Acta Cryst. (1952). **5**, 1

Scattering from Isotropic Colloidal and Macromolecular Systems

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(*Received* 22 *February* 1951 *and in revised form* 18 *May* 1951)

The theory of scattering for various idealized models of colloidal particles and macromolecules is developed in order to explain the angular scattering from systems of such particles. The scattering intensity is calculated for independent particles of the form of solid spheres, spherical shells, periodic shells, and various aggregates of spheres; and the results are compared with the scattering by gases of atoms and molecules. The scattering by non-ideal systems of non-interacting and of repelling spheres is calculated, using ideas derived from theories of scattering by non-ideal gases and liquids.

Introduction

The field of macromolecular chemistry poses some rather special problems in X-ray scattering theory, and it is the object of this paper to treat some of the simpler cases that arise. We shall be concerned particularly with the application of existing concepts in the theory of scattering to the study of colloidal systems where the overall properties are isotropic. The examination of structures showing preferred orientation, as with fibres, will be treated elsewhere.

The interpretation of the scattering of X-rays and visible light by solutions of colloids and macromolecules is formally identical with that for scattering by systems made up of atoms. There is, however, a qualitative difference between scattering by systems of atoms and by systems of large particles. The scattering material in an atom, the cloud of electrons (or the nucleus in the case of neutron scattering), is denser close to the nucleus while the effective size of the atom from the point of view of packing considerations may be determined by the outer periphery of the attenuated cloud of electrons. As a result, the intensity of scattering (in this case, the square of the atomic scattering factor f) decreases slowly with angle, and for condensed systems of atoms the structural diffraction is superposed on this slowly falling curve. In the case of colloidal particles and macromolecules, however, the scattering material is localized in a finite region which may, for example, in the case of a hard non-repelling sphere, extend uniformly to the boundary of the particle. The intensity of scattering then falls off rapidly with the angle of observation and may obscure or distort the diffraction for condensed systems of such particles.

In this paper we shall apply the theory of scattering to various idealized models of colloid particles and macromolecules in order to explain the angular scattering from solutions of such particles. In order to make the theory one of general applicability we introduce the dimensionless parameter kR, in which R is the radius of the spherical particle and $k=(4\pi/\lambda)\sin\theta$, where λ is the wave-length of the radiation in the solution and 2θ is the angle between the incident beam, assumed parallel, and the direction of scattering (i.e. twice the Bragg angle in the crystallographic case). This enables us to make a direct comparison between X-ray scattering and light scattering on the same system. For the simple dipole scattering theory to be applicable, it is necessary that the index of refraction of the particle be nearly that of the medium (Oster, 1948), a condition which is always satisfied in practice with X-rays and which is usually satisfied with visible light unless the particles have a high refractive index as, for example, with metallic colloids. The introduction of the parameter kR also enables a comparison to be made with scattering by atoms and shows qualitatively the difference in angular scattering to be expected for atoms of low and of high atomic numbers.

From the point of view of the physics of solutions, the problem divides itself into three categories: (1) ideal solutions (analogous to scattering by free atoms), (2) ideal solutions of aggregates of particles (analogous to scattering by free molecules), (3) non-ideal solutions (analogous to scattering by non-ideal gases or by monatomic or molecular liquids). We shall also introduce for the condensed systems of particles the concept of 'hydration' which is equivalent to mutual repulsion between the particles (Oster, 1950).

Isolated particles

The intensity of scattering by an ideal solution or disperse system is simply the sum of the intensities scattered by each individual molecule or particle, as, *ex hypothesi*, there is no interference between waves scattered by different particles.

The simplest type of particle to consider is that in which the density of scattering material is distributed in a spherically symmetrical fashion. The amplitude of the scattered radiation in such a case is given by

$$\frac{\int_0^\infty 4\pi r^2 G(r) \frac{\sin kr}{kr}\, dr}{\int_0^\infty 4\pi r^2 G(r)\, dr}, \tag{1}$$

(Debye, 1930), where $G(r)\,dr$ is the probability density of scattering material within a spherical shell limited by radii r and $r+dr$ referred to the centre of the particle as origin. The numerator in (1) is derived in most textbooks on X-ray optics. We have introduced in the denominator an expression proportional to the volume of the scattering material in order that the normalized amplitude F ($F=1$ for $kR=0$) be independent of the actual magnitude of the scattering, since we are concerned in the present paper only with the relative scattering at various angles.

For a solid sphere of radius R, $G(r)$ is unity for values of r from 0 to R and is zero for $r>R$. Substitution into (1) gives

$$F=3\left[\frac{\sin kR - kR\cos kR}{(kR)^3}\right] \tag{2}$$

(Rayleigh, 1914). If we call this function $\Phi(x)$, where $x=kR$, the following relation to the Bessel function of order $\frac{3}{2}$, $J_{\frac{3}{2}}(x)$, will be found useful in computing

$$\Phi(x)=3\sqrt{\frac{\pi}{2}}\left(\frac{J_{\frac{3}{2}}(x)}{x^{\frac{3}{2}}}\right).$$

Tables of the spherical Bessel function

$$S(x)=\sqrt{\frac{\pi}{2x}}\,J_{\frac{3}{2}}(x)$$

exist (*Tables of Spherical Bessel Functions*, 1947, vol. 1), and the required function may be simply derived from them by using the relation

$$\Phi(x)=\frac{3}{x}\,S(x).$$

The scattered intensity is given by $\Phi^2(x)$. The normalized intensity F^2 as a function of kR, computed in this way, is illustrated in Fig. 1, curve B. This function is a rapidly damped oscillating curve falling off as $(kR)^{-4}$ for large values of kR, with maxima at $kR=0$ and 5·75, and zero values at $kR=4{\cdot}49$ and 7·73.

It is instructive to compare the above result with the scattering by a free atom in which the apparent radius R_s for scattering is smaller than the outer radius R_a obtained from interatomic distances. Curve A in Fig. 1 gives the square of the atomic scattering factor divided by the atomic number, i.e. $(f/Z)^2$, for mercury (f values from Compton & Allison (1935, p. 781)). The radius R_a is taken to be 1·50 A. as obtained from crystallographic data. For a solid sphere the relative intensity is reduced to one half at $kR=1{\cdot}76$, whereas for an atom of mercury the half intensity is not reached until $kR_a=6{\cdot}0$. For diffraction theory a particularly important region of kR is that in the neighbourhood of $kR=\pi$, the Bragg condition for an interplanar spacing $2R$, as would be the case for the 100 planes in a primitive cubic lattice; for solid spheres the relative intensity is then only 0·0925, whereas for mercury the relative intensity is 0·70.

In certain cases, e.g. soap–water–benzene systems or solutions of proteins stained with heavy atoms, one would need to consider the possibility that the particles resemble shells more than solid spheres. For a spherical 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 in (1) gives

$$F=3\left[\frac{(\sin kR - kR\cos kR)-(\sin ckR - ckR\cos ckR)}{(1-c^3)(kR)^3}\right]. \tag{3}$$

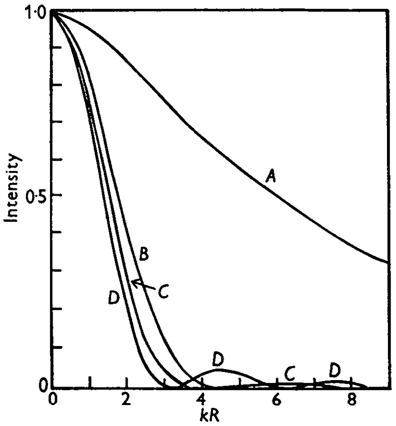

Fig. 1. Normalized intensity of scattering for independent mercury atoms ($R=1{\cdot}50$ A.) (curve A), solid spheres (curve B), spherical shells of finite thickness ($c=0{\cdot}8$) (curve C), and thin spherical shells (curve D). The maximum for curve B at $kR=5{\cdot}75$ is too low to be shown.

Fig. 1, curve C, shows F^2 for $c=0{\cdot}8$, i.e. for a shell of thickness one-fifth the outer radius of the sphere. If, in (3), we let $c\to 1$, we obtain, for an infinitesimally thin shell of radius R (Wrinch, 1946),

$$F=\frac{\sin kR}{kR}, \tag{4}$$

and F^2 for this case is given by curve D, Fig. 1. The F^2 curves in Fig. 1 fall off more rapidly the thinner the shell. This is analogous to the more rapid falling-off of $(f/Z)^2$ values as one goes from heavy atoms, where the bulk of the electrons are close to the nucleus, to light atoms, where the electrons are more dispersed.

For small values of kR the F^2 curves may be approximated by a power series, the first two terms of which are

$$1-\frac{(kR)^2}{5}p, \tag{5}$$

where $p=c^2+(c+1)/(c^2+c+1)$ for a finite shell of thickness $(1-c)R$. For an infinitesimally thin shell ($c=1$), $p=\frac{5}{3}$; for a solid sphere ($c=0$), $p=1$. Guinier (1939) has approximated the scattering for a solid sphere by a Gaussian function, which is a good representation of the curve except for large values of kR.

A particle might have an internal structure which is radially periodic. Then, as a first approximation, the density for $R > r > 0$ will be proportional to

$$G(r) = \cos^2(\pi m r/R),$$

and $G(r)$ is zero for $r > R$. The number of concentric shells is given by m, where m is an integer. Substitution into (1) gives

$$F = \frac{(2\pi m + kR)\,\Phi(2\pi m + kR) - (2\pi m - kR)\,\Phi(2\pi m - kR) + 2kR\,\Phi(kR)}{2kR}, \tag{6}$$

where $\Phi(x)$ is the function described earlier. When m is large, that is, when the inter 'plane' distance is small compared with the size of the particles, then $F \to \Phi(kR)$, the value for a solid sphere. This is also the case for any value of m when kR is small. Thus the scattering at small angles cannot help in determining the internal structure of such a particle. When kR is in the neighbourhood of $2\pi m$ (i.e. close to the Bragg condition for diffracting planes of spacing R/m) the middle term of the numerator of (6) becomes the most important term. In the neighbourhood of $kR \approx 2\pi m$, the sharpness of the band increases the larger the value of m, since the other two terms of opposite sign in the numerator then become less important.

The treatment given above for a solid sphere has been generalized by Shull & Roess (1947) to apply to solid ellipsoids of revolution in random orientation. The final results cannot be represented in closed form and depend both on the size of the particle and its axial ratio.

The results obtained in this section will apply to solutions of macromolecules, or disperse systems generally, of sufficient dilution for the assumption of an ideal system to hold.

Isolated aggregates of particles

Under certain conditions colloidal particles and macromolecules will aggregate in solution. If the system is sufficiently dilute for these aggregates to scatter independently, the observed intensity of scattering is, as previously, the sum of the intensities scattered by each individual aggregate. Random orientation of the aggregates will be assumed.

For an aggregate of n particles, each of scattering factor F, the averaged intensity of scattering will be F^2 times the double summation

$$\frac{1}{n^2}\sum_i\sum_j \frac{\sin kr_{ij}}{kr_{ij}}, \tag{7}$$

where r_{ij} is the distance between the particles i and j. This expression, due to Debye (1915), has been multiplied by the factor $1/n^2$ to obtain the scattering per particle making up the aggregate.

For two spheres in contact, (7) becomes

$$\frac{1}{4}\left[2 + 2\frac{\sin 2kR}{2kR}\right]. \tag{8}$$

This expression has a maximum (besides that at $kR = 0$) at $kR = 3{\cdot}86$, or, in the form of the Bragg relation,

$$2 \times 0{\cdot}816 \times 2R \sin\theta = \lambda.$$

For a tetrahedral arrangement of five spheres in contact, (7) becomes

$$\frac{1}{25}\left[5 + 8\frac{\sin 2kR}{2kR} + 12\frac{\sin 4\sqrt{(\frac{2}{3})}\,kR}{4\sqrt{(\frac{2}{3})}\,kR}\right], \tag{9}$$

with a maximum at $kR = 2{\cdot}5$, or $2 \times 1{\cdot}26 \times 2R \sin\theta = \lambda$.

For a first shell of nearest neighbours (12 spheres in contact with a central sphere), (7) becomes

$$\frac{1}{169}\left[13 + 72\frac{\sin 2kR}{2kR} + 6\frac{\sin 4kR}{4kR} + 12\frac{\sin 2\sqrt{(3)}\,kR}{2\sqrt{(3)}\,kR} + 6\frac{\sin 4\sqrt{(\frac{2}{3})}\,kR}{4\sqrt{(\frac{2}{3})}kR} + 12\frac{\sin 2\sqrt{(\frac{11}{3})}\,kR}{2\sqrt{(\frac{11}{3})}\,kR} + 24\frac{\sin 2\sqrt{(2)}\,kR}{2\sqrt{(2)}\,kR} + 24\frac{\sin\frac{2\sqrt{2}}{\sqrt{3}-1}kR}{\frac{2\sqrt{2}}{\sqrt{3}-1}kR}\right], \tag{10}$$

with a maximum at $kR = 2{\cdot}2$, or $2 \times 1{\cdot}43 \times 2R \sin\theta = \lambda$.

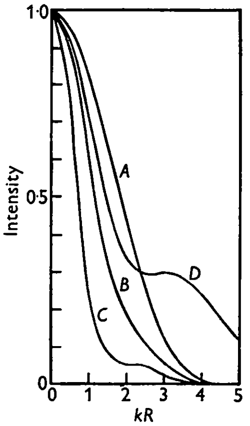

Fig. 2. Normalized intensity of scattering per sphere for independent single solid spheres (curve A), aggregates of two solid spheres in contact (curve B), centred tetrahedral aggregates of five solid spheres (curve C), and aggregates of two 'hydrated' solid spheres (curve D).

In Fig. 2 are shown the intensity curves for the aggregates of spherical particles given by (8) and (9). For the aggregate of two solid spheres in contact the maxima are swamped out by the strong influence of the F^2 factor. For the tetrahedral packing of solid spheres the diffraction is just perceptible, but the inflexion points do not correspond to the values of kR where (9) exhibits maxima. A similar result is obtained for the case of the closest packing of 13 solid spheres. With thin spherical shells the diffraction maxima are even more obscured. With an aggregate of two 'hydrated' solid spheres, each of radius $\frac{1}{2}R$ but with a radius of separation R (i.e. 700 % hydrated by volume), however, diffraction is just perceptible at

$$kR=3{\cdot}0, \text{ or } 2\times 0{\cdot}955\times 2R\sin\theta=\lambda.$$

This latter fact is analogous to that derived in the treatment of molecules by Debye & Pirenne (1938), who pointed out that diffraction maxima of biatomic molecules would be visible only for atoms of high atomic number.

For small values of kR the scattering intensity decreases more rapidly the greater the complexity of the aggregate. In the case of aggregates made up of solid spheres, the final normalized intensity per solid sphere is F^2 for a solid sphere multiplied by one of the above expressions (8), (9) or (10). For small values of kR, the result may be approximated by a power series, the first two terms of which are

$$\left.\begin{array}{l} 1-0{\cdot}53\,(kR)^2 \text{ (2 spheres)}, \\ 1-1{\cdot}28\,(kR)^2 \text{ (centred tetrahedron, 5 spheres)}, \\ 1-1{\cdot}50\,(kR)^2 \text{ (13 spheres)}. \end{array}\right\} \quad (11)$$

These approximate expressions represent the course of the low-angle scattering from dilute systems of aggregated spherical particles.

Non-independent particles

We have now to consider more dense systems, e.g. concentrated solutions, in which there is interference between waves scattered by different particles. The intensity of scattering for such a system which is isotropic over the region irradiated was first given by Zernicke & Prins (1927). We shall, however, write the expression for the normalized intensity in the slightly modified form given by Debye & Menke (1931)

$$F^2\left[1-\nu\int_0^\infty 4\pi r^2(1-g(r))\frac{\sin kr}{kr}\,dr\right], \quad (12)$$

where $\nu=N/V$ is the number of scattering particles per unit volume, and F is the scattering factor for isolated particles discussed above. The probability of finding centres of particles spherically symmetrically disposed (on an average) at a distance r from the centre of any reference particle is given by the radial distribution function $g(r)$. As pointed out by Debye & Menke, (12) should also contain a term due to the finite size of the scattering sample, the whole-volume term. For a spherical irradiated region of radius S containing N particles this term equals $NF^2\Phi^2(kS)$, where $\Phi(x)$ is the scattering function for spheres defined earlier. Since, for X-ray or light scattering, S will be of the order of 10^6 times the wave-length, this term will be important only at extremely small angles (of the order of seconds of arc) and may be neglected except when considering the scattering from samples of microscopic dimensions.

If the value of k can be made sufficiently large, the integral in (12) becomes zero and the scattered intensity is simply F^2, as for independent particles. It should, however, be noted that k can never exceed $4\pi/\lambda$.

When k is actually zero, the integral in (12) is zero and the normalized intensity of scattering at zero angle is F^2 plus the whole-volume contribution. The sum of the two is NF^2, which corresponds to the expected result that the intensity of the total exactly forward scattering is $(NF)^2$, as all amplitudes are then in phase. The simple summation is justified if the specimen is sufficiently large for the whole-volume intensity to be localized in a very narrow region; this is true for most practical cases with X-rays. Practical interest, however, centres on the *observable* intensity in the region where k is very nearly zero, but is just large enough for the whole-volume scattering to be negligible. In the following treatment of the zero-angle scattering, we are really considering the intensity of the observable particle scattering extrapolated to zero angle. This is the thermodynamically significant part of the scattering at zero angle.

According to the fluctuation theory of scattering (Smoluchowski, 1908; see also Oster, 1948) for point particles (i.e. $kR=0$) the normalized intensity equals $\nu\boldsymbol{k}T\beta$, where $\boldsymbol{k}$ is Boltzmann's constant, T is the absolute temperature, and β is the isothermal compressibility. Since, for any-sized particles, F^2 is unity for zero scattering angle ($kR=0$), then at zero scattering angle the normalized intensity (equation (12)), neglecting the contribution due to the sample being of finite extent (whole-volume term), is simply $\nu\boldsymbol{k}T\beta$. The integral in (12) then equals $\boldsymbol{k}T\beta-1/\nu$, a result obtained earlier by Zernicke & Prins (1927) (see also Yvon, 1937).

For an ideal system the equation of state per particle is $P=\nu\boldsymbol{k}T$ or $\beta=1/\nu\boldsymbol{k}T$, and (12) equals unity for $k=0$. That is, at zero angle the normalized intensity of scattering for an ideal system of particles of any size (the sample itself being of infinite extent) is unity. For a slightly imperfect system with equation of state $P/\boldsymbol{k}T=\nu+b\nu^2$, where the van der Waals covolume $b=4(\frac{4}{3}\pi R^{*3})$, and $2R^*$ is the distance of closest approach of particle centres, equation (12) becomes $(1+2b\nu)^{-1}$ at $k=0$, i.e. a value less than unity. According to the free-volume theory of liquids (Eyring & Hirschfelder, 1937) the equation of state of a liquid of hard non-interacting particles is given by

$$\frac{P}{\boldsymbol{k}T}=\frac{\nu}{1-(\nu/\nu_0)^{\frac{1}{3}}},$$

where ν_0 is the concentration of the particles in the solid state (for a closest-packed arrangement of spheres the particles occupy 74·05 % of the volume). This equation of state, which is a fair approximation to that obtained from the theory of liquids of hard non-interacting spheres of Kirkwood and of Born & Green (Kirkwood, Maun & Alder, 1950), gives for the scattered intensity at $kR=0$,

$$\nu\boldsymbol{k}T\beta=\frac{[1-(\nu/\nu_0)^{\frac{1}{3}}]^2}{1-\frac{2}{3}(\nu/\nu_0)^{\frac{1}{3}}}.$$

To compute the scattering for condensed systems at angles other than $\theta=0$ ($k=0$) is, in general, difficult because one must compute the simultaneous coherent scattering from all the particles. In some cases, however, one can compute the intensity of scattering if only interactions of pairs are considered. For example, for a very dilute system of hard spheres of radius R and distance of closest approach $2R^*$ the radial distribution function is given, to a first approximation, by $g(r)=0$ for $2R^*>r>0$ and by $g(r)=1$ for $r>2R^*$. Equation (12) then becomes

$$F^2(kR)\,[1-2\nu b\Phi(2kR^*)], \tag{13}$$

a result due to Debye (1925). The formula cannot be valid for high concentrations as Fournet & Guinier (1949) have pointed out. For a volume concentration $\frac{1}{8}\nu b$ exceeding 12·5 % the scattered intensity would be negative at $k=0$, clearly an impossible result. Thus, (13) may be regarded as a limiting expression for very low concentrations.

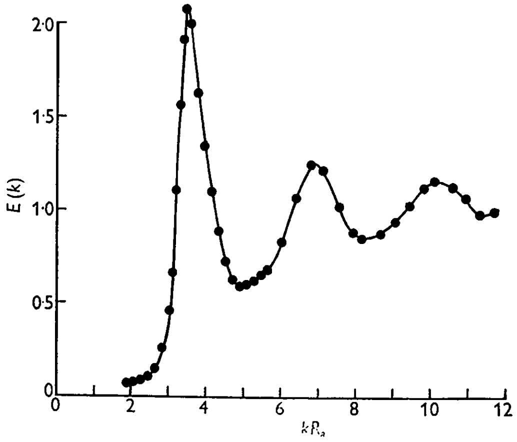

Fig. 3. $E(k)$ for liquid mercury from experimental data of Jennings ($R_a = 1{\cdot}50$ Å).

Fournet (1949) has applied the first approximation of the theory of imperfect gases of Born & Green (1946, 1947) to the problem of scattering by spheres and obtains, for the intensity,

$$F^2(kR)\,[1+2\nu b\Phi(2kR^*)]^{-1}, \tag{14}$$

which approaches (13) for small values of the volume concentration. This equation can be shown analytically to have a maximum (for $kR>0$) only when the volume concentration of the particles exceeds 33 %. This, in the case of a gas, is the density at the critical point. Although this formula circumvents the difficulties of (13) it cannot, of course, be applied to concentrations exceeding 33 %, where the simultaneous interactions of more than pairs must be considered. If the particles have short-range attractive forces, as with molecules in a gas, then at 33 %, superimposed on the curve described by (14) will be a large intensity of scattering at small values of kR since, owing to large concentration fluctuations, the local high density of particles will scatter like the aggregates of spheres described earlier (see theoretical treatment of Ornstein & Zernicke (1926) and experimental data of Noll (1932)).

Kirkwood & Boggs (1942) have derived an analytical expression, a damped oscillating function, for the radial distribution for hard non-interacting spheres which is valid up to the concentration of the solid state. The intensity of scattering for a concentrated system of hard spheres has been evaluated from (12), using the Kirkwood & Boggs theoretical radial distribution function (Oster, 1949).

We prefer, however, to use experimental figures for the angular scattering from liquid mercury to evaluate $E(k)$, the term in square brackets in (12). These figures were kindly supplied to us in advance of publication by Dr R. E. Jennings, of University College, London. They refer to liquid mercury at 22·7° C. and were obtained in a very careful investigation using the counter method for the measurement of intensity. $E(k)$ in Fig. 3 was derived from the expression

$$\frac{I}{n(f-g_K-g_L)^2},$$

where I is the corrected scattered intensity and f is the atomic scattering factor for mercury atoms (Thomas–Fermi model) as given in the *Internationale Tabellen* (1935, vol. 2, p. 573). As the wave-length of the X-radiation used (Cu $K\alpha$) was longer than the wave-length associated with the K and L absorption edges of mercury, the published f values need correction for the oscillator strengths of the corresponding electron groups (see James, 1948, p. 154). This correction term, g_K+g_L, has been taken to be 6 units for all values of $\sin\theta/\lambda$. n is a standardizing constant; R_a is taken to be 1·50 Å, the atomic radius in the solid state.

Curve A of Fig. 4 is the intensity of scattering (per sphere) for solid spheres of radius R in a system having the same relative configurations as in liquid mercury. At $k=0$ the curve should theoretically reach the value $6{\cdot}3\times10^{-3}$, since for liquid mercury at room temperature $\nu=4{\cdot}06\times10^{22}$ and $\beta=3{\cdot}76\times10^{-12}$ in c.g.s. units. The maximum of the curve is at $kR=3{\cdot}30$ or $2\times0{\cdot}95\times2R\sin\theta=\lambda$. Curve B is the intensity of scattering for a system of hydrated spheres of scattering radius R and radius of closest approach $1{\cdot}5R$. The intensity has been reduced by a factor of 10 so as to be represented on the same figure. The maximum is much sharper than that of curve A and occurs at $kR=2{\cdot}3$ or $2\times0{\cdot}91\times3R\sin\theta=\lambda$. Although at the maximum the scattering per unit sphere for this case is six times greater than that for the case of the unhydrated sphere, the absolute intensity of scattering will only be about twice as large, since the concentration of the hydrated system is about one-third that of the other. Curve C is the intensity of scattering for thin spherical shells arranged as are the atoms in liquid mercury. The maximum occurs at $kR=4{\cdot}20$ or $2\times0{\cdot}75\times2R\sin\theta=\lambda$. The alternative expressions for the positions of the maxima are given in this form for comparison with the Bragg expression $2d \sin \theta = \lambda$. It will be seen that routine use of the Bragg law would give d nearly equal to the correct value for the interparticle distance in the first two instances.

We can summarize the angular scattering results for hard spheres as follows (cf. Vineyard (1948) and Fournet & Guinier (1950)). For infinitely dilute systems the scattered intensity as a function of angle is the bell-shaped curve (B) of Fig. 1. On increasing the concentration the curve flattens and at 33 % it is a plateau, except at very small angles where it rises sharply. On further increasing the concentration a maximum occurs which becomes sharper and appears at increasingly greater values of kR until the system solidifies and a very sharp maximum appears at $kR=\pi$ (Bragg's law). The total intensity of scattering (for a given wave-length) *per sphere* is obtained by integrating (12) over the entire solid angle of scattering. The total intensity *per sphere* will decrease with increasing concentration because of the increasing importance of the coherence in relative positions of the particles, as expressed by the integral term in (12). If the system has a critical point (this depends on the magnitude of b), then at about 33 % there will be a sudden rise in intensity of scattering analogous to critical opalescence in light scattering.

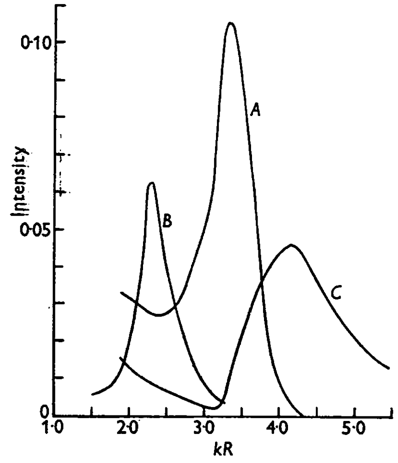

Fig. 4. Normalized intensity of scattering per sphere for hard spheres (curve A), 'hydrated' spheres (curve B), and thin spherical shells (curve C), arranged as in liquid mercury.

The effective volume of repelling particles in solution is difficult to calculate *a priori* since it is determined by several factors, e.g. the electrical charge on the particle and the salt concentration (see Oster, 1950). If, however, we determine the radial distribution function $g(r)$ by a Fourier transformation of (12), using the angular scattering data of a given solution of particles, and if, in addition, we know the osmotic pressure P of the solution as a function of concentration, we can then determine the force of interaction of the particles $F(r)$ from the equation (Kirkwood, 1935; Yvon, 1935)

$$P=\nu kT\left[1+\frac{\nu}{6kT}\int_0^{\infty} 4\pi r^2 g(r)\,F(r)\,r\,dr\right]. \quad (15)$$

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