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A Simple Method of Obtaining a Particle Mass Distribution by Inverting the X Ray Intensity Scattered at Small Angles

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hypothesis and in favor of selective absorption. This does not exclude the possibility that in some systems polymer-polymer association may occur prior to incipient precipitation. However, light scattering data should be interpreted as indicating polymer-polymer association in a solvent-precipitant mixture only after a suitable correction for the effect of selective absorption of the solvent has been made.

The increase of turbidity with added precipitant in high polymer solutions is a very great advantage in the determination of molecular weights by turbidimetry. It not only raises the relative accuracy obtainable in the measurement of absolute turbidity, but at the same time greatly reduces the slope of the conventional scattering curves. The latter circumstance enables one safely to make the linear extrapolation to infinite dilution from a smaller amount of data than would be necessary in case the data had to be relied on to determine both a high slope and the intercept. It is probable that in most cases conditions can be found which reduce the slope practically to zero, so that τ/c may be set equal to $(\tau/c)_0$. The sole condition which must be satisfied is that $\partial n/\partial\psi$ is negligible with respect to $\partial n/\partial c$ in the system considered.

TABLE II.

ψ	$\{\eta\}$	$\frac{v}{m}$	α	$(\psi_2-\psi_1)\times 100$
1	131.5	52.6	0	0
0.925	122.0	48.8	0.12	0.25
0.90	118.7	47.5	0.24	0.51
0.875	110.6	44.2	0.34	0.79
0.85	102.6	41.0	0.40	1.00

The theory presented by the writers gives a satisfactory correlation of all the observed facts. In particular it accounts for the apparently anomolous molecular weights of high polymers as obtained by the application of simple scattering theory to measurements in solvent-precipitant systems. This theory also enables us to estimate the magnitude of selective absorption in these systems.

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A Simple Method of Obtaining a Particle Mass Distribution by Inverting the X-Ray Intensity Scattered at Small Angles

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THE purpose of this note is to describe a simple and practical method of obtaining a particle mass distribution by inverting the x-ray intensity scattered at small angles by a collection of spherical particles. The method is much simpler than that published by Bauer,[1] whose procedure is complex analytically and appears to be impractical numerically.

The exact equation for the intensity scattered by a randomly-spaced distribution of spherical particles is[2]

$$I(\xi)=B\int_0^\infty M(R)R^3S(R\xi)dR, \qquad (1)$$

where B is a constant containing as factors the incident intensity, the Thomson scattering term for a single electron, including the polarization factor, and the ratio of the square of the electron density to the mass density, $M(R)dR$ is the mass contained in a group of particles having radii between R and $R+dR$, $S(x)$ is the "form factor" for one particle, and $\xi=(4\pi/\lambda)\cdot\sin\theta$ (λ = wavelength, θ = Bragg angle). The scattered intensity $I(\xi)$ is that produced by a monochromatic[3] and parallel beam defined by a pinhole having a very small cross section. If a beam defined by slits is used, suitable corrections[4] must be made.

[1] S. H. Bauer, J. Chem. Phys. **13**, 450 (1945).
[2] For example, A. Guinier, Ann. de Physique **13**, 161 (1939); R. Hosemann, Zeits. f. Physik **113**, 751 (1939).

[3] Experiments performed in this laboratory show that large errors may be introduced by the use of heterochromatic filtered radiation.
[4] A simple analytical method of making this correction has been devised by C. G. Shull, and will be published elsewhere.

The mathematical problem is: given $f(x)$ and $k(x)$ such that

$$f(x)=\int_0^\infty k(xy)g(y)dy, \tag{2}$$

determine $g(y)$. A solution can be obtained if $h(x)$ can be found such that

$$g(y)=\int_0^\infty h(xy)f(x)dx. \tag{3}$$

Titchmarsh[5] discusses this problem and shows how its solution can be obtained. Formally, the Mellin transforms of Eqs. (2) and (3) are

$$F(s)=K(s)G(1-s),$$

and

$$G(s)=H(s)F(1-s).$$

Eliminating F and G, we obtain

$$K(s)H(1-s)=1. \tag{4}$$

$h(x)$ can then be found by inverting the Mellin transform $H(s)$ given by Eq. (4), $K(s)$ being known.

Titchmarsh proves that the pair of equations

$$f(x)=\frac{d}{dx}\int_0^\infty \frac{k_1(xy)}{y}g(y)dy \tag{5}$$

and

$$g(y)=\frac{d}{dy}\int_0^\infty \frac{h_1(xy)}{x}f(x)dx \tag{6}$$

hold under quite general conditions on $f(x)$ and $g(x)$. k_1 and h_1 are such that Eqs. (5) and (6) are equivalent to Eqs. (2) and (3) if differentiation under the integral sign is permitted. The conditions for validity of Eqs. (5) and (6) given by Titchmarsh, page 226, are that $H(\frac{1}{2}+it)$ and $K(\frac{1}{2}+it)$ are both bounded, that $h_1(x)/x$ and $k_1(x)/x$ are Mellin transforms of $H(\frac{1}{2}+it)/(\frac{1}{2}-it)$ and $K(\frac{1}{2}+it)/(\frac{1}{2}-it)$, and that $f(x)$ belongs to $L^2(0,\infty)$, i.e.,

$$\int_0^\infty |f(x)|^2dx<\infty.$$

Then $g(y)$ also belongs to $L^2(0,\infty)$, and the reciprocal formulas (5) and (6) hold.

[5] E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, New York, 1937), Chapter VIII.

The function $S(x)$ in Eq. (1) may be written[6]

$$S(x)=\frac{9}{x^6}(\sin x-x\cos x)^2=\frac{9\pi}{2}\frac{J_{3/2}{}^2(x)}{x^3}$$
$$={}_1F_2(2;4,5/2;-x^2). \tag{7}*$$

In order to have $K(\frac{1}{2}+it)$ and $H(\frac{1}{2}+it)$ bounded, considerations similar to those given under part (3) on page 215 of reference 5 show that we must take[7]

$$k(x)=x^4{}_1F_2(2;4,5/2;-x^2)-(9/2). \tag{8}$$

We next calculate the Mellin transform $K(s)$, and determine $H(s)$ by use of Eq. (4). $h_1(x)$ is then calculated as the Mellin transform of $H(s)/(1-s)$, giving

$$h_1(x)=\frac{-8x}{27\pi}{}_1F_2\left(\frac{1}{2};-\frac{1}{2},\frac{5}{2};-x^2\right), \tag{9}$$

and

$$h(x)=\frac{d}{dx}h_1(x)=\frac{-8}{27\pi}{}_1F_2\left(\frac{3}{2};-\frac{1}{2},\frac{5}{2};-x^2\right). \tag{10}$$

Identifying ξ with x, R with y, $M(R)/R$ with $g(y)$, putting

$$f(x)=\xi^4I(\xi)/B-\frac{9}{2}\int_0^\infty\frac{M(R)}{R}dR,$$

and using Eqs. (8) and (9), the Eqs. (5)[7] and (6) can be written

$$I(\xi)=B\int_0^\infty M(R)R^3\times{}_1F_2(2;4,5/2;-R^2\xi^2)dR \tag{11}$$

and

$$M(R)=-\frac{8R}{27\pi B}\frac{d}{dR}\int_0^\infty R\xi^4I(\xi)\times{}_1F_2\left(\frac{1}{2};-\frac{1}{2},\frac{5}{2};-R^2\xi^2\right)d\xi. \tag{12}$$

Equation (12) gives the desired inversion.

[6] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1922), pages 54, 147, and 100.

* The use of generalized hypergeometric functions in the following is unnecessary for the case of spherical particles, but permits a direct generalization to the case of spheroidal particles.

[7] The last formula for $k(x)$ given on page 215 of reference 5 is valid only when $\alpha_1+\phi/2>0$; when $\alpha_1+\phi/2=0$ an additional term, of which the $-9/2$ in Eq. (8) is an example, must be added because of the pole of $K(s)$ at the origin. For the functions involved in the present problem, it is permissible to substitute (2) for (5), but not (3) for (6).

It can be shown[8] that

$$ {}_1F_2\left(\frac{1}{2};\ -\frac{1}{2},\frac{5}{2};\ -x^2\right)=-\frac{3\pi}{2}J_{3/2}(x)J_{-3/2}(x) $$

$$ =-\frac{3}{2x}\left[\left(1-\frac{1}{x^2}\right)\sin 2x+\frac{2\cos 2x}{x}\right]. \quad (13) $$

Also, it follows from Eq. (11) that for large ξ

$$ \xi^4 I(\xi)\sim B\int_0^\infty \frac{M(R)}{R}dR+O(\xi^{-\mu})+O(\xi^{-2}), \quad (14) $$

if

$$ M(R)=O(R^\mu) \quad \mu>0 $$[9]

for small R. Therefore, Eq. (12) can be written, differentiating under the integral sign in the finite integral,

$$ M(R)=\frac{4R}{9\pi B}\frac{d}{dR}\int_0^\infty \xi^3 I(\xi)\left[\left(1-\frac{1}{R^2\xi^2}\right)\sin 2R\xi+\frac{2\cos 2R\xi}{R\xi}\right]d\xi, \quad (15) $$

$$ =\frac{8R}{9\pi B}\int_0^{\xi_0}\xi^4 I(\xi)\left[\left(1-\frac{2}{R^2\xi^2}\right)\cos 2R\xi-\frac{2}{R\xi}\left(1-\frac{1}{2R^2\xi^2}\right)\sin 2R\xi\right]d\xi $$

$$ +\frac{4R}{9\pi B}\frac{d}{dR}\int_{\xi_0}^\infty \xi^3 I(\xi)\left[\left(1-\frac{1}{R^2\xi^2}\right)\sin 2R\xi+\frac{2\cos 2R\xi}{R\xi}\right]d\xi. \quad (16) $$

If ξ_0 is large enough the asymptotic expansion of $\xi^3 I(\xi)$ can be used in the last integral, which then can be evaluated analytically. In many cases, ξ_0 can even be chosen to make this integral vanish. The asymptotic expansion of $\xi^4 I(\xi)$ must be obtained from the measured data, and is subject to error. In a practical application, the treatment of the second term in Eq. (16) will depend upon the nature of the asymptotic behavior of $\xi^4 I(\xi)$. The mathematical situation and procedure are analogous to those encountered in inverting liquid scattering data.[10]

The general procedure described above can be applied whenever the "form factor" of the scattering particle is known and is characterized by a single size parameter. In particular, it has been applied to the calculation of the mass distribution of randomly oriented and spaced spheroidal particles having a fixed but arbitrary shape parameter v (major axes R, R, vR).

[8] Reference 6, pages 147 and 54.

[9] Actually, in order for the L^2 theory underlying (11) and (12) to be valid, we must have $\mu>\frac{1}{2}$.

[10] N. S. Gingrich, Rev. Mod. Phys. **15**, 90 (1943).