naphthalene as far as comparison is valid. The m.o. method seems to over-emphasize the amount of charge between the atoms, whilst the T.F. method tends to exaggerate the presence of the atoms at the expense of the 'bond' character. Also, as always, it should be remembered that the T.F. method gives poor results near the nuclei and at large distances, and that to some extent therefore charge contours 'flatter' its results. The results must await experimental work on the actual distribution in benzene before any more detailed discussion can be given of the relative merits of the two methods employed here.

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Particle Size Distribution from Small-Angle X-ray Scattering

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A solution of the integral equation describing the intensity of X-ray scattering at low angles by a non-uniform collection of independently scattering spherical particles is given. The final result is in a form such that the particle-size distribution can be calculated by integration. The resolvent kernel, which solves the integral equation, is shown to be a combination of half-integral order Bessel functions, and therefore obtainable from known tables. Utilizing the known scattering form for a single-sized group of spherical particles as illustration, the expected δ-function type of distribution is shown to result. The result obtained here can also be applied to the visible light scattering of dilute solutions of polydisperse macromolecules.

Introduction

During the past several years, small-angle X-ray scattering methods as a means for determining particle size have come into greater prominence. The theory of Guinier (1939, 1943, 1945; see also Hosemann 1939*a*, *b*), which served to interpret these results, was based on the independent scattering of a collimated, monochromatic beam by a system of equally sized spherical particles. The ideal character represented by such a set of assumptions, and the fact that one rarely encounters such systems within the laboratory, has stimulated research into such questions as the effect of particle shape, particle size distribution, and particle–particle interference (Patterson, 1939; Shull & Roess, 1947; Jellinek, Solomon & Fankuchen, 1946; Bauer, 1945; Roess, 1946; Yudowitch, 1949; Lund & Vineyard, 1949). Bauer (1945) and Roess (1946) have derived methods for obtaining, by analytic means, the particle-size distribution from the corrected experimental data, and Jellinek, Solomon & Fankuchen (1946) have done likewise using an approximate geometric method.

The analytical expressions obtained in both these cases are fairly complex, and, so far as is known, have not been used for this purpose. We have therefore derived an expression which allows us to obtain the particle-size distribution by numerical integration. The assumptions used are similar to those mentioned above, i.e. spherical particles and negligible interference. To take also the latter into account would necessitate the introduction of a second distribution function, that of the interparticle distances. Analysis of a set of scattering data for these two parameters would become extremely difficult.

Theory

Under the above mentioned assumptions, the theoretical scattered intensity of a collection of particles having a size distribution such that $N(R)dR$ is the number of particles with radius in the range R to $R+dR$, is given by (Hosemann, 1939*a*, *b*)

$$I(k) = K\int_0^\infty N(R)\frac{R^3}{k^3}J^2_{\frac{3}{2}}(kR)dR\ , \tag{1}$$

$$K = I_0(e^2/mc^2)^2(1+\cos^2 2\theta)4\pi^2 d^2\ ,$$

where $I(k)$ is the scattered X-ray intensity, as a function of the scattering angle. The incident X-ray beam is assumed to be collimated, or otherwise $I(k)$ is assumed to be corrected for collimation error.

The symbols, apart from the usual ones, have the following significance:

I_0 = Initial intensity of X-ray beam
$k = 4\pi \sin\theta/\lambda$
d = Electron density
2θ = Scattering angle

$J_{\frac{3}{2}}(z)$ = Bessel function of $\frac{3}{2}$ order of argument z

The factor $9\pi/2\ J^2_{\frac{3}{2}}(kR)/(kR)^3$ is the scattering function characteristic of a spherical particle.

Since the purpose of low-angle scattering measurements is the determination of particle size distribution, the problem at hand is to obtain from the theoretical equation (1) the particle size distribution in terms of the observed scattering data. We therefore rewrite equation (1) in the following form:

$$F(k) = \int_0^\infty \frac{W(R)J^2_{\frac{3}{2}}(kR)dR}{(kR)^\nu}\ , \tag{2}$$

$$F(k) = \frac{I(k)}{K}k^{3-\nu}\ ; \quad W(R) = N(R)R^{3+\nu}\ ,$$

where a term $(kR)^\nu$ has been included in both numerator and denominator of the integrand to serve as a convergence factor.

ν will be so chosen that the integrals encountered will certainly converge. Equation (2) is an integral equation (Fredholm first kind with infinite limit) with kernel $J^2_{\frac{3}{2}}(kR)/(kR)^\nu$, the argument of which is in product form. Integral equations with kernels of this type lend themselves to solution by the method of Mellin transforms, if the corresponding integrals exist (Titchmarsh, 1937).

It should be pointed out that in treating the above integral equation, the usual practice in X-ray theory has been followed here, namely the extension of the range of the variable k. k, which is an experimentally determined quantity, is by its definition bounded, $-4\pi/\lambda \le k \le 4\pi/\lambda$. In solving the integral equation, k is allowed to approach infinity. Similar extension of range is made, for example, in the application of X-rays to the structure of liquids (Gingrich, 1943) where the integral equation in question contains the sine function as kernel, and where the extension of range permits immediate application of the Fourier integral theorem. Again, in performing a Hankel transformation, Bauer (1945) likewise allows a variable $z = 2k\cos q$ to become infinite, where not only k, but q is also limited to the range $0-\frac{1}{2}\pi$.

It is not our purpose to discuss the validity of such an extension of range. It is desired, however, to indicate clearly that such extensions are currently made in X-ray problems, and that from a purely mathematical point of view the solutions obtained would be open to question. The extension in range of k greatly simplifies the problem in allowing direct use of the Mellin transform method, similar to allowing the use of Fourier and Hankel transforms in the cases cited above.

The Mellin transform of equation (2) is

$$\begin{aligned} f(s) &= \int_0^\infty F(k)k^{s-1}dk \\ &= \int_0^\infty\left\{\int_0^\infty W(R)\frac{J^2_{\frac{3}{2}}(kR)}{(kR)^\nu}dR\right\}k^{s-1}dk \qquad (3) \\ &= \int_0^\infty W(R)R^{-s}dR\int_0^\infty u^{-\nu}J^2_{\frac{3}{2}}(u)u^{s-1}du\ . \end{aligned}$$

There is no difficulty here in the interchange of the order of integration (Bromwich, 1947, p. 503). The integral on the right hand side of equation (3) has an integrand of the form $J^2_{\frac{3}{2}}(u)/u^\lambda$, and is therefore a particular example of the critical case of the Weber–Schaftheitlin integral discussed by Watson (1948). The integral converges for $4 > \mathrm{Re}(\lambda) > 2$, where Re indicates the real part, and ν in equation (3) will be considered to have a value appropriate for the condition to be fulfilled. The value of this integral is:

$$\int_0^\infty u^{-\nu}J^2_{\frac{3}{2}}(u)u^{s-1}du = \frac{1}{2(\sqrt{\pi})}\frac{\Gamma(\frac{1}{2}-\frac{1}{2}s+\frac{1}{2}\nu)\Gamma(\frac{3}{2}+\frac{1}{2}s-\frac{1}{2}\nu)}{\Gamma(1-\frac{1}{2}s+\frac{1}{2}\nu)\Gamma(\frac{5}{2}-\frac{1}{2}s+\frac{1}{2}\nu)}$$
$$\nu-3 < \mathrm{Re}(s) < \nu-1\ . \tag{4}$$

Substituting in equation (3) and solving for $W(1-s)$ we obtain

$$W(1-s) = 2(\sqrt{\pi})\frac{\Gamma(1-\frac{1}{2}s+\frac{1}{2}\nu)\Gamma(\frac{5}{2}-\frac{1}{2}s+\frac{1}{2}\nu)}{\Gamma(\frac{1}{2}-\frac{1}{2}s+\frac{1}{2}\nu)\Gamma(\frac{3}{2}+\frac{1}{2}s-\frac{1}{2}\nu)} \tag{5}$$
$$\nu-3 < \mathrm{Re}(s) < \nu-1\ ;$$

substituting $1-z$ for s, and taking the inverse Mellin transform the desired particle size distribution is obtained:

$$W(R) =$$
$$2(\sqrt{\pi})\frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty}f(1-z)\frac{\Gamma(\frac{1}{2}+\frac{1}{2}\nu+\frac{1}{2}z)\Gamma(2+\frac{1}{2}\nu+\frac{1}{2}z)}{\Gamma(\frac{1}{2}\nu+\frac{1}{2}z)\Gamma(2-\frac{1}{2}\nu-\frac{1}{2}z)}R^{-z}dz$$
$$4-\nu > \mathrm{Re}(z) > 2-\nu\ . \tag{6}$$

Application of the Parseval formula to equation (6) leads to:

$$W(R) = 2(\sqrt{\pi})\int_0^\infty \dot{F}(k)\,\mathscr{H}(kR)dk \tag{7}$$

$$\mathscr{H}(kR)=\frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty}\frac{\Gamma(\frac{1}{2}+\frac{1}{2}\nu+\frac{1}{2}z)\Gamma(2+\frac{1}{2}\nu+\frac{1}{2}z)}{\Gamma(2-\frac{1}{2}\nu-\frac{1}{2}z)\Gamma(\frac{1}{2}\nu+\frac{1}{2}z)}(kR)^{-z}dz\,.$$

The integrand has simple poles at $z = -(2m+\nu+1)$; $m = 0, 1, 2, \ldots$, in the left-hand part of the complex plane. Also for $\alpha < 0$, the integral along the line $z = \alpha+iy$ may be evaluated by means of the Cauchy residue theorem, since the integral along the line can be extended along a semi-circle of radius $N+\frac{1}{2}$ with $N \to \infty$. On this semi-circle, the integrand will vanish exponentially because of the presence of a cos (arg z) term which is always negative. We therefore choose ν to be equal to 3 and our resolvent kernel $\mathscr{H}(kR)$ becomes

$$\mathscr{H}(kR) = \frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty}\frac{\Gamma(2+\frac{1}{2}z)\Gamma(\frac{7}{2}+\frac{1}{2}z)}{\Gamma(\frac{1}{2}-\frac{1}{2}z)\Gamma(\frac{3}{2}+\frac{1}{2}z)}(kR)^{-z}dz \tag{8}$$

$$= 2\sum_{p=0}^{\infty}(-1)^p\frac{\Gamma(p+\frac{3}{2})(kR)^{2p+4}}{p!\Gamma(\frac{5}{2}+p)\Gamma(p-\frac{1}{2})}$$

$$= -\frac{2}{3\sqrt{\pi}}(kR)^4\,{}_1F_2(\tfrac{3}{2};\ \tfrac{5}{2}, -\tfrac{1}{2};\ -(kR)^2)$$

$$1 > \mathrm{Re}(z) > -1\,,$$

where ${}_1F_2(\frac{3}{2}; \frac{5}{2}, -\frac{1}{2}; -(kR)^2)$ is the generalized hypergeometric function (Watson, 1948). The distribution function $N(R)$ is thus

$$N(R) = -\frac{4}{3KR^2}\int_0^\infty k^4 I(k)\,{}_1F_2(\tfrac{3}{2}; \tfrac{5}{2}, -\tfrac{1}{2}; -(kR)^2)dk\,. \tag{9}$$

The infinite sum in equation (8) can be evaluated in terms of Bessel functions to give the distribution function in a form more amenable to calculation, which leads to

$$N(R) = \frac{\sqrt{\pi}}{2KR^3}\int_0^\infty k^3 I(k)\varphi(kR)dk \tag{10}$$

$$\varphi(x) = \frac{8}{\sqrt{x}}\left\{(2-x^2)J_{\frac{3}{2}}(2x)-\tfrac{3}{2}xJ_{\frac{1}{2}}(2x)\right\}.$$

In this form the function $\varphi(kR)$ can be readily evaluated from tables of Bessel functions, for different values of the argument. Numerical integration, utilizing these values and experimental values of $k^3I(k)$, yields for a predetermined value of R the number density corresponding to this value of R. Values of $\varphi(x)$ for x ranging from 0 to 5 are given in Table 1, and can be used in performing the numerical integration.

Table 1. *Values of* $\varphi(x)$

x	$\varphi(x)$
0	0
0·05	0·0451
0·10	−0·1508
0·15	−0·2272
0·20	−0·2701
0·25	−0·3984
0·30	−0·4938
0·35	−0·6030
0·40	−0·7032
0·45	−0·8213
0·50	−0·9400
0·60	−1·200
0·70	−1·472
0·80	−1·748
0·90	−2·008
1·00	−2·225
1·10	−2·374
1·2	−2·426
1·3	−2·353
1·4	−2·142
1·5	−1·736
1·6	−1·214
1·7	−0·7324
1·8	−0·1741
2·0	3·027
2·5	10·142
3·0	12·491
3·5	4·280
4·0	−10·952
4·5	−20·299
5·0	−12·607

Example

To illustrate the use of this result we consider the case where the experimental scattering curve is that due to a single size species of radius R_0. The experimental scattering curve should then be given by

$$I(k) = KN\frac{R_0^3}{k^3}J^2_{\frac{3}{2}}(kR_0)\,, \tag{11}$$

and the particle size distribution by

$$N(R) = \frac{\sqrt{\pi}}{2}N\left(\frac{R_0}{R}\right)^3\int_0^\infty J^2_{\frac{3}{2}}(kR_0)\varphi(kR)dk\,. \tag{12}$$

The integral in equation (12) can be conveniently integrated by the use of Mellin transforms, so that

$$N(R) = N\left(\frac{R_0}{R}\right)^3\frac{1}{2\pi i}\int_{k-i\infty}^{k+i\infty}R_0^{s-1}R^{-s}ds\,. \tag{13}$$

Now consider the Mellin transform of Dirac's δ-function

$$\int_0^\infty \delta(x-y)x^{s-1}dx = y^{s-1}\,,$$

so that

$$\delta(x-y) = \frac{1}{2\pi i}\int_{k-i\infty}^{k+i\infty}y^{s-1}x^{-s}ds\,. \tag{14}$$

Making use of this result we find that

$$N(R) = N\left(\frac{R_0}{R}\right)^3\delta(R-R_0)\,, \tag{15}$$

so that

$N(R)dR = 0$ if dR does not contain R_0

$= N$ if dR contains R_0 and the range of dR approaches zero around R_0.

After these calculations had been completed, the work of Roess (1946), mentioned previously, was examined to determine the relationship of his result to that given here. Roess's result is given for the mass distribution function, which is simply related to the number distribution. Also using Mellin transforms, he obtained a form involving the differentiation of an integral, namely,

$$M(R)=\frac{-8R}{27\pi B}\frac{d}{dR}\int_0^\infty Rk^4I(k)\,{}_1F_2(\tfrac{1}{2};\ -\tfrac{1}{2},\tfrac{5}{2};\ -k^2R^2)dR$$

$$ {}_1F_2(\tfrac{1}{2};\ -\tfrac{1}{2},\tfrac{5}{2};\ -x^2)=-\tfrac{3}{2}J_{\frac{3}{2}}(x)J_{-\frac{3}{2}}(x)\,. \qquad (16)$$

Formally differentiating under the integral sign, we obtain, except for differences between the two types of distribution, the result shown in equation (10).

Although X-ray scattering has been discussed here, it is well known that an equation similar to equation (1) has been applied to the determination of size of spherical particles by visible light-scattering (Debye, 1944). It follows that the results obtained here should be applicable to dilute polydisperse solutions of spherical macro-molecules, in which particle–particle interference effects may be neglected.

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The Crystal Structure of Potassium Trioxalatochromate (III), $K_3[Cr(C_2O_4)_3]\,.\,3\,H_2O$

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The crystal structure of $K_3[Cr(C_2O_4)_3].3H_2O$ is monoclinic $P2_1/c$–C^5_{2h} with four formula units in a cell of dimensions $a = 7{\cdot}71$, $b = 19{\cdot}74$, $c = 10{\cdot}40$ Å, $\beta = 108°\ 0'$. The structure has the pseudo space group $C2/c$–C^6_{2h}, which was used throughout this investigation. By evaluating the functions $\sigma(x, y)$ and $\sigma(y, z)$, projections of the structure on two crystallographic planes were obtained.

The configuration of the two stereo isomeric complex ions $[Cr(C_2O_4)_3]$ is described. The three oxalato groups in a complex ion are planar, their inner oxygen atoms form a slightly distorted octahedron round the central chromium atom. It is shown that both ionic and hydrogen bonds link the complex ions in the structure. The errors introduced by treating the structure in the wrong space group are estimated not to be very serious, so that the investigation gives a clear picture of the general features of the structure.

1. Preparation and crystal data

The material used in this investigation was prepared by Mr R. W. Burley (1950) of the Leather Industries Research Institute, Grahamstown, South Africa. The crystallographic data of this compound were investigated by Jaeger (1919). We found his data to be substantially correct, except that his unit cell has very nearly three times the volume of our cell. The crystals are monoclinic holohedral and dark blue in colour. They usually crystallise as thick prismatic needles with large, well developed {031} faces. Jaeger calls these the {110} faces. In the literature this compound is usually described as $K_3[Cr(C_2O_4)_3].3H_2O$ (Jaeger, 1919; Wyrouboff, 1900; Rammelsberg, 1854; Schabus, 1854). The crystals are, however, unstable. They lose water in a dry atmosphere, decomposing into a crystalline powder, whereas in a humid atmosphere they absorb water and become liquid. The exact number of water molecules associated with a formula unit is therefore undetermined. Although the crystals were coated with perspex films during photographic exposures, the uncertainty of their exact water content when an exposure was started still