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Scattering from Cylindrically Symmetric Systems

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Expressions for the intensity of scattering by systems composed of infinitely long cylindrical particles are derived. Four types of independent scattering regions are considered: (1) isolated cylindrical rods, with and without internal radial structure; (2) aggregates of parallel rods with fixed locations; (3) systems of parallel rods with variable locations; (4) two-dimensional crystals. The effect of random and specific orientation of independent scattering regions in discussed. The results are applicable to low-angle X-ray scattering from fibres and from macromolecular or micellar solutions.

In a previous paper (Oster & Riley, 1952) we considered the scattering of X-rays and visible light by isotropic systems and confined our treatment to those cases which possess spherical symmetry. We shall now extend our examination to assemblies which possess cylindrical symmetry and in which the fundamental particles are very long compared with the wavelength λ of the radiation used. On the macroscopic scale such systems may be isotropic or anisotropic. In the former case they are collections of cylindrically-symmetric domains in random orientation; in the latter, the domains themselves have preferred orientation. Micellar solutions are an example of the first type and completely oriented fibres of the second. We shall show that there is a close analogy between the expressions for the intensity of scattering by cylindrically symmetric systems and those for the equivalent spherically symmetric cases discussed in our first paper. The results obtained in the present paper are not only applicable to X-ray scattering and diffraction by certain macromolecular and colloidal systems but also to visible-light scattering and diffraction by macroscopic systems having cylindrical symmetry.

A peculiar feature of systems of long rod-shaped particles is the correlation in orientation which sets in if the concentration exceeds a certain critical value, depending on the particle length and the forces of interaction (Onsager, 1949; Oster, 1949). Very long particles will, even in fairly dilute solution, show correlation in orientation, the rods being nearly parallel over rather large domains. Fibres in bundles can usually be rendered parallel, at least in local regions, by stretching and rolling the sample. These properties of elongated particles considerably simplify the mathematics of the problem as it then reduces to a two-dimensional calculation.

In this paper we shall calculate the angular distribution of scattered intensity for (1) isolated cylindrical rods, with and without internal radial structure, (2) aggregates of parallel rods with fixed locations, (3) systems of parallel rods with variable locations as expressed generally by a radial distribution function, and (4) two-dimensional crystals consisting of an infinite periodic array of parallel rods. As in the previous paper, we shall eliminate the scale factor by writing all expressions in terms of the dimensionless variable kR in which R is the radius of the cylinder and $k = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of the radiation in the medium and 2θ is the angle of scattering.

In order that the problem be reduced to two-dimensions, we shall consider only systems in which the fundamental units are cylindrical rods of infinite length and in which, within any independent scattering domain, the rods are perfectly parallel. The intensity of scattering is then localized in a plane. In the sections which immediately follow, it will be assumed that the long axes of the rods are at right angles to the incident beam and the expressions derived for the scattering refer to angles measured in the equatorial plane. In the last section, the question of random and specific orientation will be discussed.

Since we are dealing with systems possessing cylindrical symmetry, the resolution of the scattering problem is expressible in terms of Bessel functions. The properties of $J_0(x)$ and $J_1(x)$, the Bessel functions of zero and first order respectively, are given by Watson (1948). The numerical values used in computing were taken from the Harvard *Tables of Bessel Functions* ... (1947).

Independent particles

By analogy with the method used by Debye (1930) to derive the atomic scattering factor for three-dimensional systems of spherical symmetry, the scattered amplitude F from an infinitely long (compared with the wavelength) cylindrically symmetric system is given by

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$$F = \frac{\int G(r) e^{ikr\cos\alpha} da}{\int G(r) da}, \tag{1}$$

in which $G(r)da$ is the probability that the scattering material lies in the element of area $da = rd\alpha dr$, where r is the radial distance in the equatorial plane and α is the polar angle in this plane. Since we are concerned only with the relative scattering at various angles, we have introduced the normalizing factor in the denominator so that the amplitude is unity at zero angle ($k = 0$). The integration is to be performed over the entire plane, the limits being α from 0 to 2π and r from 0 to ∞. Now, since

$$\int_0^{2\pi} e^{ikr\cos\alpha} d\alpha = 2\pi J_0(kr), \tag{2}$$

equation (1) becomes

$$F = \frac{\int_0^{\infty} 2\pi r G(r) J_0(kr) dr}{\int_0^{\infty} 2\pi r G(r) dr}. \tag{3}$$

Wrinch (1946) has also derived this relation in a study of rotational symmetry of Fourier transforms.

For an isolated solid rod of radius R, $G(r)$ is unity for $R > r > 0$ and is zero for $r > R$. Substitution into equation (3), making use of the identity

$$\int_0^R r J_0(kr) dr = \frac{R}{k} J_1(kR), \tag{4}$$

gives

$$F = \frac{2J_1(kR)}{kR}. \tag{5}$$

This result is identical with the expression, first derived by Airy (1835), for Fraunhofer diffraction by a circular aperture. It has been applied by Guinier (1939) to the case of low-angle X-ray scattering by oriented ramie fibres. The more detailed treatment given below, however, takes into account the relative positions of the fibres.

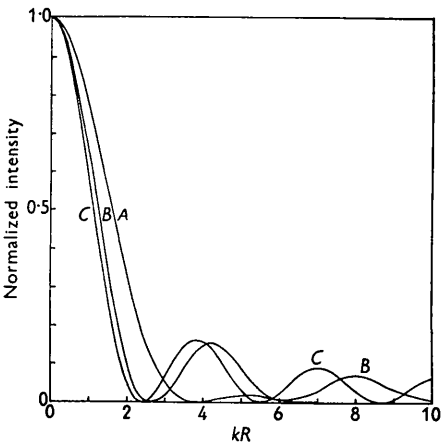

Fig. 1. Normalized intensity of scattering for independent: solid cylinders (curve A), cylindrical shells of finite thickness ($c = 0{\cdot}8$) (curve B), and thin cylindrical shells (curve C).

The normalized intensity F^2 as a function of kR for solid cylinders is illustrated in Fig. 1 (curve A). This function is a rapidly damped oscillating curve which, for large values of kR, approaches

$$\frac{8}{\pi(kR)^3}\cos^2(kR - \tfrac{3}{4}\pi). \tag{6}$$

Maxima in the intensity appear at kR=0, 5·14, 8·42, etc. For a solid cylinder the normalized intensity is reduced to one-half at $kR = 1{\cdot}61$ as compared with $kR = 1{\cdot}76$ in the case of a solid sphere of the same radius.

For a cylindrical shell of thickness $(1-c)R$ where $1 > c > 0$, $G(r)$ is zero for $cR > r > 0$, unity for $R > r > cR$, and zero for $r > R$. Insertion into equation (3) gives

$$F = 2\left[\frac{kRJ_1(kR) - ckRJ_1(ckR)}{(kR)^2(1-c^2)}\right]. \tag{7}$$

In Fig. 1 (curve B) is shown the intensity F^2 for $c = 0{\cdot}8$, that is, for a shell of thickness one-fifth of the outer radius of the cylinder. This function has maxima at $kR = 0$, 4·25, 8·05, etc. and is reduced to one-half its zero-angle value at $kR = 1{\cdot}25$.

If the equation (7) we let c tend to unity, we obtain F for an infinitesimally thin cylindrical shell of radius R:

$$F = J_0(kR). \tag{8}$$

This is equivalent to the result obtained by Rayleigh (1888) for Fraunhofer diffraction by a circular line aperture. The intensity F^2 for this case (Fig. 1, curve C) is a more slowly damped oscillating function than that for the solid cylinder, and for large values of kR approaches

$$(2/\pi kR)\cos^2(kR - \tfrac{1}{4}\pi). \tag{9}$$

The very pronounced maxima appear at $kR = 0$, 3·83, 7·02, 10·17, etc. The intensity is reduced to one-half its zero-angle value at $kR = 1{\cdot}12$.

As will be seen by comparing the three curves drawn in Fig. 1, at small values of kR the F^2 curves fall off more rapidly the more the scattering matter is removed from the center of the particle. For small values of kR, the expression for F given in equation (7) may be expanded in a power series. The first two terms of the square of this series, corresponding to the intensity F^2, are given by

$$F^2 = 1 - \tfrac{1}{4}(kR)^2(1+c^2), \tag{10}$$

where $(1-c)R$ is the thickness of the shell. For solid cylinders, this simplifies to $1 - \frac{1}{4}(kR)^2$. More generally, the square of equation (3) may, for small values of k, be approximated by

$$F^2 = 1-\frac{k^2}{2}\frac{\int_0^\infty r^3G(r)dr}{\int_0^\infty rG(r)dr}. \qquad (11)$$

For a cylinder of radially periodic structure with $G(r) = \cos^2(\pi mr/R)$ for $r < R$ and zero for $r > R$, where m is the number of concentric shells, (11) becomes

$$F^2 = 1-\tfrac{1}{4}(kR)^2\left(1+\frac{3}{\pi^2m^2}\right). \qquad (12)$$

Hence, for small angles the scattering is practically independent of the internal radial structure of the cylinders. The complete expression for the periodic shell case can be obtained by using equation (3) and integrating by parts, making use of well-known relations between $J_0(x)$ and $J_1(x)$. The solution is a complicated algebraic expression involving k, $2\pi m/R$, $J_0(kR)$ and $J_1(kR)$, the most important term of which becomes greater the less the difference between k and $2\pi m/R$. In other words, the intensity F^2 becomes large as kR tends to $2\pi m$, a condition which may be written as $\lambda = 2(R/m)\sin\theta$, analogous to Bragg's law for a set of diffracting planes of spacing R/m.

The above treatments for the scattering by isolated circular cylinders may be generalized to deal with the case of cylinders of elliptical cross section. The results are expressible in terms of Mathieu functions of analogous type to the Bessel functions given above, with k and the length of the long axis of the ellipse and its ellipticity as parameters.

Isolated aggregates of cylinders

Let us consider an isolated assembly of identical long cylindrical particles in perfect parallel orientation with their long axes normal to the incident beam and located in fixed positions relative to one another. By analogy with the scattering from polyatomic gases (Debye, 1915), we have for the normalized intensity of scattering by n cylinders, each with scattering factor $F(kR)$, where the centres of the pth and qth cylinders are at a distance s_{pq} apart:

$$\frac{1}{n^2}F^2(kR)\sum_p^n\sum_q^n e^{iks_{pq}\cos\alpha}. \qquad (13)$$

If all rotational orientations about an axis parallel to the lengths of the cylinders are equally probable, each term is integrated between the limits 0 and 2π for α. Using equation (2), we obtain for the normalized intensity of scattering:

$$\frac{1}{n^2}F^2(kR)\sum_p^n\sum_q^n J_0(ks_{pq}). \qquad (14)$$

For two parallel cylinders (14) becomes

$$\tfrac{1}{4}F^2(kR)[2+2J_0(2\gamma kR)], \qquad (15)$$

where we have introduced the 'swelling' parameter γ defined by $s/2R$, s being the interparticle distance separating the centres of nearest neighbours. This parameter takes into account that the particles may not be in contact owing to interparticle repulsion or 'hydration'. In Fig. 2 we have plotted intensity curves

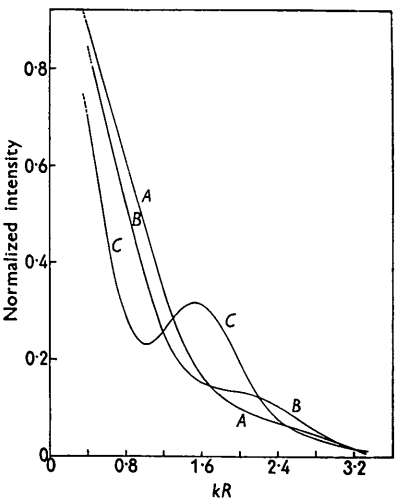

Fig. 2. Normalized intensity of scattering per cylinder for independent aggregates of two solid cylinders: (*A*) $\gamma=1{\cdot}00$, (*B*) $\gamma = 1{\cdot}25$, (*C*) $\gamma = 2{\cdot}00$.

for the aggregate of two solid cylinders with $\gamma=1{\cdot}00$, 1·25, and 2·00. In the first (contact) case (curve *A*) no interference maximum is observed. In the third case (curve *C*), where the two cylinders are separated by a gap equal to their diameters, there is a distinct maximum at $kR = 1{\cdot}53$. In other words, $\lambda=2{\cdot}05s\sin\theta$, which means that Bragg's law is very nearly obeyed.

For seven cylinders in a central hexagonal arrangement, the expression for the scattered intensity becomes

$$\tfrac{1}{49}F^2[7+24J_0(x)+6J_0(2x)+12J_0((\sqrt{3}/3)x)], \qquad (16)$$

where $x = 2\gamma kR = ks$. In Fig. 3 the intensity of

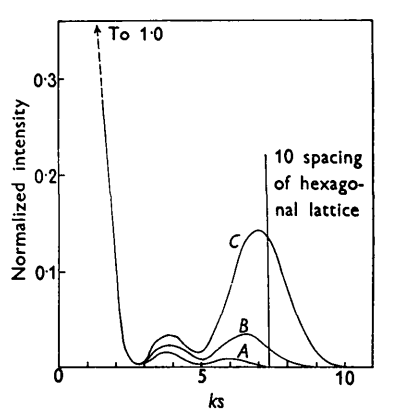

Fig. 3. Normalized intensity of scattering per cylinder for independent aggregates of seven solid cylinders in hexagonal array ($s = 2\gamma R$): (*A*) $\gamma = 1{\cdot}00$, (*B*) $\gamma = 1{\cdot}25$, (*C*) $\gamma = 2{\cdot}00$.

scattering is given as a function of ks for such an arrangement of solid cylinders with $\gamma = 1{\cdot}00$, $1{\cdot}25$, and $2{\cdot}00$. It is evident that the diffraction bands are more pronounced the larger the gap between the particles; at the same time, the maximum of the main band moves toward a spacing corresponding to that of the 10 planes in a 2-dimensional hexagonal lattice of infinite extent. The subsidiary maximum, which has no equivalent in the case of the infinite lattice, is a result of the small number of particles in the system.

For small values of kR, the intensity for two solid cylinders is given, on approximating (15), by

$$1-\tfrac{1}{4}(kR)^2(1+2\gamma^2)\,. \tag{17}$$

Similarly, (16) is given approximately by

$$1-\tfrac{1}{4}(kR)^2(1+\tfrac{4}{7}\gamma^2)\,. \tag{18}$$

Non-independent particles with arbitrary location

We shall now consider a system of parallel identical cylindrical particles of infinite length in which the particles are free to occupy any position. Once again, the problem reduces to a consideration of circular diffracting regions lying in a plane normal to the long axes of the cylinders. The probability that the centre of the pth particle lies in the element of area da_p while that of another lies in the element da_q, both elements of area being in the same plane, is $g(r_{pq})da_p da_q/A^2$, where r_{pq} is the distance between the two elements and A is the total area. The normalized intensity of scattering by such a two-dimensional system (cf. Zernike & Prins (1927) for the equivalent three-dimensional case) is

$$F^2(kR)\left[1-N\int\int(1-g(r_{pq}))e^{ikr_{pq}\cos\alpha}\frac{da_p}{A}\frac{da_q}{A}\right]. \tag{19}$$

For a radially symmetric distribution, r is referred to any element of area as centre, and (19) becomes

$$F^2(kR)\left[1-\nu\int_0^{2\pi}\int_0^{\infty}r(1-g(r))e^{ikr\cos\alpha}d\alpha\,dr\right], \tag{20}$$

or, by use of equation (2),

$$F^2(kR)\left[1-\nu\int_0^{\infty}2\pi r(1-g(r))J_0(kr)dr\right], \tag{21}$$

where $g(r)$ is the radial distribution function in the plane normal to the long axis of the cylinders, $\nu=N/A$ is the density of particle centres in this plane, and the scattering sample is assumed to be of infinite extent.

From a given observed normalized intensity I, we can determine $g(r)$ by inverting the integral of (21) by means of the Fourier–Bessel theorem (Watson (1948, p. 453). Writing $I/F^2-1 = i(k)$, we have

$$2\pi\nu(g(r)-1) = \int_0^{\infty}ki(k)J_0(kr)dk\,. \tag{22}$$

The evaluation of $g(r)$ from the observed values of I as a function of k is carried out by standard numerical methods, e.g. by planimetry. The factor F^2 discussed earlier is determined from the form of the scattering of the oriented individual particles or of a sufficiently loose packing of such oriented particles so that interference of the particles is not important.

As seen in (21), the greater the correlation in position of the particles, the more the intensity is reduced from that for the isolated particles, F^2. To illustrate the interference effect, we may consider the idealized case in which $g(r)$ is zero for $s > r > 0$, where s is the closest distance of approach of the centres, which may be greater than $2R$. Substitution into (21) and making use of equation (4) gives for the normalized intensity:

$$F^2(kR)\left[1-\nu\pi s^2\left(\frac{2J_1(ks)}{ks}\right)\right]. \tag{23}$$

Two-dimensional crystals

We shall next consider the case where the centres of the cylindrical particles occupy the lattice points of a two-dimensional hexagonal crystal of infinite extent. Owing to the oscillatory nature of the F^2 factors, peculiar intensity relationships for the crystal reflexions can occur, which are markedly dependent on the degree of lateral swelling. The effect is most marked in the case of cylindrical shells, where $F^2 = [J_0(kR)]^2$. The following spacing equation applies to such assemblies:

$$d_{hk} = \sqrt{\left(\frac{3}{h^2+hk+k^2}\right)}\gamma R\,, \tag{24}$$

or

$$kR = \frac{2\pi}{\sqrt{3}}\frac{\sqrt{(h^2+hk+k^2)}}{\gamma}\,,$$

where h and k are the Miller indices. The volume concentration for a hexagonal array of solid cylinders is $\pi/2(\sqrt{3})\gamma^2$ which, at contact (closest packing), becomes 0·905.

Fig. 4 shows the relative intensities, for hollow cylinders arranged in a hexagonal lattice, of reflexions from the first eight sets of hk planes. The effect of multiplicity of reflecting planes is not included. The calculations refer to five different values of $\gamma=s/2R$, where s is the unit-cell dimension. The abscissae represent the reciprocal of the interplanar spacing d_{hk}, scaled down to the same value for easy comparison. In other words, instead of expanding the lattice we have contracted the radius of the cylinders, keeping s constant. It is clear that the relative intensities do not fall off smoothly toward higher orders as they would with spherical particles. Indeed, for $\gamma = 1{\cdot}5$, the 10 spacing is absent, and is only barely perceptible for $\gamma = 1{\cdot}75$. These effects might well be important in the case of macromolecular particles and colloidal micelles containing heavy atoms at the periphery or for tightly coiled helical particles, and some caution

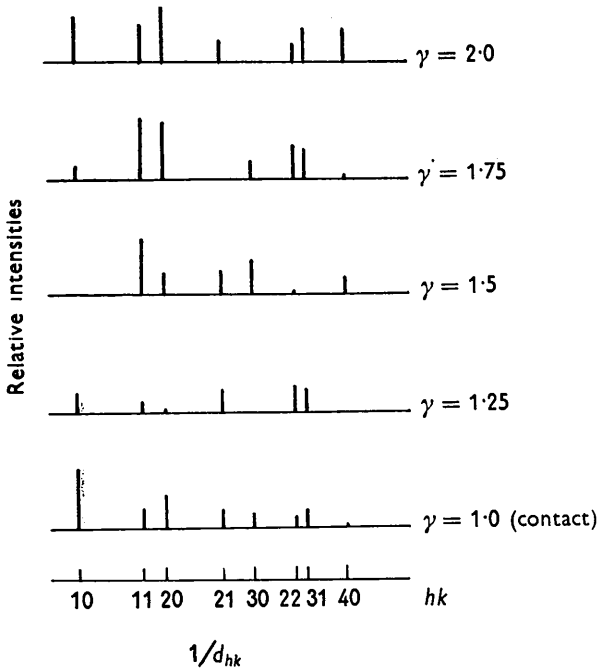

Fig. 4. Relative intensities for thin cylindrical shells arranged in a two-dimensional hexagonal lattice as a function of reciprocal interplanar spacing for various values of γ. Bottom line gives values for point scatterers.

would be advisable in interpreting diffraction results from such systems.

Orientation of independent regions

In the previous sections it has been assumed that the incident and scattered beams lie in the plane perpendicular to the long axis of the cylinders and that the only freedom of movement allowed to the systems is that of rotation about a normal to this plane. We shall now deal with the more general case.

For the reasons given earlier, the intensity function for a given independent scattering region is localized in a plane, and the direction and intensity of scattering are defined by the intersection of this plane with the sphere of reflexion in reciprocal space. As any one unit or domain, considered in isolation, is anisotropic, its orientation needs to be known in order to derive the spatial distribution of intensity.

Let us first consider systems consisting of independent scattering regions, all parallel as regards their particle axes but with random rotational orientation about a line parallel to each of these axes. The averaged intensity function will then have radial symmetry about its origin. Fig. 5 shows how this planar averaged intensity function of kR intersects the sphere of diameter $4\pi R/\lambda$. It is clear that diffraction can occur up to the maximum angle defined by $kR = 4\pi R/\lambda$, when the plane of the intensity function contains the diameter OQ and the scattering point P is at $Q(2\theta = \pi)$, i.e. when the cylindrical axes are perpendicular to the incident beam. The diffracted rays then lie in a plane containing the incident beam. In the general case, the function-plane cuts the sphere in a circle of smaller diameter than $4\pi R/\lambda$ and this restricts the angular range of diffraction. The diffracted rays describe a cone $MOPL$ of axis MT which would intersect a flat film, placed in the usual way at right-angles to the incident beam QMO, in an ellipse passing through the centre. The intensity is symmetrical about the plane OML, and MT is the direction of the particle axes. If, now, we let the independent scattering regions, assumed to be large in number, have completely random orientation, the circular line of constant scattering power PRS becomes the surface of a sphere of centre O and intersects the sphere of reflexion in a circle, the plane of which is at right angles to QMO. Rays of equal intensity therefore describe a cone whose axis is the direction of the incident beam, and the angular distribution of intensity in any plane containing the incident beam is, as regards relative intensity, the same as in the special case when the particle axes are perpendicular to the main beam, although in that case the diffraction is limited to one plane only. In other words, the expressions derived in the previous sections apply also to an assembly of a large number of randomly oriented independent scattering domains. They would not, however, apply to the general case of arbitrary specific orientation just discussed and illustrated in Fig. 5.

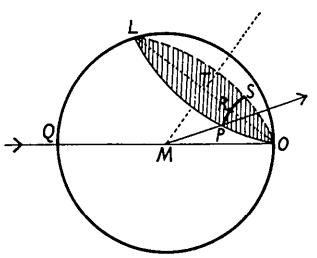

Fig. 5. Ewald scattering sphere (see text for explanation).

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