizable. Let us now evaluate the probability $p_{kj}\, dv_k\, dv_j$. We know that the probability of occurrence of an ensemble of two events is equal to the probability of

the first multiplied by the probability of the second *as modified by the knowledge that the first event exists*. The probability of occurrence of the first event, finding a particle in dv_k, is $(N_0/V_0)\,dv_k$. When this is realized:

1. The remaining $N_0 - 1$ particles are distributed through a volume $V_0 - dv_k$.

2. If the centers of the two volumes dv_k and dv_j, each containing a particle, are separated by a distance r, the centers of the particles are separated by a distance approximately equal to r. It is obvious that the different distances (and uniquely the distances, if the matter being examined is composed of only one phase) cannot all be equally probable; if the particles are spheres of radius R, the distance between particles cannot be less than $2R$. This behavior will be described by a function $P(r)$ such that

$$p_{kj}\,dv_k\,dv_j = \frac{N_0}{V_0}\,dv_k\,\frac{N_0 - 1}{V_0 - dv_k}\,P(|\mathbf{R}_k - \mathbf{R}_j|)\,dv_j \qquad (48)$$

The manner in which $P(r)$ has been introduced shows that this function will tend towards unity as r increases, for then the condition discussed above disappears or, rather, does not play a part. We can neglect dv_k with respect to V_0, and usually 1 is negligible compared to N_0 (see §2.4).

By introducing *the average volume offered to each particle*, $v_1 = (V_0/N_0)$, a quantity characteristic of the ensemble of particles, equation 48 reduces to

$$p_{kj}\,dv_k\,dv_j = \frac{dv_k}{v_1}\frac{dv_j}{v_1}\,P(r_{kj}) \qquad (49)$$

and the desired average of the double sum becomes

$$\overline{\sum_k \sum_{j \neq k} \cos[\mathbf{h}\cdot(\mathbf{R}_k - \mathbf{R}_j)]} = \int_V \int_V \frac{\sin hr_{kj}}{hr_{kj}}\,P(r_{kj})\,\frac{dv_k}{v_1}\frac{dv_j}{v_1} \qquad (50)$$

2.2.1.4. General Expression for the Scattered Intensity

Since $P(r)$ tends toward unity as r increases, the structure of the ensemble of particles might be better characterized by the function $(1 - P(r))$, this function being different from zero only for small values of r. By making the substitution $P(r) = 1 - (1 - P(r))$ equation 50 takes on the following form:

$$\overline{\sum_k \sum_{j \neq k} \cos[\mathbf{h}\cdot(\mathbf{R}_k - \mathbf{R}_j)]} = \int_V \int_V \frac{\sin hr_{kj}}{hr_{kj}}\frac{dv_k}{v_1}\frac{dv_j}{v_1}$$
$$- \int_V \int_V \frac{\sin hr_{kj}}{hr_{kj}}[1 - P(r_{kj})]\frac{dv_k}{v_1}\frac{dv_j}{v_1}$$

Let us examine separately each of these terms.

First term: The contribution of this term to the total scattered intensity is

$$I_1(h) = I_e(h)\overline{F(h)}^2 \int_V \int_V \frac{\sin hr_{kj}}{hr_{kj}}\frac{dv_k}{v_1}\frac{dv_j}{v_1}$$

which (cf. equation 15) can be interpreted as representing the intensity scattered by a "particle" of volume V with a uniform electronic density, $\rho = \overline{F(h)}/v_1$. Given the size of this particle, $I_1(h)$ is effectively *zero for all observable angles*. (Fournet [48] discusses the reasoning of Compton and Allison (1935) on this subject.)

It is important to note the simple, general interpretation of the term $I_1(h)$. A further discussion of this factor is given by James (1948), where the scattering of a spherical volume is considered. To find simply and schematically the limit h_0, beyond which $I_1(h)$ is negligible, it might be considered that for $h = h_0$ the largest phase difference between rays scattered by two points in the particle will be of the order of 2π radians. Then, if the average dimension of the volume irradiated is designated by D_0, h_0 is determined by $h_0 = 2\pi/D_0$.

Second term: Let us consider first the integration with respect to dv_k:

$$\int_V \frac{\sin hr_{kj}}{hr_{kj}}[1 - P(r_{kj})]\frac{dv_k}{v_1}$$

Since the function $[1 - P(r_{kj})]$ approaches zero rapidly as r increases, by neglecting boundary effects this term can be written as

$$\int_0^\infty \frac{\sin hr}{hr}[1 - P(r)]\frac{4\pi r^2}{v_1}\,dr \qquad (51)$$

independent of the index j. The further integration with respect to j then results simply in multiplying equation 51 by a factor $\int \frac{dv_j}{v_1}$, which is equal to $\overline{N}$, the average number of particles in the irradiated volume V. The final relation for the scattered intensity is thus (Fournet [44])

$$\overline{I(h)} = I_1(h) + I_e(h)\overline{N}\left\{\overline{F^2(h)} - \frac{\overline{F(h)}^2}{v_1}\int_0^\infty \frac{\sin hr}{hr}[1 - P(r)]4\pi r^2\,dr\right\} \qquad (52)$$

$I_1(h)$ is completely unobservable, and so for $h > h_0$ this becomes

$$\overline{I(h)} = I_e(h)\overline{N}\left\{\overline{F^2(h)} - \frac{\overline{F(h)}^2}{v_1}\int_0^\infty \frac{\sin hr}{hr}[1 - P(r)]4\pi r^2\,dr\right\} \qquad (53)$$

If the particles considered are spherically symmetric, we have seen

(§2.1.2) that there is no distinction between the average of the square of the structure factor $\overline{F^2(h)}$ and the square of the average of the structure factor $\overline{F(h)}^2$. For this case equation 53 can be simplified to the following:

$$\overline{I(h)} = I_e(h) \overline{N} F^2(h) \left\{ 1 - \frac{1}{v_1} \int_0^\infty [1 - P(r)] \frac{\sin hr}{hr} 4\pi r^2 \, dr \right\} \qquad (54)$$

This expression was derived by Zernicke and Prins [309] and by Debye and Mencke [269]. Equation 53 thus appears as a generalization of this last expression.

The integral figuring in equations 53 and 54 has the dimensions of a volume. We shall define this as the *volume of perturbation*, $v_2(h)$:

$$v_2(h) = \int_0^\infty [1 - P(r)] \frac{\sin hr}{hr} 4\pi r^2 \, dr$$

We shall see in §2.2.3.1 that this function, which has also been called the "characteristic volume" (Porod [137]), is actually a function of two variables: $v_2 = v_2(h, v_1)$.

To summarize, we have shown that the scattered intensity can be expressed as a sum of two terms:

$$\overline{I(h)} = I_e(h) \overline{F(h)}^2 \int_V \int_V \frac{\sin hr_{kj}}{hr_{kj}} \frac{dv_k}{v_1} \frac{dv_j}{v_1}$$
$$+ I_e(h) \overline{N} \left\{ \overline{F^2(h)} - \frac{v_2(h)}{v_1} \overline{F(h)}^2 \right\}$$

the first of these terms being negligible with respect to the second for $h > h_0$. The value of h_0 is defined by the relation $h_0 D_0 = 2\pi$, D_0 being the average dimension of the irradiated volume. In the remainder of this section we shall designate by "intensity $I(h)$" *only the second term* of equation 52, and when a misunderstanding is possible we shall employ the expression "observable intensity" to denote this second term.

2.2.2. WIDELY SEPARATED PARTICLES

The general expression which we have just established shows the influence of interparticle interferences, through the intermediary of $v_2(h)$, on the scattered intensity. Let us now consider in detail the case of rather widely separated particles, for which the expression for the intensity takes on a particularly simple form. We shall later indicate the criterion which defines "widely separated particles," but for the moment we can indicate that a good example of such a system is a gas under low pressure.

2.2.2.1. Expression for the Scattered Intensity

If the particles are widely separated, the average volume v_1 offered to each will be large. Any irregularities of the function $[1 - P(r)]$ demonstrate that certain interparticle distances are favored while others are less probable. These irregularities are the more marked, the more closely the particles are packed, for, in order to contain more matter in a given volume, the degree of organization of this matter must be increased.

We see thus for two reasons that the ratio of $v_2(h)$ to v_1 is very small for widely separated particles. More rigorously, the part of $v_2(h)$ involving the integration from $r = 0$ to r equal to the smallest particle diameter will not vary as the particles become more separated, but, since v_1 increases, the corresponding part of the ratio of $v_2(h)$ to v_1 decreases. In the limit of large separations, we find the classical result

$$\overline{I(h)} = I_e(h) \overline{N} F^2(h) \qquad (55)$$

where we recall that this expression, derived from equation 53, is valid only for $h > h_0$ (h_0 has been defined on p. 34).

The intensity of radiation scattered by an ensemble of widely separated particles is thus identical on a relative scale to the mean intensity scattered by one isolated particle; in obtaining the intensity relative to an ensemble of particles it is necessary only to multiply the intensity scattered by one particle by the average number of particles, $\overline{N}$.

Realizing the practical importance of this simple result, it is opportune to underline its significance and to recognize its limits of validity. Later (§2.2.3.2) we shall demonstrate the connection existing between this expression and the equation of state for ideal gases, $pv_1 = kT$.

Let us compare equation 55 with a well-known problem in optics. It is often indicated in the literature that the intensity of scattering by identical elements distributed at random is formed by the addition of the intensities scattered by each element. This is not always correct, for if $h = 0$, we are led to the result $\overline{I(0)} = \overline{N} \, \overline{F^2(0)}$, whereas the exact result is known to be $\overline{I(0)} = \overline{N^2} \, \overline{F^2(0)}$. The usual reasoning behind the above statement consists of describing the double sum

$$\sum_k \sum_{j \ne k} \cos (\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j))$$

as containing as many positive terms as negative terms, so that consequently the sum is zero. But if $h = 0$ all the cosine terms are equal to unity and this reasoning is no longer true. As a criterion for applicability we can say that this reasoning is correct when the largest phase difference between particles reaches 2π radians; that is, if D_0 is the average dimension of the volume offered to the particles, the reasoning is correct when

$h > (2\pi/D_0) = h_0$. This is simply a restatement of the result that was established in §2.2.1.3.

The classical reasoning is a little too simplified, if not incorrect, and it should be replaced with that due to Lord Rayleigh (1919), who tries first to calculate the probability that the intensity will be between I and $I + dI$ and then afterwards calculates the average intensity. By correcting one error and slightly modifying the reasoning of Lord Rayleigh to render it applicable to the problem of X-ray scattering, equation 55 can be obtained as a first approximation when $h > h_0$. The corrective terms that appear are negligible when $\bar{N}$ is very large (Fournet [48]).

Remarks

For the simple case of widely separated, spherical particles, the scattered intensity (see equation 47) is given by

$$\overline{I(h)} = I_e(h)F^2(h)\{\bar{N} + \sum_k \sum_{j \neq k} \cos{(\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j))}\}$$

Let us compare the mathematical structure of the square of the structure factor of the particle, $F^2(h)$, with the bracketed term. The intensity scattered by a spherically symmetric particle, whose p scattering centers each have the same scattering factor f, can be described as (cf. equation 3)

$$I_e(h)F^2(\mathbf{h}) = I_e(h)f^2 \sum_l \sum_m \cos{(\mathbf{h} \cdot \mathbf{M}_l \mathbf{M}_m)}$$
$$= I_e(h)\{pf^2 + f^2 \sum_l \sum_{m \neq l} \cos{(\mathbf{h} \cdot (\mathbf{r}_m - \mathbf{r}_l))}\} \quad (56)$$

The previous discussion shows that the second term is negligible with respect to the first when h is greater than $h_1 = 2\pi/d$, d being the average dimension of the particle. For angles where h is the order of $h_1/10$, however, each of the terms of equation 56 has approximately the same value, so that the term pf^2 is negligible compared to the double sum.

The total scattered intensity is thus

$$I(h) = I_e(h)f^2 \{p + \sum_l \sum_{m \neq l} \cos{(\mathbf{h} \cdot (\mathbf{r}_m - \mathbf{r}_l))}\}$$
$$\times \{\bar{N} + \sum_k \sum_{j \neq k} \cos{(\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j))}\} \quad (57)$$

The symmetry of this relation is evident; mathematically the description is the same, whether for an ensemble of points in a particle or for an ensemble of particles, but the physical results are very different.

For $0 < h < h_0$, the values of the bracket concerning the ensemble of particles are not interesting to the physicist, since they cannot be reached experimentally. For $h_0 < h < h_1$, the values of the bracket concerning the ensemble of points in a particle are *essential* and permit the determination of the radius of gyration. For an angle of the order of $h_1/10$ and for quasi-homogeneous particles, the second term of the first bracket and the first term of the second bracket are the terms that are important in this expression. The two parts of this equation are shown separately in Fig. 10, in which curve a refers to the first factor and curve b to the second.

2.2.2.2. Remarks on the Babinet Principle of Reciprocity

This principle will be considered at this point not because it is applicable uniquely to ensembles of widely separated particles but rather because our recent concern with just such ensembles permits us to treat it very quickly.
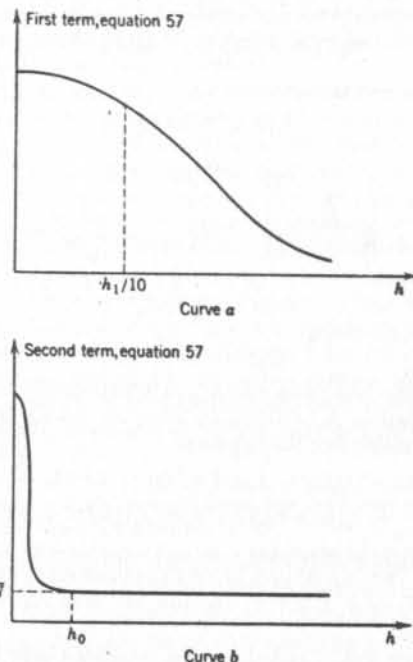

Fig. 10. A graphical representation of the two factors of equation 57. For clarity h_0 has been greatly exaggerated.

Let us first recall the simplest enunciation of Babinet's theorem: complementary objects produce the same diffraction effects. The concept of complementary objects will be more precisely defined in the following paragraph, but we can give a simple illustration of a pair of such objects: a screen pierced with circular holes, and an ensemble of circular discs, each disc corresponding in size and position to a particular hole.

The general expression for the amplitude scattered by matter contained in a volume V is

$$A_1(\mathbf{h}) = A_e(h)\int_V \rho_1(\mathbf{r})e^{-i\mathbf{h}\cdot\mathbf{r}} d\mathbf{r}$$

where $\rho_1(\mathbf{r})$ is the electronic density in the volume element $d\mathbf{r}$ whose position is fixed by the vector $\mathbf{r}$. Let us now consider a complementary space, whose electronic density $\rho_2(\mathbf{r})$ is defined as: $\rho_2(\mathbf{r}) = \rho_0 - \rho_1(\mathbf{r})$, where ρ_0 is a constant. The amplitude scattered by this complementary space is then

$$A_2(\mathbf{h}) = A_e(h)\int_V [\rho_0 - \rho_1(\mathbf{r})]e^{-i\mathbf{h}\cdot\mathbf{r}}\,d\mathbf{r}$$

The problem now is to compare

$$I_1(\mathbf{h}) = A_1(\mathbf{h})\,A_1^*(\mathbf{h})$$

and

$$I_2(\mathbf{h}) = A_2(\mathbf{h})\,A_2^*(\mathbf{h})$$

If we write

$$A_0(\mathbf{h}) = A_1(\mathbf{h}) + A_2(\mathbf{h}) = A_e(h)\int_V \rho_0 e^{-i\mathbf{h}\cdot\mathbf{r}}\,d\mathbf{r}$$

then the function,

$$I_0(\mathbf{h}) = A_0(\mathbf{h})\,A_0^*(\mathbf{h})$$

is a maximum for $h = 0$

$$[I_0(0) = I_e(0)V^2\rho_0^2]$$

decreases rapidly with increasing h, and effectively becomes zero beyond an angle defined by $h_0 = 2\pi/D_0$, D_0 being the average dimension of V.

We can now calculate the following:

$$I_2(\mathbf{h}) = [A_0(\mathbf{h}) - A_1(\mathbf{h})][A_0^*(\mathbf{h}) - A_1^*(\mathbf{h})]$$

$$= I_1(\mathbf{h}) + I_0(\mathbf{h}) - A_1(\mathbf{h})A_0^*(\mathbf{h}) - A_0(\mathbf{h})A_1^*(\mathbf{h}) \qquad (58)$$

If $h > h_0$, $I_0(\mathbf{h})$ is effectively zero, and consequently $A_0(\mathbf{h})$ and $A_0^*(\mathbf{h})$ are also zero. Then $I_1(\mathbf{h}) = I_2(\mathbf{h})$, the usual statement of the reciprocity principle. However, if $h < h_0$, equation 58 shows that this principle is no longer true.

Thus the principle of reciprocity can be applied only to calculate the intensity scattered at angles such that the corresponding values of h are greater than the limit $2\pi/D_0$. The dimension D_0 refers to the average dimension of the volume in which a "complementary" electronic density is defined.

In the experimental systems generally used for the study of low-angle scattering, *the principle of reciprocity can be applied to an ensemble of particles* (that is, an ensemble of cavities in a homogeneous medium can be considered equally well in place of an ensemble of particles), since the intervening dimension is defined by the transverse dimension of the beam, generally of the order of 1 mm. wide, but *it cannot be applied to each single particle* (as, for example, replacing a spherical particle of 100 A diameter containing a concentric spherical cavity of 20 A diameter by a simple

sphere of 20 A diameter). This latter method has been employed by some authors, leading to incorrect results; we cite for example the article of Kratky and Porod ([108], p. 45ff), in which these authors tried to evaluate the intensity scattered by a "finite packing of lamellae" of submicroscopic dimensions by replacing the lamellae with the interstices contained between them. In a later article, however, Porod is in agreement with the ideas expressed here.

Another application of these ideas is the calculation of the scattering from particles which, instead of being in a vacuum, are *immersed in a homogeneous medium* of electronic density ρ_0 (for example, the solvent of a colloidal suspension). The scattering body can be considered as the superposition of a continuous medium of density ρ_0 and particles of density $\rho - \rho_0$. The scattered amplitude is the sum of the amplitudes scattered by the continuous medium and by the fictitious particles. *The first of these is zero* throughout the region accessible to experiment. The observed scattering is therefore simply that due to the particles of density $\rho - \rho_0$. All the equations which have been established are thus valid on condition that ρ is considered as *the difference between the electronic density of the particle and that of the surrounding medium*. The small-angle scattering becomes zero if the particles have a density equivalent to that of the surrounding medium, even if they have a quite different atomic structure.

2.2.3. INFLUENCE OF THE CLOSER PACKING OF PARTICLES
2.2.3.1. General Considerations

We have just treated the simple case of widely separated particles, in which the total scattered intensity, proportional to the intensity relative to a single particle, generally decreases continuously with increasing scattering angle. It is only for the very particular case of particles with a strongly marked internal structure (for example, CCl_4 molecules) that intensity maxima at non-zero angles can be observed for widely separated particles.

It is well known that numerous liquids whose elementary particles possess simple structures give rise to maxima of intensity at non-zero angles. Zernicke and Prins [309] established their well-known formula (equation 54) in order to explain these results. We should point out that it is difficult to study the effect of the closer packing of particles on the scattering distribution from this equation; when the concentration of matter increases, v, decreases, *but there is also an unknown change in the function $P(r)$.* Writing the equation for the intensity in the form given by Zernicke and Prins could lead to the assumption that the concentration of matter has no influence on the function $P(r)$. To eliminate the

possibility of this assumption, we propose to modify slightly the expression of the Zernicke-Prins formula, writing:

$$I(h) = I_e(h)\overline{N}\,F^2(h)\left\{1 - \frac{1}{v_1}\int_0^\infty [1 - P(r, v_1)]\frac{\sin hr}{hr}\,4\pi r^2\,dr\right\} \quad (59)$$

in which the functional dependence of $P(r, v_1)$ appears explicitly.

Numerous authors have studied the influence of the mutual approach of particles on the distribution of scattered radiation, assuming *a priori* a function $P(r)$ more or less well chosen but independent of the concentration of the matter. Among the latest attempts we may cite that of Yudowitch [186]. We believe that it is difficult to determine the validity of the results thus obtained, for in these studies of the influence of concentration on the intensity $I(h)$, one of the most important functions determining this intensity has been assumed *a priori* to be independent of concentration.

The real problem then in any such study is to obtain the function $P(r, v_1)$. This problem is difficult. We feel certain that its solution will require a profound analysis of the thermodynamics of ensembles of particles. We can hope that by such an approach, equations 53 and 54, which may be called "Zernicke-Prins type equations," concerning only the geometry of the ensembles of particles, can be transformed into "thermodynamic equations" by the introduction of certain intrinsic characteristics of the particles.

It is first necessary to find variables that can intervene in a definition of $P(r)$. We have already noted one such variable, v_1. The function $P(r)$ is connected to the *probability* of seeing a certain configuration of two particles realized, so that the calculation of probabilities introduces itself naturally into the problem. If Boltzmann statistics are employed we need to introduce both the temperature and the potential energy $\Phi(r)$ of a pair of particles whose centers are separated by a distance r.

The problem of calculating the function $P(r)$ from v_1, T, and $\Phi(r)$ is the central problem of the latest kinetic theories of fluids (Yvon (1935), Kirkwood (1935), Born and Green [259]). Our own problem is not limited simply to the case of fluids; we are interested to a large extent in solutions of large molecules, suspensions, etc. In each of these cases the functions $P(r)$ and $\Phi(r)$ can always be defined. We shall introduce later the variable, pressure, and the equation of state of the matter being considered. This presents no difficulty in problems concerning gases or liquids. Moreover, it is well known that in solutions the osmotic pressure plays a role analogous to that of pressure in fluids and that the equation of state of *ideal* solutions can be expressed in the form $pv_1 = kT$. If there is difficulty in extending these concepts to the study of emulsions,

we can always formally define the pressure by evaluating the change of free energy of the system with respect to the total volume offered.

In the different kinetic theories of fluids cited above, the integral equation determining $P(r)$ is of the form,

$$P(r) = F\left(\frac{P(r)}{v_1}, \frac{\Phi(r)}{kT}\right) \quad (60)$$

where F designates an integration of the functions $P(r)/v_1$ and $\Phi(r)/kT$. In establishing this equation it has been necessary to make a physical approximation known as the "principle of superposition." We shall not give the details of this principle, for these can be found in the article of Kirkwood and Boggs (1942) in which this principle is described and employed for the first time. We may describe equation 60 as having been established in a very general manner from considerations of classical Boltzmann statistics, the only assumption being that of the validity of the principle of superposition.

2.2.3.2. Scattered Intensity and the Equation of State

We have just seen that the kinetic theories of fluids furnish a relation between $P(r)$ and $\Phi(r)$; this shows the manner in which the relation between the function $I(h)$ and $\Phi(r)$ can be established. At this point it seems advantageous to introduce the equation of state, a more familiar quantity than the corresponding mutual potential energy function. This can be written in the following form (Green [273], Yvon (1949)):

$$p = \frac{kT}{v_1} - \frac{1}{6v_1^2}\int_0^\infty P(r)\Phi'(r)\,4\pi r^3\,dr \quad (61)$$

If the integral is neglected, this reduces simply to the ideal gas law,

$$p = \frac{kT}{v_1} = \frac{N_A kT}{N_A v_1} = \frac{RT}{V}$$

where N_A is Avogadro's number.

Let us first consider the case for which the function $\Phi(r)$ is identically equal to zero. The equation determining $P(r)$ then states that $P(r) \equiv 1$. Two important relations resulting from this particular function $P(r)$ can now be derived:

1. The expression for the scattered intensity becomes (see equation 53)

$$\overline{I(h)} = I_e(h)\overline{N}\,\overline{F^2(h)} \quad (55)$$

the result for widely separated particles.

2. The equation of state, obtained from the general expression of equation 61, becomes

$$pv_1 = kT \tag{62}$$

the ideal gas law.

This result shows that the domains of validity of equation 55 and equation 62 are the same. These two expressions are rigorously true only for point particles, small even on the angstrom scale, as is required when the potential energy is defined as $\Phi(r) = 0$, independent of r. In §2.2.3.4 we shall discuss the conditions under which equation 55 is a good approximation.

Let us remark also that if an attempt is made to find a function $P(r)$ which is independent of r_1 and which is to be defined by equation 60, the only possible solution will be found to be $P(r) = 1$.

Now let us leave the case of widely separated particles and try to treat the general case. By developing $P(r, r_1)$ in a series expansion with r_1 as the variable, we find

$$P(r, r_1) = P_0(r) + r_1 P_1(r) + \cdots$$

where the term $P_0(r)$ is identical to $e^{-\Phi(r)/kT}$.

Thus a first approximation of equation 60 is

$$P(r, r_1) = e^{-\Phi(r)/kT} \tag{63}$$

For this approximation the equation of state becomes

$$pv_1 = kT \left[1 - \frac{(2\pi)^{3/2}}{2} \frac{\beta(0)}{v_1} \right]$$

and the scattered intensity distribution is (cf. equation 54)

$$I(h) = I_e(h)\overline{N} F^2(h) \left[1 + \frac{(2\pi)^{3/2}}{v_1} \beta(h) \right] \tag{64}$$

where the function $\beta(h)$ is defined by the relation

$$h\beta(h) = \frac{2}{\sqrt{2\pi}} \int_0^\infty r\alpha(r) \sin hr \, dr \tag{65}$$

with

$$\alpha(r) = e^{-\Phi(r)/kT} - 1$$

An approximate solution for hard spheres of radius R and volume v_0, with no interactions other than impenetrability, has been considered by Debye [265]. With the probability function defined (cf. equation 63) as

$$P(r) = 0 \quad 0 < r < 2R$$
$$P(r) = 1 \quad r > 2R$$

equations 31 and 64 lead to the following expression for the scattered intensity:

$$I(h) = I_e(h)N\Phi^2(hR) \left[1 - \frac{8v_0}{v_1} \Phi(2hR) \right] \tag{66}$$

where the function $\Phi(x)$ is described by equation 31. We shall consider the validity of this expression in §2.2.3.3.

The solution $P(r, v_1) = e^{-\Phi(r)/kT}$ has been proposed as a general solution by Raman (1924), who believed that the solution was exact. His oversight was the following: if an ensemble of only two particles is considered, the probability that these particles are at a distance r from one another is truly $e^{-\Phi(r)/kT}$, but, if an ensemble of a large number of particles is considered, the probability that any two particles are at a distance r cannot be the same, since interactions with the other particles must be taken into account.

A second approximation of equation 60 based on the more complete theories of Born and Green [259] leads to the following result (Fournet [44], [45], [49]):

$$I(h) = I_e(h)\overline{N} \left\{ \overline{F^2(h)} + \overline{F(h)}^2 \frac{\epsilon\beta(h)}{v_1(2\pi)^{-3/2} - \epsilon\beta(h)} \right\} \tag{67}$$

where ϵ designates a constant approximately equal to unity.

For the simple case of spherically symmetric particles, equation 67 becomes

$$I(h) = I_e(h)\overline{N} F^2(h) \frac{v_1}{v_1 - (2\pi)^{3/2}\epsilon\beta(h)} \tag{68}$$

Let us emphasize that equations 67 and 68 have been derived from certain results of the theory of Born and Green with no additional physical hypotheses or mathematical simplifications.

A simple outline of the derivation of equation 67 is as follows:
The modification added by Rodriguez (1949) to the simple calculation of Green consisted in writing

$$P(r) = e^{-\Phi(r)/kT} e^{f(r)} \tag{69}$$

In obtaining $f(r)$ from equation 60 the value of the function $\alpha(r) = e^{-\Phi(r)/kT} - 1$ is assumed to be different from zero only for small values of r, and in certain cases the product $\alpha(r) f(r)$ is assumed to be replaceable by the terms $\alpha(r) (\epsilon - 1)$, thus defining $(\epsilon - 1)$ as a mean value of $f(r)$ for small values of r. From this, the function $f(r)$ can be described by the Fourier transform

$$rf(r) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty \frac{\epsilon^2 h\beta^2(h)}{v_1(2\pi)^{-3/2} - \epsilon\beta(h)} \sin hr \, dh \tag{70}$$

neglecting terms in $f^3(r)$, $f^2(r)$, etc.

The calculation of $v_2(h)$ requires a knowledge of the function $[P(r) - 1]$. From equation 69,

$$P(r) - 1 = [\alpha(r) + 1][1 + f(r) + \cdots] - 1$$

or

$$P(r) - 1 \approx \epsilon\alpha(r) + f(r)$$

Thus we can write

$$-\frac{v_2(h)}{v_1} = \frac{1}{h}\frac{(2\pi)^{3/2}}{v_1}\frac{2}{\sqrt{2\pi}}\int_0^\infty r[\epsilon\alpha(r) + f(r)]\sin hr\, dh$$

which, by means of equations 65 and 70, becomes

$$-\frac{v_2(h)}{v_1} = \frac{1}{h}\frac{(2\pi)^{3/2}}{v_1}\left[\epsilon h\beta(h) + h\frac{\epsilon^2\beta^2(h)}{v_1(2\pi)^{-3/2} - \epsilon\beta(h)}\right] \qquad (71)$$

Equation 67 is easily found from this last equation.

Let us try to analyze quite generally the different relations which we have established by employing a criterion often used in the statistical theory of ensembles (theory of fluids, the order-disorder transformations in alloys, magnetism): the inclusion in the calculation of particles in units, pairs, triplets, etc. We must point out that a perfect theory should take account of all such possible groups.

Equation 55, correct for widely separated particles, takes account of particles only in units; that is, all interactions between particles have been neglected.

The discussion we have given of the work of Raman with respect to equation 64 shows that this expression takes into account particles considered in units and in pairs; that is, interactions between particles have been limited to a sum of interactions between pairs of particles isolated in space.

In considering the validity of equations 67 and 68 we must first point out that the Kirkwood-Boggs principle of superposition used in establishing equation 60 is presented in the form of a relation, good to a first approximation, between the properties of particles considered in pairs and the properties of particles considered in triplets. Now in the form that Rodriguez has given to the theory of Born and Green, one determines the second approximation to the function $f(r)$, defined by equation 60 and the relation

$$P(r) = e^{-\Phi(r)/kT}e^{f(r)}$$

The first approximation, that of $f(r) \equiv 0$, furnished the solution of Raman, which takes into account only the influence of doublet terms. Thus we can affirm that equations 67 and 68, established from the theory of Born and Green, take account of triplet terms at least to a first approximation, contrary to the opinion of Oster and Riley [128].

To summarize these results, we have listed the expressions of certain equations of state and the corresponding expressions for the scattered intensity.

Summary

EQUATION OF STATE	SCATTERED INTENSITY
$pV = RT$	$I(h) = I_e(h)\overline{N}\overline{F^2(h)}$
$pV = RT\left[1 - \dfrac{(2\pi)^{3/2}\beta(0)}{2v_1}\right]$	$I(h) = I_e(h)\overline{N}\overline{F^2(h)}\left[1 + \dfrac{(2\pi)^{3/2}}{v_1}\beta(h)\right]$
Born and Green	$I(h) = I_e(h)\overline{N}\overline{F^2(h)}\dfrac{1}{1 - \dfrac{(2\pi)^{3/2}}{v_1}\epsilon\beta(h)}$

2.2.3.3. Limiting Value for the Intensity Scattered at Very Small Angles

We have just examined the relation between the equation of state and the scattered intensity, $I(h)$. Let us now restrict the problem to determining which thermodynamic variables are related to $I(0)$. From a previously established relation, equation 53, we find

$$I(0) = I_e(0)\overline{N}\left\{n^2 - n^2\frac{v_2(0)}{v_1}\right\} = I_e(0)\overline{N}n^2\left\{1 - \frac{v_2(0)}{v_1}\right\}$$

n being the number of electrons contained in a particle.

The function $v_2(0)$ can be evaluated as follows: we have seen (§2.2.1.3) that $p_{kj}\,dv_k\,dv_j$ represents the probability that there is at the same time a particle in dv_k and a different particle in dv_j. The double integral of $p_{kj}\,dv_k\,dv_j$ extended over the domain V should then give the average number of pairs of particles existing in the volume V. Designating by N the number of particles in V at a certain instant, we find that

$$\int_V\int_V p_{kj}\,dv_k\,dv_j = \int_V\int_V P(r_{kj})\frac{dv_k}{v_1}\frac{dv_j}{v_1} = \overline{N(N-1)} = \overline{N^2} - \overline{N}$$

since the average of a sum always equals the sum of the averages of each term.

Now by introducing the function $(1 - P(r))$ in terms of these quantities, we have

$$\overline{N^2} - \overline{N} = \int\frac{dv_k}{v_1}\int\frac{dv_j}{v_1} - \int\frac{dv_j}{v_1}\int[1 - P(r_{kj})]\frac{dv_k}{v_1}$$

By making use of the calculations employed in §2.2.1.4, and neglecting only very small terms, we obtain the following expression:

$$\overline{N^2} - \overline{N} = \overline{N^2} - \overline{N}\int_0^\infty[1 - P(r)]\frac{4\pi r^2}{v_1}\,dr$$

from which we find

$$\frac{1}{v_1}\int_0^\infty[1 - P(r)]\,4\pi r^2\,dr = \frac{v_2(0)}{v_1} = \frac{-\overline{N^2} + \overline{N}^2 + \overline{N}}{\overline{N}} = 1 - \frac{\overline{N^2} - \overline{N}^2}{\overline{N}}$$

With this value of $v_2(0)$, we find that

$$I(0) = I_e(0)n^2(\overline{N^2} - \overline{N}^2) = I_e(0)n^2\overline{(N - \overline{N})^2} \tag{72}$$

This result was first established by the work of Einstein and Smoluchowski; other papers developing this topic which might be cited are those of Zernicke and Prins [309], Bhatia and Krishnan (1948), Yvon (1947), and Fournet and Guinier [53].

Equation 72, which is a result of the hypotheses H_1 and H_2 imposed on the structure of ensembles of particles, shows that the *observable* scattered intensity (see p. 35) at very small angles is a consequence of the existence of fluctuations in the sample. A thermodynamic description of $I(0)$ can be found by recalling a classical result of the kinetic theory of gases,[1]

$$\frac{kT}{V}\beta + \cdots = \overline{\left(\frac{N - \overline{N}}{N}\right)^2} = \frac{\overline{(N - \overline{N})^2}}{\overline{N}^2} + \cdots \tag{73}$$

where β is the isothermal coefficient of compressibility,

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

V being the total volume offered to the gas. If N is large and the matter is not near its critical point, the terms neglected in equation 73 are small when one writes

$$I(0) = I_e(0)n^2\overline{N}\frac{kT}{v_1}\beta \tag{74}$$

thus establishing a simple *relation between $I(0)$ and the isothermal compressibility.*

Values for $I(0)$ have been predicted by several different theories. The expression given by Debye for a model of hard spheres is (cf. equation 66)

$$\overline{I(0)} = I_e(0)n^2N\left(1 - \frac{8v_0}{v_1}\right)$$

where v_0 is the volume of each sphere. (The coefficient, 8, has been omitted in several references in the literature.) The maximum value of v_0/v_1, that for close-packed hexagonal or cubic systems, is 0.74, leading to the prediction of negative intensities for a large domain ($v_0/v_1 > 0.125$). The *linear* model of Kratky and Porod [108], with assumptions similar to those of Debye, leads to a similar factor: $(1 - 2l_0/l_1)$, $[2^3 = 8]$; since the maximum possible value of l_0/l_1 is unity, again negative intensities are possible.

[1] See, for example, R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford, 1946, p. 647.

Equations 67 and 68 give negative results if v_1 is smaller than $(2\pi)^{3/2}\epsilon\beta(0)$. This is not a valid criticism, however, since Fournet [49] has shown that the passage of the Zernicke-Prins type equation to equations 67 and 68 is possible only if there are no roots to the following equation:

$$v_1 - (2\pi)^{3/2}\epsilon\beta(h) = 0$$

When roots to this equation exist, as happens for liquids, equation 67 is no longer correct and must be replaced by another which does not predict negative intensities (for details, see the article of Fournet cited above).

2.2.3.4. Thermodynamic Expression for the Intensity

Let us now consider the general possibilities of employing equation 68,

$$I(h) = I_e(h)\overline{N}F^2(h)\frac{v_1}{v_1 - (2\pi)^{3/2}\epsilon\beta(h)} \tag{68}$$

in a study of spherical particles.[1] Fournet [45], [49] has employed this equation together with the potential energy function $\Phi(r)$ determined by Lennard-Jones (1937) to predict correctly the scattering by gaseous and liquid argon at 150° K.; this is shown in Fig. 11. When considering a fluid of hard spheres, for which $\beta(h)$ can be calculated, equation 68 becomes

$$I(h) = I_e(h)\overline{N}\Phi^2(hR)\frac{1}{1 + \frac{8v_0}{v_1}\epsilon\Phi(2hR)} \tag{75}$$

The corresponding curves are given in Fig. 12 for various values of $(8v_0\epsilon/v_1)$. Let us recall that, in practice, ϵ can be taken as equal to 1.

We can now establish a precise criterion for defining the term "widely separated particles." Equation 68 can be written in the form

$$I(h) = I_e(h)\overline{N}F^2(h)\frac{1}{1 - \frac{(2\pi)^{3/2}\epsilon\beta(h)}{v_1}}$$

which allows us to say that the equation relative to widely separated particles is accurate to within n per cent when the ratio $(2\pi)^{3/2}\epsilon\beta(h)/v_1$ has the value of n per cent.

A certain characteristic behavior of the scattered intensity can be predicted from the mathematical structure of equation 68. If the value

[1] We shall consider only spherically symmetrical particles in this paragraph in order to simplify the discussion. For the general case, as expressed by equation 67, the results are analogous.
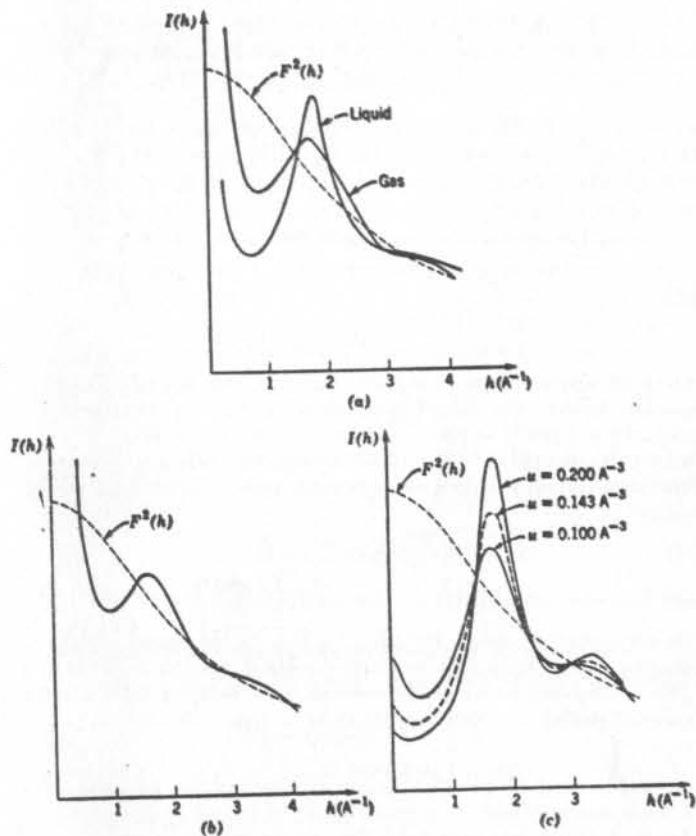
(a)

(b)

(c)

Fig. 11. (a) Experimental curves of the scattering by liquid and gaseous argon at pressures near the condensation pressure at 149.3° K. (Eisenstein and Gingrich [40]). The dotted curve represents the square of the structure factor, $F^2(h)$.   (b) Theoretical curve (equation 68) of the scattering from gaseous argon at 149.3° K. and at condensation pressure.   (c) Theoretical curves of the scattering from liquid argon of several densities at 149.3° K.   ($u = (2\pi)^{3/2}\epsilon(v_1)^{-1}$ [see equation 68]).

of $\beta(h)$ is zero when h equals some value h_1, the reduced intensity, $I(h)/\bar{N}I_e(h)$, evaluated at h_1 is a constant, $F^2(h_1)$, regardless of the concentration of the matter. This fact, predicted from equation 68, is verified quite well by the results found for argon by Eisenstein and Gingrich [40], when their results are considered on the basis of one
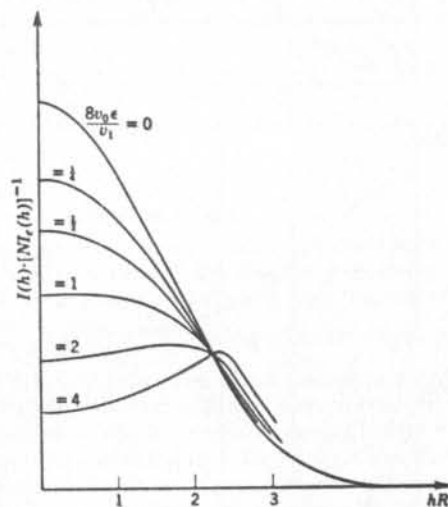
Fig. 12.   Scattering curve for non-interacting hard spheres (equation 75).

temperature (see Fig. 7 of the reference cited); the condition of a common temperature for the curves is necessary, since $\beta(h)$ depends on the temperature, as is shown in equation 65.

If the coefficient of $F^2(h)$ in equation 68 is considered, it is seen that the maxima of this function always occur at the same angles (those such that $\beta(h)$ is a maximum), regardless of the concentration of scattering matter; the only effect of a change in concentration is to accentuate the maxima to a greater or lesser degree. This same result is found if the expression derived from only the first approximation is used. (Personal communication from G. W. Brindley.)

A detailed study of equation 68 by Fournet [48] has shown that for the general case, in which $F^2(h)$ decreases in the observable region with increasing h, the intensity maxima are produced at larger and larger angles, the greater the concentration of scattering matter. This is illustrated in Fig. 13, in which we have plotted representative curves of
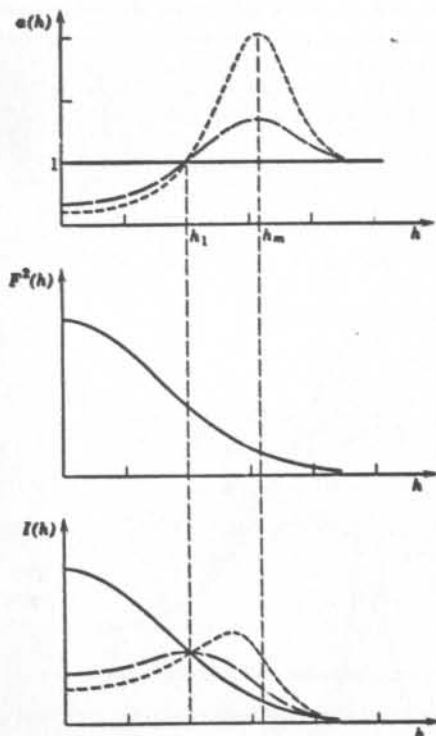
Fig. 13. Scattering from a fluid for three different concentrations of particles. The solid curves correspond to a very low concentration, the dashed curves to an average concentration, and the dotted curves to a high concentration. Note that the maxima of $a(h)$, the interparticle interference function, and $I(h)$, the observed intensity, occur at different scattering angles.

the terms involved as a function of h for three values of v_1; the solid curves refer to the case of v_1 approaching infinity (i.e., widely separated particles), the dashed curves refer to a smaller value of v_1, and the dotted curves to still smaller values of v_1 (i.e., still higher concentrations). The first function, the interparticle interference function

$$a(h) = \frac{v_1}{v_1 - (2\pi)^{3/2} \epsilon \beta(h)}$$

is equivalent to $\dfrac{I(h)}{I_e(h)\ N F^2(h)}$; the second is the function $F^2(h)$; and the third, the product $F^2(h)a(h)$, is proportional to the intensity. It can be seen that the product of the continually decreasing function $F^2(h)$ and the function $a(h)$, with its only slightly accentuated maximum, results in a function $I(h)$ having a still more diffuse maximum situated at a smaller value of h than that for the original function, $a(h)$, for each of these cases. The position of the observed maximum thus depends markedly on the function $F^2(h)$, that is, on the structure of the particle. The position of the intensity maximum depends in a very complex way on the structure of the *arrangement* of the particles *and* on the particular *structure of each particle*.

2.2.3.5. Fluids and Crystals

In an examination of a crystalline substance by means of an experimental method such as Debye-Scherrer photography, we find that the function for a perfect crystal which plays the role of $a(h)$, that is, the function $\dfrac{I(h)}{I_e(h)N F^2(h)}$, is identically equal to zero except for certain specific values of h, at which points it takes on very large values. The product of this function with the function $F^2(h)$ then gives a function $I(h)$ which shows the same structure as $a(h)$, in that it also is identically zero except for certain specific values of h. The positions of the intensity maxima (the Debye-Scherrer lines in this example) are identical to those of the function $a(h)$ and thus can immediately furnish information on the structural arrangement of the particles (see Fig. 14). This illustrates one of the essential differences between the classical problems of X-ray crystallography and the problems that are treated here: the degree of order in a crystal is in general such that the function $I(h)/F^2(h)$ presents sharp maxima. As a result the maxima of the function $I(h)$ occur at the same values of h as the maxima of the function $I(h)/F^2(h)$. *This result does not apply to fluids, for they are much less ordered than any crystal.*

We should like now to offer a physical explanation of the fact that the maximum of the function $I(h)/F^2(h)$ is produced at a constant angle for a fluid, independent of its concentration. For this very qualitative explanation let us make the approximation that $P(r) = e^{-\Phi(r)/kT}$. The factor of physical importance in this problem is the arrangement of particles around any one particle. At very low concentrations the probability of finding a particle in a volume element dv_j is dv_j/v_1. If it is known that this element, dv_j, is at a distance r from another particle, the probability
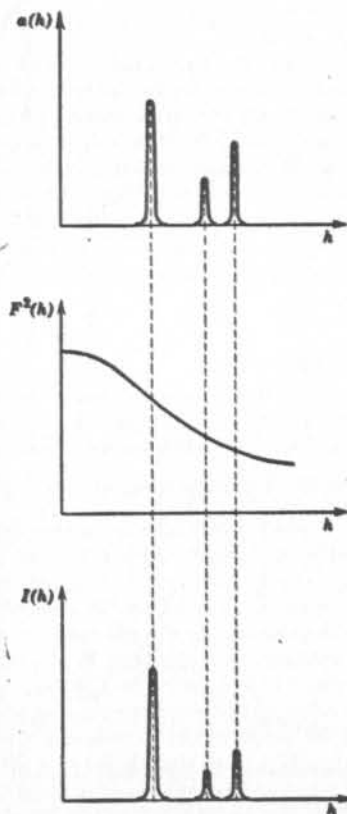
Fig. 14. Scattering from perfect crystals. The maxima of $a(h)$ and $I(h)$ occur at the same scattering angles.

becomes $(dv_s/v_1)e^{-\Phi(r)/kT}$, and the probability density, $d(r)$, from its definition, is $(1/v_1)\, e^{-\Phi(r)/kT}$. We have plotted this probability density in Fig. 15 for two concentrations, v_1' and v_1''. Whereas the mean probability density increases when the concentration increases, the ratio of probability densities for arbitrarily chosen r_1 and r_2 remains a constant. Since the position of the maximum of $I(h)/F^2(h)$ is related to this ratio of probability densities, it can thus be understood that the position of the maximum will remain invariant.

To summarize, we have shown that there is a great deal of difference between the behavior of the function directly connected to the arrangement of particles, $I(h)/F^2(h)$, and the function $I'(h)$ which is observed experimentally. In §4.1.2.2 we shall return to this point to discuss its important consequences in the interpretation of experiments.
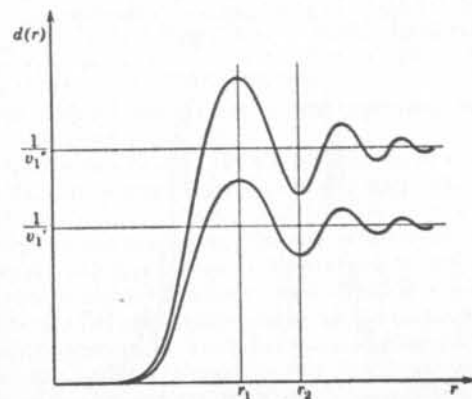
Fig. 15. A schematic representation of the probability density $d(r)$ for two different concentrations of particles.

2.2.3.6. Secondary Maxima

In the course of experiments on the scattering of X-rays by suspensions of latex, Yudowitch [186] and Danielson, Shenfil, and DuMond [25] found several maxima in the scattering curve (Fig. 16). A study of this same suspension by electron microscopy showed that the latex globules were spherical and very regular in size, variations in diameter being less than 10 per cent. These globules were relatively close-packed, so that an explanation based on the theoretical development of §2.2.3.4 can readily explain the principal maximum, the maximum at the smallest angle. The other maxima, which we shall refer to as secondary maxima, appear to be more difficult to interpret.

Yudowitch advanced the hypothesis that these secondary maxima were due to the particular form of the square of the particle structure factor, $F^2(h)$. Let us re-examine the function $F^2(h)$, considering the latex globules as analogous to hard spheres of constant electronic density, this being the same model that we have heretofore designated as "Debye's model."

The intensity scattered by one such sphere is given by the relation

$$F^2(h) = \Phi^2(hR) = \left[3 \frac{\sin hR - hR \cos hR}{h^3 R^3} \right]^2 \qquad (31)$$

The positions of the maxima and minima of this function are then given by the solutions of the equation

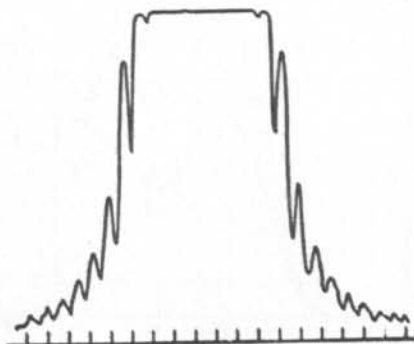$$2\Phi(u)\Phi'(u) = 2\Phi(u) \frac{(u^2 - 3)\sin u + 3u \cos u}{u^4} = 0$$

Fig. 16. A microphotometer curve of the diffraction pattern of latex particles showing the secondary diffraction rings. Intervals at the bottom correspond to a scattering angle of 3 minutes of arc (Danielson, Shenfil, and DuMond [25]).

where $u = hR$. The solutions corresponding to the minima are those for which $\Phi(u) = 0$. The positions of the maxima are given as solutions of the equation

$$\tan u_m = \frac{3u_m}{3 - u_m^2} \qquad (76)$$

At these positions we note that

$$\Phi^2(u_m) = \frac{\sin^2 u_m}{u_m^2} = \frac{9}{u_m^4 + 3u_m^2 + 9} \qquad (77)$$

A first approximation to the solutions of equation 76 is found by placing $u_m = k\pi$, where the first maximum is that for $k = 0$, the second for $k = 2$, the third, $k = 3$, etc. A better, second-order approximation (except for $k = 0$) is obtained in writing

$$u_m = k\pi - (3/k\pi) \qquad (78)$$

the corresponding intensities being given by

$$I(u_m) = \frac{9}{k^4\pi^4} + \frac{81}{k^6\pi^6} \qquad (79)$$

Thus we can establish the following table:

Index of Maximum	1	2	3	4	5	6
k	0	2	3	4	5	6
u_m, equation 78		5.80	9.10	12.33	15.52	18.69
u_m, exact	0.000	5.76				
$10^3 \times I_m$, equation 79		7.37	1.28	0.39	0.15	0.07
$10^3 \times I_m$, exact	1000	7.45				

It should be noted that the second-order approximation gives correct values even for $k = 2$.

Evidently the ratio of $I(u_m)$ at its first maximum, at zero angle, to the value of $I(u_m)$ at its second maximum is very large, actually a value of 1.3×10^2, but, more important, the ratio of the intensities of any two other successive maxima is small; the ratio of the second to the third is only about 5. It is thus possible to observe experimentally several of the maxima that theory predicts for the case of *widely separated* particles.

Next the effect of interparticle interference should be considered. We shall employ equation 75, which has been established for the case of particles with no mutual interaction other than impenetrability; though this represents an approximation, it should be sufficient for the larger angles. Neglecting constant factors (see §2.2.3.4), the scattered intensity is

$$I_2(u) = \frac{\Phi^2(u)}{1 + \frac{8v_0}{v_1} \epsilon\Phi(2u)}$$

Expanding this function, $I_2(u)$, around the point $u = k\pi + x$, we find that to a second approximation this function is a maximum for

$$u = k\pi - (3/k\pi) + \cdots$$

the same result as that found for the maxima of $\Phi^2(u)$. The values of the intensity maxima are (cf. equation 79):

$$I_2(u_m) = \frac{9}{k^4\pi^4} + \frac{81}{k^6\pi^6} + \frac{27c}{4k^6\pi^6}$$

where c designates the ratio $(8v_0\epsilon/v_1)$, which has a maximum value of about 6.

We see thus that for this model *the positions and magnitudes of the secondary maxima are only slightly modified in passing from a very dilute system to a dense system.* This is not true for the principal maximum; the principal maximum occurs at zero angle for dilute solutions, and as the

concentration increases it is displaced towards larger angles, occurring at values of u between 0 and 2.5 for systems of average concentration.

The explanation of the secondary maxima observed by Yudowitch is thus given by a complete calculation of interparticle interferences. These maxima are present in the representative curves of $F^2(h)$ for a single particle, and interparticle interferences, instead of removing these maxima, actually reinforce them slightly, as is shown in Fig. 17.
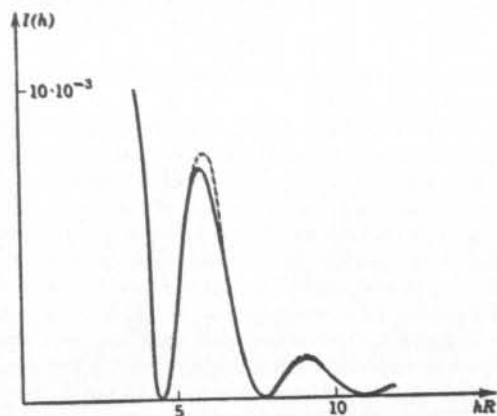

Fig. 17. Scattering from hard spheres. The solid curve represents the intensity scattered by a single sphere of radius R at large value of hR (see Fig. 6). The dotted curve represents the scattered intensity per sphere for a dense group of spheres $((8v_i\epsilon)/v_1 = 5)$.

We must point out that this explanation of the secondary maxima is based on the choice of a model of the particles, but the hard-sphere model seems particularly valid for suspensions of latex globules.

Let us now consider as a second example the secondary maxima that can be observed in the scattering curves of liquid or gaseous argon as determined by Eisenstein and Gingrich (Fig. 11). A comparison of these curves with the square of the structure factor shows immediately that these secondary maxima are due uniquely to interparticle interferences.

2.2.3.7. Remarks on Fourier Transformations

When considering two mutually reciprocal spaces that are connected by a Fourier transformation, as, for example, the real space containing the particles and the reciprocal space of the variable h, in which densities are

related to scattered intensities, it is known that an unevenness in density in one space corresponds to a periodic variation of density in the other space, with the period in the second space being related to the position of the unevenness in the first. We know thus that a Debye-Scherrer line, which is a discontinuity in h space, is determined by the periodic distribution of certain crystallographic planes in real space, and the position
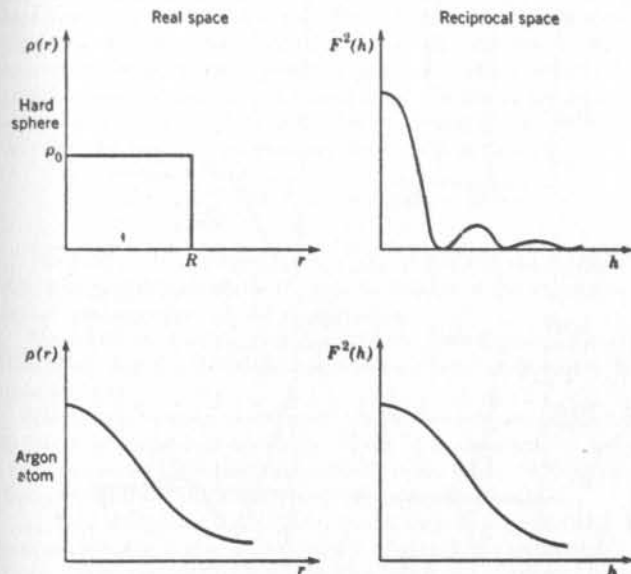
Fig. 18. Schematic curves of $\rho(r)$ and $F^2(h)$ for a hard sphere and for an argon atom. The unevenness in $\rho(r)$ for the hard sphere causes a certain periodicity in its $F^2(h)$.

of the line is determined by the period, or distance between consecutive planes, in real space (Bragg's law). These remarks can now be applied in a discussion of the intensity scattered by a hard homogeneous sphere and by an atom of argon. Both particles are characterized in the real space by the electronic density $\rho(r)$ at a distance r from the center of a particle and in the h space by the function $F(h)$, related to $\rho(r)$ by a Fourier integral (see §2.1).

Since the density $\rho(r)$ is more uneven, in a general sense, for hard spheres than for argon atoms, the graph of $F^2(h)$ for hard spheres will

demonstrate a certain periodicity not found in the corresponding curve for argon, as is seen in Fig. 18.

Let us now consider an ensemble of hard spheres and an ensemble of argon atoms. The effects of interparticle interferences, which must be taken into account, will be determined in real space in terms of the potential $\Phi(r)$ associated with the forces acting between two particles
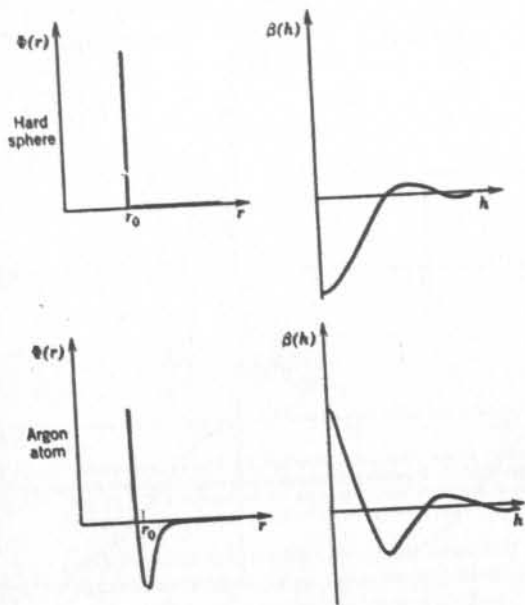

Fig. 19. Schematic curves of $\Phi(r)$ and $\beta(h)$ for hard spheres and for argon atoms. The argon interaction potential is the more uneven, so its function $\beta(h)$ has the more marked periodic character.

separated by a distance r. We have previously shown that the influence of $\Phi(r)$ is felt through the intermediary of a function $\beta(h)$, which is defined as the Fourier transform of $\alpha(r)$, where $\alpha(r) = e^{-\Phi(r)/kT} - 1$. Thus we can say immediately that, since the curve of $\Phi(r)$ with respect to argon is the most uneven, the function $\beta(h)$ of argon will have the more marked periodic character. This is shown in Fig. 19.

The scattered intensity is found by combining the functions $F^2(h)$ and $\beta(h)$ (see §2.2.3.2). The above discussion shows why the secondary

maxima from argon are due almost entirely to interparticle effects, whereas form and internal structure are the predominant factors for the case of hard spheres.

2.2.4. PARTICLES UNRESTRICTED BY HYPOTHESES H_1 AND H_2

We have assumed from the beginning of §2.2 that the scattering matter being examined satisfies hypotheses H_1 and H_2. We should like now to remove these restrictions. If the details of the calculations which led to equation 47 are considered, it is seen that the second part of our hypothesis—that which excludes all possible relations between relative positions and probabilities of orientations of particles (i.e., all possible relations between positions and structure factors)—has enabled us to calculate the averages by describing the average of the factor

$$\sum_{k} \sum_{j \neq k} F_k(\mathbf{h}) F_j(\mathbf{h}) \cos (\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j))$$

as the product of the averages of $F_k(\mathbf{h})$, $F_j(\mathbf{h})$, and $\cos(\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j))$. The first part of hypothesis H_1 gave knowledge of the average of $F(\mathbf{h})$, which was convenient for our considerations.

We should like now to try to consider the general problem in order to determine the characteristic magnitudes that are involved in this question.

The general relation, equation 46, shows that only information *relative to pairs of particles* is necessary. Thus it is sufficient to define the statistical correlations existing between two particles. We shall describe these by means of the development offered by Fournet [48]:

$p_1(F, \mathbf{h})$ designates the *a priori* probability density function of the scattering factor F of a particle for a scattering angle corresponding to $\mathbf{h}$. We shall assume this function to be identical for all particles. If we have no information concerning the surroundings of a particle, the probability that its scattering factor for a given value of $\mathbf{h}$ is contained between the values F_0 and $F_0 + dF_0$ is equal to $p_1(F_0, \mathbf{h}) dF_0$.

$p_2(F_j, F_k, \mathbf{r}, \mathbf{h})$ designates the probability density function of the scattering factor F_j of a jth particle for a scattering angle corresponding to $\mathbf{h}$ when it is known that the scattering factor for the same angle of a kth particle has a value F_k, where $\mathbf{R}_k - \mathbf{R}_j = \mathbf{r}$. As a consequence of the indistinguishability of particles, p_2 must be the same for the same vector $\mathbf{r}$, regardless of the position of the center of the kth particle.

There is no contradiction in stating that the probability density p_1 is the same for all particles, while defining p_2 as has been done above, if it is realized that the function p_2 concerns ensembles of factors F_k and F_j,

whereas p_1 governs the factor F_k or F_j, considered by itself. The relation between p_1 and p_2 can be expressed as

$$\int_0^\infty p_2(F_j, F_k, r, h)p_1(F_k, h) \, dF_k \equiv p_1(F_j, h) \tag{80}$$

Now let us consider the intensity of radiation scattered by an ensemble of identical, arbitrarily shaped particles,

$$I(h) = I_e(h)\overline{\sum_k \sum_j F_k(h)F_j(h) \cos(h \cdot (R_k - R_j))} \tag{81}$$

We can group separately the terms for which $k = j$. An analogous problem has been treated in §2.1.2, in which the result for the sum of these terms was shown to be

$$I_e(h)\overline{N} \; \overline{F^2(h)} = I_e(h)\overline{N} \int_0^\infty F^2 p_1(F, h) \, dF$$

In the general term of equation 81 for which $k \neq j$ there are found three types of variables:

1. The scattering factor F_k (F_j is related to F_k by means of the functions p_2).
2. The angle $\measuredangle h(R_k - R_j)$.
3. The distance $|R_k - R_j|$.

In order to evaluate the group of terms for which $k \neq j$ we shall perform successive integrations over each of these variables.

Average of the Variable F_k

Let us consider first only the functions F_k as variables. The group of terms of equation 61 for which $k \neq j$ can now be written as

$$\sum_k \sum_{j \neq k} \left\{ \cos(h \cdot (R_k - R_j)) \int_0^\infty F_k p_1(F_k, h) \int_0^\infty F_j p_2(F_j, F_k, r, h) \, dF_j \, dF_k \right\} \tag{82}$$

We shall assume that correlation between values of the scattering factors does not occur for large distances of separation; the knowledge of F_k gives no information about F_j if $|R_k - R_j|$ is large compared to nearest neighbor distances.

It now follows that $p_2(F_j, F_k, r, h)$ tends toward the function $p_1(F_j, h)$ for large r. Thus it is useful to express the quantity p_2 as

$$p_2(F_j, F_k, r, h) = p_1(F_j, h) - \{p_1(F_j, h) - p_2(F_j, F_k, r, h)\} \tag{83}$$

On replacing p_2 by this expression, equation 82 breaks down into two terms:

First term: This term describes the scattering when the structure factors F_k and F_j follow the same law of probability, independent of one another. We have already solved an analogous problem (§2.2.1.2), which gave as a result

$$\overline{F(h)}^2 \left\{ \sum_k \sum_{j \neq k} \cos(h \cdot (R_k - R_j)) \right\}$$

where

$$\overline{F(h)} = \int_0^\infty F p_1(F, h) \, dF$$

Second term: This term is of the form

$$-\sum_k \sum_{j \neq k} \{b(r, h) \cos(h \cdot (R_k - R_j))\}$$

where

$$b(r, h) = \int_0^\infty \int_0^\infty F_k p_1(F_k, h)\{p_1(F_j, h) - p_2(F_j, F_k, r, h)\}F_j \, dF_j \, dF_k \tag{84}$$

The bracketed term in the integrand approaches zero when $|r|$ becomes large, and consequently the function $b(r, h)$ behaves in the same manner. Thus in evaluating this second term we can neglect boundary effects and treat the summation over the index j as independent of k:

$$-\sum_k \sum_{r \neq 0} b(r, h) \cos(h \cdot r)$$

where the sum extends over all vectors r which exist in the sample (except $r = 0$). The sum over k then results simply in multiplying this result by the average number of particles. The final expression for the scattered intensity is then

$$\overline{I(h)} = I_e(h)\overline{N}\left\{ \overline{F^2(h)} - \sum_{r \neq 0} b(r, h) \cos(h \cdot r) \right\}$$
$$+ I_e(h)\overline{F(h)}^2 \left\{ \sum_k \sum_{j \neq k} \cos(h \cdot (R_k - R_j)) \right\} \tag{85}$$

or

$$\overline{I(h)} = I_e(h)\overline{N}\left\{ [\overline{F^2(h)} - \overline{F(h)}^2] - \sum_{r \neq 0} b(r, h) \cos(h \cdot r) \right\}$$
$$+ I_e(h)\overline{F(h)}^2 \sum_k \sum_j \cos(h \cdot (R_k - R_j)) \tag{86}$$

Average with Respect to the Angle $\measuredangle h(R_k - R_j)$

Keeping the magnitudes of the distances fixed, let us assume that all orientations of the vector r are equally probable. The function p_2 then depends only on the distance r between centers k and j. The terms in $\cos(h \cdot r)$ on averaging will then be replaced by terms in $\sin hr/hr$ (a

calculation illustrated several times, viz., equation 7). The resulting expression for the intensity is

$$\overline{I(\mathbf{h})} = I_e(h)\overline{N}\left\{[\overline{F^2(\mathbf{h})} - \overline{F(\mathbf{h})}^2] - \sum_{r \neq 0} b(r, \mathbf{h}) \frac{\sin hr}{hr}\right\}$$

$$+ I_e(h)\overline{F(\mathbf{h})}^2 \sum_k \sum_j \frac{\sin hr_{kj}}{hr_{kj}} \tag{87}$$

Average with Respect to Distance r

For this final averaging we proceed as in §2.2.1.3, defining a function $P(r)$ which is related to the probability of finding the centers of two different particles at a distance r. When no external field is applied, all orientations of a vectorial distance $\mathbf{r}$ are equally probable, so that we can begin with equation 87, modified only so that the term $-\overline{N}I_e(h)\overline{F(\mathbf{h})}^2$ is included in the double sum over k and j. Analogous problems have already been treated in §2.2.1.4.

The summations of equation 87 must be replaced by integrations, taking into account the probability of realization of the different distances, r. By replacing $P'(r)$ with $1 - [1 - P(r)]$ and considering only angles for which $h > h_0$ (§2.2.1.4), only the term in $[1 - P(r)]$ need be considered in the third term of equation 87. This reasoning cannot be applied to the second term of equation 87, since $b(r, \mathbf{h})$ tends to zero as r becomes large. The final expression is thus (Fournet [48])

$$\overline{I(\mathbf{h})} = I_e(h)\overline{N}\left\{\overline{F^2(\mathbf{h})} - \frac{\overline{F(\mathbf{h})}^2}{v_1}\int_0^\infty [1 - P(r)]\frac{\sin hr}{hr} 4\pi r^2\, dr\right.$$

$$\left. - \frac{1}{v_1}\int_0^\infty P(r)b(r, \mathbf{h})\frac{\sin hr}{hr} 4\pi r^2\, dr\right\} \tag{88}$$

The first two terms of this expression are identical to those derived on the assumption of complete independence between the orientations and the positions of the particles. The term in $b(r, \mathbf{h})$ thus appears as a corrective term, necessary for the description of the general case.

The complete expression, equation 88, must be used, for example, in calculating the intensity scattered by a dense ensemble of identical ellipsoids of axes $2R$, $2R$, and $2\nu R$. The scattering factor of an ellipsoid for a given scattering angle, 2θ, depends on the orientation of the ellipsoid. If it is known that the distance between the centers of two ellipsoids is $2R$, the axes of these ellipsoids cannot be oriented in a completely arbitrary manner, and, consequently, their scattering factors must be related. We can see by this example how a relation between scattering factors

F_k and F_j and the distance between their centers can be introduced. It is this dependence which introduces the supplementary term in equation 88.

We have just seen that in the general case, in which the orientations and the positions of particles are related, the expression for the scattered intensity contains *two characteristic functions, $P(r)$ and $b(r, \mathbf{h})$. This makes it impossible to determine separately these characteristic functions from the experimental curve of $\overline{I(h)}$.* Equation 88 can serve only to predict intensities for certain models.

To proceed further it would probably be necessary to introduce thermodynamic considerations, defining a potential energy of interparticle forces not as a function $\Phi(r)$ but rather as $\Phi(r, \varphi)$, where at least one angular variable is necessary, and then relating the functions $P(r)$ and $b(r, \mathbf{h})$ to this potential. This problem has not yet been undertaken.

Remarks

In establishing equation 86 we have allowed only the structure factors to undergo variations, so that a simple interpretation can be given to this equation by applying it to a study of crystals and neglecting thermal effects.

The third term of equation 86 represents the intensity scattered by the sample under inspection, if it is supposed that all the scattering centers are identical, with scattering factors $F(\mathbf{h})$. The first term varies only slowly with h, while the second term can present intensity maxima that will probably be less sharp than those created by the third term. From this we can see the essential role of the function $b(r, \mathbf{h})$, a function that is analogous to the Patterson distribution function for crystal structure analyses. If we assume that each of the three intensity terms can be separated, all the information obtainable from experiments will be contained in the function $b(r, \mathbf{h})$.

In the study of crystals it is often assumed that the structure factors of different atoms all follow the same law, $F(h)$, the magnitudes depending on a coefficient equal to the atomic number Z of the atom considered. If we assume this to be true, all the formulas we have developed can be considerably simplified, for the functions p_1 and p_2 can be treated as being functions uniquely of the Z_k.

The function $b(\mathbf{r}, \mathbf{h})$ becomes

$$b(\mathbf{r}, \mathbf{h}) = b(\mathbf{r}, h) = F^2(h)\sum_k \sum_j Z_k p_1(Z_k)[p_1(Z_j) - p_2(Z_j, Z_k, \mathbf{r})]Z_j$$

$$= F^2(h)c(\mathbf{r})$$

The final result is then (Fournet [48])

$$\overline{I(\mathbf{h})} = I_e(h)\overline{N} F^2(h)\{[\overline{Z^2} - \overline{Z}^2] - \sum_{r \neq 0} c(\mathbf{r}) \cos (\mathbf{h} \cdot \mathbf{r})\}$$

$$+ I_e(h)F^2(h)\overline{Z}^2 \sum_k \sum_j \cos (\mathbf{h} \cdot (\mathbf{R}_k - \mathbf{R}_j)) \tag{89}$$

The function $c(\mathbf{r})$ can always be calculated from any given model. We have employed this technique in the recalculation of the scattering by a linear model of an alloy with partial short-range order, a model first studied by Guinier and Griffoul (1948). We quickly obtained the same results as those given by these authors.

Equation 86 can be easily used to obtain the intensities scattered by more complicated models. This equation, a particular case of which has been given by

Mac Gillavry and Strijk (1946), can be viewed as a generalization of the expression obtained by von Laue (1941) in considering completely disordered metallic solid solutions, in which all scattering centers were assumed to follow independently the same law. When bound by this assumption, p_k is equal to p_1 and the function $b(\mathbf{r}, \mathbf{h})$ becomes identically zero. The second term of equation 86 disappears and, on noting that the two types of atoms, A and B, are present in proportions p_A and p_B the Laue equation is obtained:

$$\overline{F^2} - \bar{F}^2 = p_A F_A{}^2 + p_B F_B{}^2 - (p_A F_A + p_B F_B)^2$$
$$= p_A p_B (F_A - F_B)^2$$

2.3. SCATTERING BY GROUPS COMPOSED OF SEVERAL TYPES OF PARTICLES

This problem is quite complicated, and the few equations that can be derived have not yet been employed in experimental studies.

2.3.1. GENERAL THEORY

Simple calculations, in every way analogous to those which have been developed in §2.2.1.4, give the following relation for the scattered intensity (Fournet [48]):

$$I(h) = I_e(h)\bar{N} \left\{ \sum_k p_k \overline{F_k{}^2(h)} \right.$$
$$\left. + \sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)} \frac{1}{v_1} \int_0^\infty [P_{kj}(r) - 1] \frac{\sin hr}{hr} \, 4\pi r^2 \, dr \right\} \quad (90)$$

where $F_k(h)$ designates the structure factor of the particle of type k; p_k, the probability that one of the $\bar{N}$ particles is of the type k; v_1, the average volume offered to each particle, regardless of its type; and $P_{kj}(r)$, a probability function analogous to the function $P(r)$ defined in §2.2.1.3, which applies to a pair of particles of type k and j. Evidently

$$P_{kj}(r) = P_{jk}(r)$$

This general expression can best be appreciated by comparing it with equation 53, the expression applicable to an ensemble of identical particles. From the first terms we obtain

$$\overline{F^2(h)} = \sum_k p_k \overline{F_k{}^2(h)}$$

while from the second terms

$$\overline{F(h)}^2 = \sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)}$$

and

$$\overline{F(h)}^2 P(r) = \sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)} P_{kj}(r)$$

By a simple substitution we now find

$$P(r) = \frac{\sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)} P_{kj}(r)}{\sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)}}$$

which demonstrates that in the general case a function equivalent to $P(r)$ but dependent on the single variable r does not exist.

It is equally impossible to obtain information by means of a Fourier transformation. Equation 90 can be written in the form

$$\frac{I(h)}{I_e(h) \bar{N}} - \sum_k p_k \overline{F_k{}^2(h)} = \sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)} \frac{1}{v_1} \int_0^\infty [P_{kj}(r) - 1] \frac{\sin hr}{hr} \, 4\pi r^2 \, dr$$

The right side of the equation depends on the variable h not only in the term $\sin hr/hr$ but also in $\overline{F_k(h)}$ and $\overline{F_j(h)}$, and this prevents the effective application of a Fourier transformation. Results can be obtained by this technique only if the assumption is made that $F_k(h) = a_k f(h)$, that is, that the functions $F_i(h)$ differ only by a constant factor. On making this assumption, we find

$$\frac{I(h)}{I_e(h) \bar{N}} - f^2(h) \sum_k p_k a_k{}^2 = f^2(h) \sum_k \sum_j p_k p_j a_k a_j \frac{1}{v_1} \int_0^\infty [\overline{P(r)} - 1] \frac{\sin hr}{hr} \, 4\pi r^2 \, dr$$
$$(91)$$

with
$$\overline{P(r)} = \frac{\sum_k \sum_j p_k p_j a_k a_j P_{kj}(r)}{\sum_k \sum_j p_k p_j a_k a_j} \quad (92)$$

from which the function $\overline{P(r)}$ can easily be obtained by means of a Fourier transformation.

With the exception of this case, which itself would be hard to interpret, it is difficult to use equation 90 without supplying some model.

2.3.2. WIDELY SEPARATED PARTICLES

When the concentration of scattering matter becomes small equation 90 reduces to the following form:

$$I(h) = I_e(h)\bar{N} \sum_k p_k \overline{F_k{}^2(h)} \quad (93)$$

which describes the total intensity as being given simply by the addition of the intensities scattered by each of the different types of particles, each

weighted by its respective probability. On expressing each $\overline{F_k{}^2(h)}$ by the approximate law of Guinier (equation 39), equation 93 becomes

$$I(h) = I_e(h)\overline{N} \sum_k p_k n_k{}^2 \left[1 - \frac{h^2 R_{0k}{}^2}{3} + \cdots \right]$$

$$= I_e(h)\overline{N}[\sum_k p_k n_k{}^2] \left[1 - \frac{h^2}{3} \frac{\sum_k p_k n_k{}^2 R_{0k}{}^2}{\sum_k p_k n_k{}^2} + \cdots \right] \qquad (94)$$

This relation shows that the total curve can still be represented by an exponential function if the Guinier approximation is valid for all of the individual particles, particularly those that are the largest.

These conditions are rarely satisfied in practice. Thus, it is more interesting to consider the tails of the scattering curves. The principal part of the curve of $\overline{F_k{}^2(h)}$ at large values of h for a homogeneous particle of density ρ_k and external surface S_k is given by the function $(2\pi\rho_k{}^2 S_k)/h^4$ (equation 26). The extra terms acting as damped oscillations contain the functions $\cos h R_{1k}$ and $\sin h R_{1k}$, where R_{1k} is the maximum dimension of the kth particle. When the curves for a large number of particles of different dimensions are added together, it is probable that *the sum of the oscillating terms will be zero*. In fact, such oscillations have never been observed on a scattering curve unless the particles of the sample were extremely uniform in size (Fig. 16). The asymptotic behavior of the observed curve is then

$$I(h) = I_e(h)\overline{N}[\sum_k p_k \rho_k{}^2 S_k] \frac{2\pi}{h^4} \qquad (95)$$

This shows that, for a given angle within the domain of validity of equation 26, *the scattered intensity is proportional to the total surface of the group of diffracting particles* if all particles have the same electronic density.

In this discussion we have assumed that the particles were separated sufficiently so that there were no interparticle interferences. In §2.4.3 we shall see that equation 95 is also valid for the case of *packed* powders.

2.3.3. INFLUENCE OF THE CLOSER PACKING OF PARTICLES

Evidently one can try to effect the same sort of generalization of equation 90 as was done with equation 53, the equation of the scattering relative to a single species of particle. The first step is to generalize the theory of Born and Green (Fournet [51], and Rushbrooke and Scoins

(1951)) so as to allow the consideration of this case. The general expression can be obtained in placing

$$P_{kj}(r) = e^{-\frac{\Phi_{kj}(r)}{kT} + f_{kj}(r)}$$

Next the functions $g(h)$ and $\beta(h)$ are defined as

$$h g_{kj}(h) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} r f_{kj}(r) \sin hr \, dr$$

$$h \beta_{kj}(h) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} r(e^{-\Phi_{kj}(r)/kT} - 1) \sin hr \, dr$$

These two functions are connected by the set of relations

$$\frac{v_1}{(2\pi)^{3/2}} g_{kj}(h) = \sum_i p_i \{g_{ki}(h) + \epsilon_{ki}\beta_{ki}(h)\} \epsilon_{ij}\beta_{ij}(h)$$

where the ϵ_{jk} designates a mean value of $(f_{jk}(r) + 1)$ near the origin, $r = 0$.

With the introduction of these functions, equation 90 becomes

$$I(h) = I_e(h)\overline{N} \left\{ \sum_k p_k \overline{F_k{}^2(h)} + \frac{(2\pi)^{3/2}}{v_1} \sum_k \sum_j p_k p_j \overline{F_k(h)} \, \overline{F_j(h)} [g_{kj}(h) + \epsilon_{kj}\beta_{kj}(h)] \right\}$$

$$(96)$$

The scattered intensity then depends only on the functions $F_k(h)$ and $\beta_{kj}(h)$, since the $g_{kj}(h)$ are expressible in terms of the $\beta_{lm}(h)$. We have given the complete expression for the intensity scattered by ensembles of two types of spherically symmetric particles in another article (Fournet [48]). This complicated equation was applied to *mixtures of homogeneous spheres of the same matter but of radii R and 2R*; the curves representing the variation of scattered intensity as a function of angle are given in Fig. 20. Two parameters were included in the calculation: k, the ratio of the volume occupied by the particles to the total volume offered them; and x, the ratio of the mass of smaller particles to the total mass of the particles. Short-dashed curves correspond to $k = 0.5$, long-dashed curves to $k = 0.125$, and full-line curves to the case of infinitely separated particles.

For each concentration, x per cent, the curves have been normalized so that the ordinate at $h = 0$ is equal to unity. The essential feature of the curves is that *for constant k, the intensity curves are more sharply varying, the more homogeneous the mixture.*

We believe that this statement is generally true; it is difficult to conceive of a not too compact heterogeneous mixture manifesting a
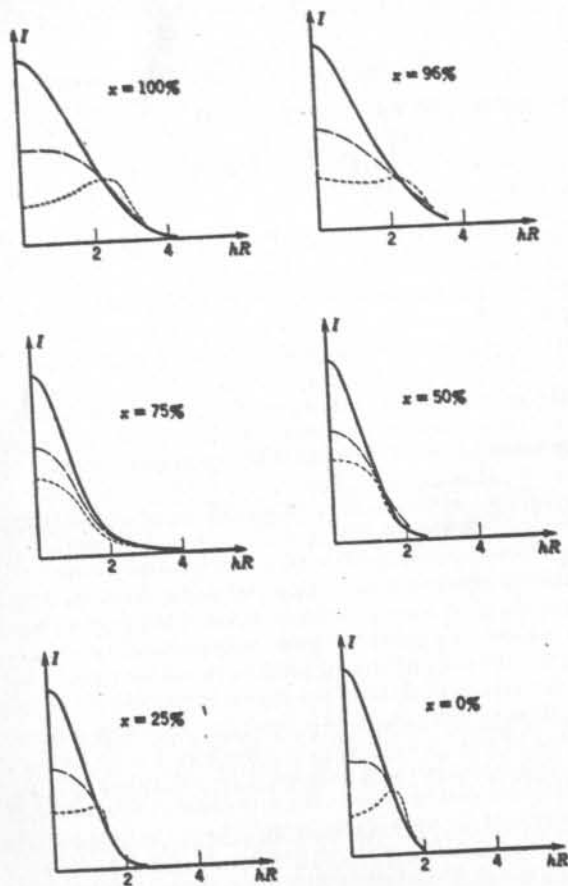
Fig. 20. Scattered intensity from mixtures of spheres of radii R and $2R$. The parameter x denotes the ratio of the mass of the small spheres to the total mass of the mixture, and k represents the ratio of the effective volume of the spheres to the volume occupied by the mixture. ———, $k = 0$; — — —, $k = 0.125$; – – – – , $k = 0.500$.

reasonable degree of order. In our model, the curve for $k = 0.5$ possesses a maximum only if the mass of smaller particles represents more than 95 per cent or less than 25 per cent of the total mass.

We must remark that this model was based on spherical particles, and that consequently there was a favorable opportunity for observing intensity maxima. In generalizing the conclusion drawn from a study of this example, it thus would be a temptation to state: *in a mixture of non-identical particles of arbitrary forms and with random distribution (no long-range order) it is improbable that the packing of particles will lead to large changes in the scattering curves and that thus the laws for widely separated particles can furnish the orders of magnitude of the scattering phenomena.*

This idea is in agreement with the calculations of Hosemann [81], [84], who showed that, for arbitrary particles and conveniently chosen functions $P_{kj}(r)$, the packing of the particles caused little change in the distribution of scattered intensity. We refer the reader to these works for the details of the calculations and results.

Conclusions contrary to these have been given by Kratky and Porod [108], [137], in considering the influence of packing on an ensemble of heterogeneous particles. However, they considered uniquely a *linear model* composed of a series of parallel plates of different thicknesses situated at variable distances from one another. In the limiting case the space is completely occupied by the plates, causing the central scattering at observable angles to disappear entirely. The packing of particles thus creates notable changes in the distribution of scattered intensity. We believe that this is a result which depends on the *linear character* of the model.

2.4. GENERAL CASE

There are often substances which give rise to strong small-angle scattering that cannot be described as a group of well-defined particles arranged in a more or less close-packed fashion. This is true, for example, of matter which displays submicroscopic porosity, such as activated carbon. The physical characteristic that can accurately define these substances is the electronic density $\rho(\mathbf{x})$ found at the point defined by the vector $\mathbf{x}$. The intensity scattered by such a substance is then given by the general relation

$$I(\mathbf{h}) = I_e(h) \left[\int_V \rho(\mathbf{x}) e^{-i\mathbf{h}\cdot\mathbf{x}} \, d\mathbf{x} \right]^2 \qquad (97)$$

V being the volume irradiated by the X-rays. It is well known that it is not possible to determine $\rho(\mathbf{x})$ from the experimental data. Indeed,

low-angle scattering experiments made with different samples taken from a given material give the same experimental curve. Thus it is obvious that the central scattering depends on some statistical property of $\rho(x)$ that defines the state of heterogeneity or porosity of the substance. It is particularly interesting to try to determine the general characteristics that are necessary for the production of an observable scattering at small angles. When considered in this general form, the problem presents special difficulties; we shall first discuss these difficulties and then present the results of the attempts that have been made in this field.

2.4.1. LIMITING VALUE OF THE SCATTERED INTENSITY AT VERY SMALL ANGLES

The property we shall try to calculate is the "experimental" limit of the scattered intensity as the scattering angle tends to zero, that is, the
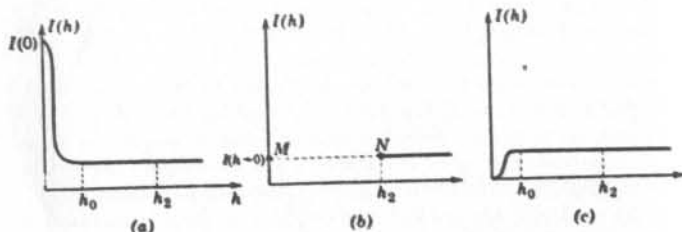
Fig. 21. (a) Schematic representation of a real scattered intensity distribution. (b) The observable intensity and its extrapolated value at $h = 0$. (c) A possible result for a calculated intensity distribution.

intensity that can be obtained by extrapolation of the results of measurements which, as will be seen later, cannot be extended to angles smaller than several minutes of arc, even with the most perfect experimental system.

Let us recall some results of our discussion of an ensemble of particles. The curve of the scattered intensity shows a very important singularity in the neighborhood of $h = 0$, since for extremely small values of h the amplitudes of the waves scattered by all the electrons in the scatterer add together and the scattered intensity approaches the value,

$$I(0) = I_e(0)n^2\overline{N^2} \tag{98}$$

The width of this central peak, defined by the parameter h_0 (see Fig. 21a), depends on the dimensions of the volume V explored by X-rays and is smaller by several orders of magnitude than the minimum observable angle.

A correct calculation of the desired "limiting intensity" should give a formula which reproduces the real curves down to a value of h equal to h_2, the experimental limit, and then, eliminating the central peak, remains practically independent of h (Fig. 21b) in the range between h_2 and 0. This, for example, is the result obtained in the calculations of §2.2.3.3, which pertained to the particular case of an ensemble of particles contained in a volume V_0 large with respect to the volume V of the scatterer explored by the X-rays. The result of this calculation gave

$$I(h \to 0) = I_e(0)n^2(\overline{N^2} - \overline{N}^2) \tag{72}$$

Frequently it can happen that, in trying to eliminate the central peak, a term will be discarded in the course of the calculation which will bring about a marked change in the curve, such as that depicted in Fig. 21c. Such a formula does not give correctly the limiting value of the intensity when h is made equal to zero. It can be quite correct for $h > h_0$, but it will not be useful, since the intensity cannot be easily calculated if h is non-zero.

In the case of an ensemble of particles, the intensity $I(0)$ for $h = 0$ is of the order of $\overline{N^2}$, while the limiting value should be of the order of $\overline{N^2} - \overline{N}^2$, that is, of the order of $\overline{N}$. (This limit is exact for the case of ideally separated particles, viz., equation 55.) Thus we see that in the region of very small angles the limiting intensity, which will be expressed as the difference between the exact expression for the intensity and another term which must be made more definite, is of the order of $1/N$ times the actual intensity. This order of magnitude indicates immediately *the rigor and exactness that must be maintained in all phases of the calculations.*

As an illustration of the effects of a slight inexactness, let us reconsider the reasoning that we have developed in §2.2.1.3 and §2.2.1.4. We have assumed that the volume V_0 is large with respect to the volume V. If we vary V_0 (and thus N_0, the total number of particles), keeping V and v_1 constant, equation 72 predicts a limiting intensity of zero when $V_0 = V$; this is then a good example of the type of curve represented in Fig. 21c.

In order to obtain a relation which will more accurately describe this case, the manner in which the function $P(r)$ was introduced must be reviewed, noting specifically that the probability $p_{kj} dv_k dv_j$ is defined by the relation

$$p_{kj} dv_k dv_j = \frac{N_0}{V_0} dv_k \frac{N_0 - 1}{V_0 - dv_k} P(r_{kj}) dv_j$$

The infinitesimal volume element, dv_k, is always negligible as compared with V_0, but *this cannot always be said for the comparison of unity with respect to N_0, particularly when V and V_0 are approximately equal* (and,

thus, N and N_0). On reconsidering the complete calculation, beginning with the relation

$$p_{hj}\, dv_k\, dv_j = \frac{dv_k}{v_1}\frac{dv_j}{v_1}\frac{N_0-1}{N_0}\, P(r_{kj})$$

we obtain as an expression for the observable intensity (cf. equation 53)

$$\overline{I(h)} = I_e(h)\overline{N}\left\{\overline{F^2(h)} - \overline{F(h)}^2\frac{1}{v_1}\frac{N_0-1}{N_0}\int_0^\infty [1-P(r)]\frac{\sin hr}{hr}4\pi r^2\, dr\right\} \quad (99)$$

In the limit as $h \to 0$, we then find

$$\frac{v_2(0)}{v_1} = \frac{N_0}{N_0-1} - \frac{\overline{N^2}\dfrac{N_0}{N_0-1} - \overline{N}^2}{\overline{N}}. \quad (100)$$

which gives as an expression for the limiting value of the observable intensity (Fournet [48])

$$I(h \to 0) = I_e(0)n^2\left[(\overline{N^2} - \overline{N}^2) + \frac{\overline{N}^2}{N_0}\right]$$

$$= I_e(0)a^2\left[\overline{N^2} - \overline{N}^2 + \overline{N}\frac{V}{V_0}\right] \quad (101)$$

The factor $(\overline{N^2} - \overline{N}^2)$ is of the order of $\overline{N}$, so that, when V/V_0 is small with respect to unity, equation 101 is to a first approximation equivalent to our earlier result, equation 72. The advantage of equation 101 is that a reasonable result is permitted in the case for which $V = V_0$.

$$I_{V=V_0}(h \to 0) = I_e(0)n^2N$$

We can see by this example how approximations which at first sight are quite logical can completely upset the results of this type of calculation.

We have defined the limiting intensity by an extrapolation of a part of the curve of Fig. 21b, but we have not yet determined whether this quantity has any physical meaning. We know, for example, that the actual curve has a shape which depends on the form of the sample, whereas the limiting intensity should depend only on the statistical properties of the distribution of scattering centers in the sample. It is not obvious that the operation of extrapolation as described should lead to such a result. In any event, we have not yet clearly defined a criterion for the determination of the extrapolated part of the curve (part MN of Fig. 21b). Questions such as these form the obstacles encountered when an attempt is made to resolve the problem of low-angle scattering as calculated from the electronic density function.

As a first approach, let us offer without real proof a qualitative

treatment; then we shall present the solution given by Debye and Bueche [322] and that of Porod [137] for a more particular case.

We want to calculate the scattered intensity for a value h_2 near the minimum observable angle (for example, $2\theta = 1'$). Let us divide the irradiated volume V into a series of M equal volumes, $v_1, v_2, \cdots v_m$, where each volume is of the order of $\left(\frac{2\pi}{h_2}\right)^3$. (In the example chosen, $v_i \approx 1\mu^3$ for Cu $K\alpha$ radiation; this is still small with respect to the volume V which is of the order of $1\,\text{mm}^3$. in ordinary experiments.) The amplitude of the radiation scattered by the volume element v_i is then $A_i(h)$. We shall assume that there will be negligible interference effects among the waves scattered by the different volume elements when $h > h_2$; this hypothesis is reasonable for the phase difference between waves will always be much larger than 2π since the centers of the volumes are separated by distances greater than $2\pi/h_2$. Consequently a very probable value for the total intensity is simply the sum of the elementary intensities, $I = \sum_i |A_i|^2$. In other words, the observed intensity is effectively M times the average intensity scattered by an elemental volume. This result is analogous to that for the problem of a variable number of particles, N, in a volume V (§2.2.3.3), except that the observed intensity is determined by an average over space instead of an average over time as N fluctuates in a constant volume V.

Thus by analogy we are led to the following description of the limiting observed scattered intensity. It is proportional to the mean square fluctuation in the number of electrons in the volume v_i, and will be zero if the number of electrons in the different volumes v_i is fixed. If ρ_i is the electronic density of the volume v_i and $\bar{\rho}$ is the average density as determined by all the volume elements, the observed scattered intensity will be proportional to

$$M\frac{V^2}{M^2}\overline{(\rho_i - \bar{\rho})^2} = V\overline{v_i(\rho_i - \bar{\rho})^2} \quad (102)$$

The volumes $v_i = V/M$ do not really intervene as such, since the mean square fluctuation is inversely proportional to the volume v_i, but their consideration is essential in determining the magnitude of the volume to be used in the calculation of ρ_i.

Equation 102 shows that the *limiting low-angle scattering is a consequence of the heterogeneities in the scattering medium*, but it also allows for the stipulation that this heterogeneity must exist on a scale of several tens to several thousand angstroms if the scattering is to be observable. Let us give several examples of the application of this simple rule. The fact

that matter is formed of atoms instead of being continuous is not a cause of low-angle scattering since the corresponding density fluctuations are averaged out in a volume of the order of $1\mu^3$. A lattice with periodic perturbations of density (for example, a period of the order of 50 A) is heterogeneous, but it produces no small-angle scattering since the volume v_i contains a large number of periods, and hence the average density in this volume is approximately constant.

A typical case is offered by the Al–Ag alloy that will be studied further in §6.4.3.1. The silver atoms assemble themselves into spherical clusters while remaining on the sites of the solid solution lattice. Around these clusters is left a spherical shell lacking in silver. The shell diameter is of the order of 50 A, and a large number of these clusters are randomly distributed throughout the solid solution.

This alloy gives a pattern of central scattering containing a diffuse ring whose radius corresponds to a Bragg distance of the order of 25 A, but *the scattered intensity decreases toward the center*, and careful measurements show that it approaches zero. If the small silver clusters exist in the average solid solution without being accompanied by the shell-like regions lacking in silver, only a normal central scattering is observed. Equation 102 furnishes the explanation of these facts. In the first case the cluster contains a number of excess atoms which is just the number of atoms lacking in the shell-like region. The volumes v_i in which the densities ρ_i should be examined are large with respect to the cluster dimensions; thus they contain the same number of silver atoms as they would if the solution were homogeneous. On this scale there are no electronic density fluctuations and the intensity scattered at the center should be zero. If there is no spherical shell around these clusters, these clusters will play the role of particles with an electronic density different from that of the surrounding medium; if the clusters are distributed at random in the solid solution and are not too closely packed, they give rise to a central scattering which is characteristic of their size.

2.4.2. CALCULATION OF THE SCATTERED INTENSITY AS A FUNCTION OF $\rho(\mathbf{x})$

We shall now briefly present the solution of Debye and Bueche [322]. These authors define a function $\eta(\mathbf{x})$ by means of the relation

$$\rho(\mathbf{x}) = \rho_0 + \eta(\mathbf{x})$$

where ρ_0 designates the average density of the substance. We can then write

$$\int \eta(\mathbf{x})\, d\mathbf{x} = 0$$

By means of equation 97 we can immediately write the expression for the scattered intensity as (cf. §2.1.1)

$$I(\mathbf{h}) = I_e(h) \int_V \int_V [\rho_0 + \eta(\mathbf{x}_k)][\rho_0 + \eta(\mathbf{x}_j)] e^{-i\mathbf{h}\cdot(\mathbf{x}_k - \mathbf{x}_j)}\, d\mathbf{x}_k\, d\mathbf{x}_j$$

Recognizing the difficulties discussed previously, we shall take account of more details in our calculation than was done by the original authors. We will divide the intensity expression into the four terms corresponding respectively to terms in ρ_0^2, $\rho_0\eta(\mathbf{x}_k)$, $\rho_0\eta(\mathbf{x}_j)$, and $\eta(\mathbf{x}_k)\eta(\mathbf{x}_j)$ and consider each term separately.

First term:

$$I_1(\mathbf{h}) = I_e(h)\rho_0^2 \int_V \int_V e^{-i\mathbf{h}\cdot(\mathbf{x}_k - \mathbf{x}_j)}\, d\mathbf{x}_k\, d\mathbf{x}_j$$

We have already studied analogous terms (p. 34) and have seen that they correspond to intensities that are practically zero for all observable angles, since V is the order of 1 mm³.

Second and third terms: Since the second and third terms are complex conjugates, we can write

$$I_2(\mathbf{h}) + I_3(\mathbf{h}) = 2\mathrm{Re}\left\{ I_e(h)\rho_0 \int_V \eta(\mathbf{x}_k)\, d\mathbf{x}_k \int_V e^{-i\mathbf{h}\cdot(\mathbf{x}_k - \mathbf{x}_j)}\, d\mathbf{x}_j \right\}$$

or

$$I_2(\mathbf{h}) + I_3(\mathbf{h}) = 2 I_e(h)\,\mathrm{Re}\left\{ \int_V \eta(\mathbf{x}_k) e^{-i\mathbf{h}\cdot\mathbf{x}_k}\, d\mathbf{x}_k \int_V \rho_0 e^{i\mathbf{h}\cdot\mathbf{x}_j}\, d\mathbf{x}_j \right\}$$

Therefore

$$I_2(\mathbf{h}) + I_3(\mathbf{h}) < 2 I_e(h)\, |A_1^*(\mathbf{h})|\cdot\left|\int_V \eta(\mathbf{x}) e^{-i\mathbf{h}\cdot\mathbf{x}}\, d\mathbf{x}\right|$$

The first factor $|A_1^*(\mathbf{h})|$ is the modulus of the amplitude from which $I_1(\mathbf{h})$ is derived. As we shall see below, the second factor is just the modulus of $A_4(\mathbf{h})$, the amplitude corresponding to the fourth term. Therefore I_2 and I_3 as well as I_1 are negligible as compared with I_4.

Fourth term:

$$I_4(\mathbf{h}) = I_e(h) \int_V \int_V \eta(\mathbf{x}_k)\eta(\mathbf{x}_j) e^{-i\mathbf{h}\cdot(\mathbf{x}_k - \mathbf{x}_j)}\, d\mathbf{x}_k\, d\mathbf{x}_j$$

Let us place $\mathbf{x}_j = \mathbf{x}_k + \mathbf{r}$. The above equation then transforms to

$$I_4(\mathbf{h}) = I_e(h) \int_V \int_V \eta(\mathbf{x}_k)\eta(\mathbf{x}_k + \mathbf{r}) e^{i\mathbf{h}\cdot\mathbf{r}}\, d\mathbf{x}_k\, d\mathbf{r}$$

Let us consider first the integral with respect to $\mathbf{x}_k$,

$$\int_V \eta(\mathbf{x})\eta(\mathbf{x} + \mathbf{r})\, d\mathbf{x}$$

This integral depends uniquely on r. For $r = 0$, the value of the integral is proportional to $\overline{\eta^2}$, the mean value of the square of the density fluctuations, since

$$\int_V \eta(\mathbf{x})\eta(\mathbf{x}) \, d\mathbf{x} = \int_V \eta^2(\mathbf{x}) \, d\mathbf{x} = \overline{\eta^2} V$$

Conforming to the notation of Debye and Bueche, let us define a function $\gamma(r)$ by the relation

$$\int_V \eta(\mathbf{x})\eta(\mathbf{x} + \mathbf{r}) \, d\mathbf{x} = \overline{\eta^2} V \gamma(\mathbf{r}) \tag{103}$$

The equation for $I_e(\mathbf{h})$ then takes the form

$$I_e(\mathbf{h}) = I_e(h)\overline{\eta^2} V \int_V \gamma(\mathbf{r}) e^{i\mathbf{h}\cdot\mathbf{r}} \, d\mathbf{r}$$

This integral can undergo two modifications:

1. For large $\mathbf{r}$ there is no relation between the fluctuations of $\eta(\mathbf{x})$ and $\eta(\mathbf{x} + \mathbf{r})$; the function $\gamma(\mathbf{r})$ thus tends to zero as r increases. The integration over the domain V can then be replaced by an integration over an infinite region.

2. It can often be assumed that, in the region of vectors $\mathbf{r}$ of small magnitude, the only domain in which $\gamma(\mathbf{r})$ is different from zero, the properties of $\gamma(\mathbf{r})$ depend only on the magnitude r.

The final expression for the intensity is then

$$I(h) = I_e(h) = I_e(h)\overline{\eta^2} V \int_0^\infty \gamma(r) \frac{\sin hr}{hr} 4\pi r^2 \, dr \tag{104}$$

This is the expression developed by Debye and Bueche to describe the intensity scattered by the matter under examination.

Let us consider the limiting value of $I(h)$ as $h \to 0$:

$$I(0) = I_e(0) \int_V \int_V \eta(\mathbf{x}_k)\eta(\mathbf{x}_l) \, d\mathbf{x}_k \, d\mathbf{x}_l$$

$$= I_e(0) \int_V \eta(\mathbf{x}_k) \, d\mathbf{x}_k \int_V \eta(\mathbf{x}_l) \, d\mathbf{x}_l \tag{104a}$$

The integral $\int \eta(\mathbf{x}) \, d\mathbf{x}$ is zero in a large volume on the average, but the irregularity of the distribution of matter in the volume V irradiated by X-rays gives it a value which fluctuates around zero. The two integrals of equation 104a are taken over the same volume; the two factors are thus *not* independent, and the average of the product is *not* the product of the average of each factor. Therefore, although the average value of each integral is zero, the average value of $I(0)$ is *not* zero. A calculation shows that the limiting value for the intensity scattered at zero-angle is given by equation 102.

2.4.3. MATTER OF UNIFORM DENSITY AND RANDOM DISTRIBUTION

Porod [137] studied a more particular system, that of a sample made up of a random distribution of matter of constant density. The density $\rho(\mathbf{x})$ in the volume V of the sample can take only two values, ρ and 0. If c is the fraction of the volume occupied by matter, the average density of the sample is ρc. In the parts occupied by matter $\eta = \rho(1 - c)$, and in the empty regions $\eta = -\rho c$. Therefore

$$\overline{\eta^2} = \rho^2 c(1 - c) \tag{105}$$

Porod defines the distribution of matter by a function, $Z(r)$, which represents the probability that a point in the volume at a distance r from a point *occupied* by matter is itself also *occupied*. It is assumed that this probability is a function only of the distance r (an isotropic sample) and that there is no long-range order, so that $Z(r)$ tends toward c as r approaches infinity. We can therefore put

$$Z(r) = c + (1 - c)\gamma(r) \tag{106}$$

where the function $\gamma(r)$, called the *characteristic function* of the sample, has the value unity when r is zero and approaches zero as r becomes very large. This is identical to the function Debye and Bueche introduced by the definition

$$\int \eta(\mathbf{x})\eta(\mathbf{x} + \mathbf{r}) \, d\mathbf{x} = \overline{\eta^2} V \gamma(r) \tag{103}$$

In order to show this, let us first point out that $Z'(r) = (1 - c) + c\gamma(r)$ represents the probability that a point in the volume at a distance r from a point in empty space (unoccupied) is itself also in empty space. This can be verified easily by equating the two relations each of which describes the probability of one point being occupied and the other unoccupied,

$$c(1 - Z(r)) = (1 - c)(1 - Z'(r))$$

Now in order to calculate the integral in equation 103 we must first set up a table of probabilities for the different situations at points $\mathbf{x}$ and $\mathbf{x} + \mathbf{r}$.

Nature of Points $\mathbf{x}$ and $\mathbf{x} + \mathbf{r}$		Value of $\eta(\mathbf{x})\eta(\mathbf{x} + \mathbf{r})$	Probability of Occurrence
Occupied	Occupied	$\rho^2(1 - c)^2$	$cZ(r) = c^2 + c(1 - c)\gamma(r)$
Occupied	Empty	$-\rho^2 c(1 - c)$	$c(1 - Z(r)) = c(1 - c)(1 - \gamma(r))$
Empty	Occupied	$-\rho^2 c(1 - c)$	$(1 - c)(1 - Z'(r)) = c(1 - c)(1 - \gamma(r))$
Empty	Empty	$\rho^2 c^2$	$(1 - c)Z'(r) = (1 - c)^2 + c(1 - c)\gamma(r)$

Now by carrying out the integration

$$\frac{1}{V} \int \eta(\mathbf{x}) \eta(\mathbf{x} - \mathbf{r}) \, d\mathbf{x} = \rho^2 c(1 - c)\gamma(r)$$

where equation 105 has been used, it can be seen that equations 103 and 106 define the same function.

Thus the scattered intensity can be determined immediately from equation 104,

$$I(h) = I_e(h) V \rho^2 c(1 - c) \int_0^\infty \gamma(r) \frac{\sin hr}{hr} 4\pi r^2 \, dr \tag{107}$$

This expression can be linked to the equation relative to a single particle, equation 21. Let us consider a very dilute system of identical particles of arbitrary orientations. The probability $Z(r)$ is then approximately equal to the function we have called the characteristic function of a particle, $\gamma_0(r)$ (see p. 12), since by virtue of the dilution of the system there is only a negligible chance of finding an occupied point outside of the particular particle in which the origin point is chosen. Then since $1 - c \approx 1$ and c is negligible, equation 106 gives $\gamma(r) = \gamma_0(r)$. In addition Vc is the total volume of particles, $N r_0$. Therefore equation 107 is equivalent to equations 21 and 55.

Mathematically, $I(h)$ is determined entirely by a knowledge of $\gamma(r)$. However, the calculation of $\gamma(r)$, very complex for an isolated particle, is rarely possible for systems of particles of a given arrangement. Conversely, the characteristic function of the sample can be determined from the experimental measurement of $I(h)$. This function $\gamma(r)$ contains all the information that can be obtained from the small-angle scattering experiments, but unfortunately this function does not give a direct image of the structure and is quite far from defining it. The effects of both the form of the particles and their mutual arrangement are intermixed in the single function $\gamma(r)$. Theories are discussed in §2.2.3 which have as their object the separation of these two effects.

Nevertheless, several parameters having simple and precise interpretations can be obtained from $\gamma(r)$, as was done for the function of a single particle.

$\gamma(r)$ is equal to unity when r is zero and tends asymptotically to zero as r becomes large. It can take on negative values, greater than $-c/(1 - c)$, while the function for an isolated particle is always positive.

1. The slope of the curve at the origin is

$$\left(\frac{d\gamma}{dr}\right)_{r=0} = \frac{1}{1 - c} \left(\frac{dZ}{dr}\right)_{r=0}$$

The slope of $Z(r)$ at $r = 0$ can be calculated for the complex system in the same way as for the isolated particle. If S is the total surface area of the matter contained in the volume V, the real volume of matter being only Vc, then from equation 24

$$\left(\frac{dZ}{dr}\right)_{r=0} = -\frac{1}{4} \frac{S}{Vc}$$

Therefore

$$\left(\frac{d\gamma}{dr}\right)_{r=0} = -\frac{1}{4c(1 - c)} \frac{S}{V} = -\frac{1}{4c(1 - c)} S_{sp}$$

where S_{sp}, the specific surface, is the surface area per unit volume of the sample. From this, following the reasoning leading to equation 26, the asymptotic behavior of the intensity curve is found as

$$I(h) \approx I_e(h) \frac{2\pi \rho^2 S}{h^4} \tag{108}$$

The absolute value of the scattered intensity in the tail of the curve depends only on the total surface area of the matter in the sample. If the object is made up of n identical particles of volume v and surface s, the total free surface S is always approximately equal to ns, whatever the degree of aggregation of the particles, provided that these are of some arbitrary form and that they will not become distorted. The intensity can be written as

$$I(h) = I_e(h) n \rho^2 (2\pi s / h^4)$$

It is equal to n times the average intensity scattered by one particle. This shows that at large angles interparticle interferences are negligible, even for particles of uniform size. It is therefore valid to apply equation 95 to dense systems. This does *not* mean that the intensity curve at *small* angles will not be modified considerably by the action of particles drawing closer together. Let us point out also that the above argument will not be valid for particles in the form of broad platelets parallel to one another, since the packing together of such particles can make the interfaces disappear, decreasing the total surface and thus the scattered intensity by a large amount. We have already mentioned (p. 70) that the effect of interferences for one-dimensional systems is much larger than for a powder of irregular grains.

2. The area of the curve $\int_0^\infty \gamma(r) \, dr$ can be calculated either from the integral $\int_0^\infty h I(h) \, dh$ (see equation 29) or from the total energy E scattered

in the low-angle region for a given incident beam intensity (see equation 30). Equation 107 gives

$$\frac{l_c}{2} = \int_0^\infty \gamma(r)\, dr = \frac{1}{4\pi V \rho^2 c(1-c)} \int_0^\infty \frac{h I(h)}{I_e(h)}\, dh \tag{109}$$

and

$$\frac{l_c}{2} = \int_0^\infty \gamma(r)\, dr = \frac{1}{2V\rho^2 c(1-c)} \frac{1}{\lambda^2 p^2} \frac{E}{I_e(h)} \tag{110}$$

where p is the distance from the sample to the film. l_c is a parameter that has been called the *distance of heterogeneity* by Kratky and Porod. In an isolated particle $\bar{l}$ (equation 25) represents a mean value of the diameters passing through every point of the particle in all directions, but what is the geometrical significance of l_c for an arbitrary system? Let us draw a straight line in an arbitrary direction *from a point in matter*. This line will be divided into segments which are alternately occupied and unoccupied by matter. The ratio of the total length of occupied segments to that of unoccupied segments is equal to the ratio of the occupied and unoccupied volumes, that is, $c/(1-c)$. The *probable occupied length* in a line of length L drawn from the point chosen as origin is found from the definition of $Z(r)$ (equation 106) to be

$$\int_0^L Z(r)\, dr = Lc + (1-c) \int_0^L \gamma(r)\, dr$$

$$\cong Lc + (1-c) \int_0^\infty \gamma(r)\, dr$$

This length is larger than the mean occupied length Lc of an arbitrary section of length L, because by imposing the condition that the section L starts from a point occupied by matter the chances of finding an occupied section are increased. This excess length is simply $(1-c)\,(l_c/2)$.

3. In the general case there is a normalization relation analogous to equation 28,

$$\int_0^\infty h^2 I(h)\, dh = 2\pi^2 I_e(h) \rho^2 V c(1-c) \tag{111}$$

4. The roles played by c and $(1-c)$ in equation 107 are symmetric. In addition the characteristic function $\gamma(r)$ is the same for an object and for its complementary object (Fig. 66, p. 192). Therefore the same scattered intensity is found for two complementary objects in the angular region in which equation 107 is valid (§2.2.2.2).

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3. EXPERIMENTAL EQUIPMENT

3.1. GENERAL CONSIDERATIONS

The object of an X-ray scattering experiment, whether in the small-angle region or in the usual domain of investigation, is the determination of the variation of the intensity scattered by a sample as a function of the scattering direction, this direction in general being defined by two parameters. In the important particular case in which the scattering is circularly symmetric about an axis coincident with the incident beam, only one parameter, the scattering angle, is involved, and the object of the experiment is simply the determination of the relative value of $I(h)$, with $h = (4\pi \sin \theta)/\lambda$.

Experiments can also furnish a second quantity, less frequently employed, which is the absolute value of the scattering coefficient, σ. This is defined by means of the relation, $I = I_0 \sigma \, dm \, d\Omega$, where I is the power scattered by the particle of mass dm in the solid angle $d\Omega$, and I_0 is the intensity of the incident beam striking the sample. The sample is assumed to be small enough to be non-absorbing.

3.1.1. OPERATIONAL PRINCIPLES

The method employed to realize the objectives discussed above is not different in principle from that used in all experiments in X-ray crystallography. Special difficulties are encountered, however, in investigating the scattering at very small angles.

1. *Geometrical Definition of the Incident Beam.* Following the notation of Fig. 22, let MM' be the portion of the sample which is irradiated. Each point of the sample will receive a beam of rays whose divergence depends on the constitution of the incident beam. Rays will converge at the point of observation P which have been scattered by each of the points of the sample through angles varying in an interval $2d\theta$ about a mean value, 2θ. The interval $d\theta$ is practically independent of θ, so that good definition of the scattering angle in relative value is more difficult to obtain, the closer a scattering angle of zero is approached.

Furthermore, there will always be an angular region inaccessible to experiment; this is the region between N and N' of Fig. 22, in which the scattered radiation received at any point is completely overshadowed by the much greater intensity of the direct beam at this point. Thus, to

investigate scattering at small angles, it is necessary to *reduce both the cross section and the divergence of the primary beam*, the restriction being greater, the smaller the limiting angle of observation that is desired. As a result, the beams employed are much less intense than those used in ordinary techniques, so that a determination of the best geometrical conditions is essential.
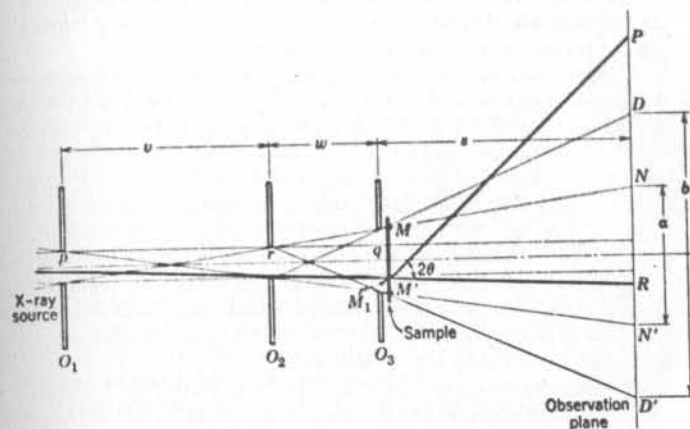
Fig. 22.   Slit system for a small-angle scattering apparatus.

2. *Parasitic Scattering.* The measurement of the intensity received at the point of observation is a correct measure of the intensity scattered by the sample only if there is no parasitic scattering. The term parasitic scattering refers to the radiation received at the point of observation when the sample is withdrawn from the beam. If a Geiger counter or ionization chamber is employed as a detector, the parasitic scattering can easily be subtracted from the observed scattering to give the corrected value, but this procedure is acceptable only if the correction is small. If photographic detection is employed, it is very difficult to make the correction by the above procedure. *The reduction of the parasitic scattering is thus the second important requirement*, and here again the suppression is more difficult, the smaller the angles at which scattering is to be observed.

Thus we can say that the quality of a small-angle scattering apparatus is characterized by the power of the beam for a given fineness of dimensions and by the angle beyond which all parasitic scattering is eliminated.

A third critical property of such an apparatus is the spectral purity of the primary radiation. We shall consider successively equipment without and with monochromatization, showing the different domains of application of each.

3.1.2. INFLUENCE OF THE MONOCHROMATIZATION OF THE PRIMARY RADIATION

Use may be made of either filtered or crystal monochromated radiation, depending on the nature of the sample to be studied.

1. The total radiation from the anode, with the usual filtering to remove the $K\beta$, may be used in a study of low-angle crystalline diffraction effects that are analogous to the usual high-angle phenomena, differing only in that the effective lattice spacings are very large. These patterns contain lines, spots, or rings at well-defined angles, and the corresponding intensities are considerably larger than those at intermediate angles on the patterns. Thus, as with ordinary diffraction patterns, the diffraction effects due to the characteristic radiation emerge from the continuous background of diffraction and scattering caused by the continuous spectrum. Often the primary objective of such a study is to determine the position of the lines or spots, and in these circumstances even a rather strong parasitic scattering may be tolerated.

2. The opposite case is the study of continuous scattering of the type that has been described in the first part of this book. This continuous scattering is often extremely weak and is superposed on the scattering of various other origins, such as the inactive parts of the sample (the solvent, for example, when the scattering of particles in solution is studied). Given the actual state of the theory, it is essential in this type of problem to have a precise evaluation of the function $I(h)$.

It is easy to see that in certain cases the influence of the continuous spectrum may be considerable, since, in addition to the intensity $I(h)$ due to the principal radiation of wavelength λ_0, one will also observe a scattering of the form

$$\int I\left(\frac{\lambda_0}{\lambda} h\right) f(\lambda)\, d\lambda$$

where $f(\lambda)$ is the distribution function of the energy in the continuous spectrum. The effect of all the continuous spectrum can thus be large with respect to that of the characteristic radiation. Experiments by several authors have proved that an investigation cannot be made free from all objection without the use of monochromatized radiation.

When Geiger-counter detection is used, the elimination of the continuous spectrum by the double filter method of Ross (Kirkpatrick (1939)) is often

sufficient, but this method is not easily applied with photographic techniques. The most practical and the most general method of producing monochromatic radiation involves the use of a *crystal monochromator*. Since the use of a monochromator profoundly modifies the geometry of the equipment, we shall study separately the system with collimation, designed for studies of crystalline diffraction, and the system with monochromatization, especially adapted to the study of the continuous scattering.

3.2. SYSTEMS EQUIPPED WITH COLLIMATORS

The beam (see Fig. 22) is defined by two apertures, O_1 and O_2, separated by a distance r, which are placed before a source of radiation large enough to illuminate the entire opening. As the edges of O_2 are touched by the direct beam, they are sources of scattered and diffracted radiation. Thus it is necessary to protect the plane of observation by introducing a third aperture, O_3, at a distance w from O_2, *whose edges closely approach but do not touch the incident beam*. Apertures O_2 and O_3 then define the region DD' which is not exempt from parasitic scattering. The sample is placed after O_3, as close to it as the supports will permit. The sample and the opening O_3 are thus at approximately the same distance from the plane of observation; this distance is denoted by s.

We want to determine the form and dimensions to give to the various apertures in order to obtain the "best results" for our measurements. We must first specify the known quantities of the problem and the criterion of quality to be required. This cannot be done until the nature of the pattern given by the sample has been specified.

3.2.1. COLLIMATOR FORMED BY TWO SLITS

Let us consider the simple problem of the study of the equatorial line of a crystalline "fiber pattern." Our attention is thus devoted to diffraction effects in only one dimension. The collimator openings can then be infinitely long slits parallel to the "fiber axis" (perpendicular to the plane of Fig. 22), and the diffraction spots will appear as lines. We shall impose the following conditions:

1. Let us define the angular uncertainty of the pattern as the variation in scattering angle of the rays arriving at a point P in the plane of observation. Such rays scattered from an incident ray M_1R are scattered through an angle equal as a first approximation to PR/s, whatever the position of the diffracting point M_1 on the sample. Thus the maximum variation of the scattering angle, $2\Delta\theta$, for the group of rays converging at P (the

angular uncertainty of the pattern), is measured by the quantity, $A = a/s$, where a is the width of the primary beam in the plane of observation, and s is the sample-to-film distance. The largest lattice spacing which can give rise to a line distinct from the direct beam will then be

$$d_{max} = \lambda/A$$

2. The scattering angle inside of which parasitic radiation is found is $B/2 = b/2s$, where b is the width of the part DD' of the film receiving scattered radiation in the absence of a sample. The upper limit of the lattice spacings which will register outside of all parasitic scattering is then $d'_{max} = 2\lambda/B$. Obviously B is larger than A, and usually it is larger than $2A$, so that $d'_{max} < d_{max}$.

3. Either Geiger-Müller counters or photographic plates may be employed as detectors, but the conditions that apply to each are different.

(i) If a Geiger-Müller counter is used, it must be equipped with an entrance slit so that the divergence of the rays scattered by a point on the sample that enter the counter is fixed and clearly less than A ($A/10$, for example). If this condition is satisfied, it is possible, at least theoretically, to correct the observed pattern for the effect of the width of the direct beam (see §3.4).

For a given angular uncertainty, A, the counter slit width is proportional to s. Since, for constant A, s can be arbitrarily chosen without affecting the measured power, it is then advantageous to employ a large value of s so that the counter slit can be more easily constructed. The only restriction is that s must be less than a limiting value, s_c, determined by the mechanical conditions and obstructions.

(ii) The limitations of the photographic method arise from the grain size of the film, which is always rather large for emulsions sensitive to X-rays. X-ray patterns cannot be usefully enlarged by a factor of 10. The resolving power of these films is of the order of a hundredth of a millimeter; thus the exploring slit of the microphotometer should have a width of this order of magnitude, ϵ. Consequently the sample-to-film distance s has a *lower* limit, s_p, such that ϵ/s_p is clearly smaller than A (for example, $A/10$, as suggested in the preceding case).

4. The study of very small angles necessitates the use of beams which are very narrow and, consequently, of low power. It is essential for the success of the experiment that the system be found which allows the most powerful beam, while satisfying the geometrical conditions previously enumerated. Specifically, it is necessary to try to maximize the number of photons received by a counter placed at the center of a diffraction line or to maximize the blackening of this line on a film. The most desirable

form for a sample is that of a small plate intercepting the entire beam, the thickness being chosen in accordance with its absorption coefficient. (It is well known that the optimum thickness is that for which the ratio of the transmitted to incident intensity is the factor, $1/e \approx 1/3$.) Now, for simplicity let us assume that the point of observation is in a region of the pattern in which the variation of intensity with angle is very small, as, for example, in the center of a rather wide diffraction line. Then, for a given slit width, the intensity of the radiation entering the counter will be proportional to the total power of the primary beam incident on the sample per unit collimator slit height, I_1. When photographic detection is employed, the blackening at the same point will be proportional to I_1/s (we are considering one-dimensional diffraction effects, so the factor $1/s$ rather than $1/s^2$ intervenes). *These are the factors that must be maximized respectively in the construction of the collimator when the detector is a Geiger counter or a photographic film.*

Bolduan and Bear [205], in an analogous calculation, chose a criterion which seems to us to be on a less general level; they maximized *not the total power* of the incident beam *but rather the intensity* of the radiation striking the plane of observation at the center of the direct beam. Their conclusions are clearly different from those we shall draw. This shows that, if in a given experimental problem some of our assumptions are not satisfied, it will be necessary to discard our conclusions and to make an analogous calculation with appropriately modified factors.

5. The source of X-rays is assumed to be an X-ray tube with a rectangular focal spot of large length and of width l, so oriented that the long dimensions of the focal spot and the slits are parallel. The emerging rays make an angle, α, with the plane of the target. If the power per unit area delivered to the target by the incident electrons is $\mathscr{P}$, the intensity of the emitted X-rays will be proportional to $\mathscr{P}/\alpha$, if α is larger than a limiting value, α_0, of the order of $1°$ or $2°$ (Bolduan and Bear [205]). We shall fix α at this optimum value, α_0, and we shall place the first slit of the collimator close to the focal spot; the width, p, of the slit O_1 is then determined as the projection of the focal spot, $l\alpha_0$.

Let r be the width of the second slit, O_2, which is placed at a distance v from O_1. The power of the beam defined by the collimator O_1O_2 will then be proportional to

$$\frac{\mathscr{P}}{\alpha_0} p \frac{r}{v} = \frac{\mathscr{P}lr}{v}$$

The third slit, O_3, of width q, is placed at a distance w from O_2. Let us recall that the ratio a/s has been denoted by A and the ratio b/s by B.

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