The same calculations were performed for a doublet made out of two symmetric Gaussian profiles ($k=0{\cdot}15$ both for left side and right side). The matching of the results was as above. This time the sine Fourier coefficients had to come out as zero, and in fact, in both cases, they were smaller than 10^{-4}. This also means that the Fourier coefficients of $I_1(n)$ were calculated around the center of gravity even when the input data was that of $I(n)$ where $I(n)=I_1(n)+I_2(n)$.

In the present work we assumed that $R=I_1/I$ was known. However, R can be easily calculated. It has been shown (Gangulee, 1970) that R can be determined by defining a 'residue' by

$$\text{Residue}=\sum_{n=1}^{n}|I'_1(n)|-I'_n(n)$$

where $I'_1(n)$ is the synthesized $I_1(n)$ profile assuming a given value of R. This 'residue' will be minimum for the correct value of R. The 'experimental' profile was calculated using $R=0{\cdot}67$. Then the profile $I_1(n)$ was calculated using different values of R and the corresponding 'residues' were determined. The plot of the 'residue' *versus* R had a minimum (residue$=0$) at $R=0{\cdot}67$ which is the true value of R.

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The Moments of a Powder Diffraction Profile in the Kinematic Tangent-Plane Approximation

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The nth moment of the diffraction line profile of a small or imperfect crystal is obtained in terms of the derivatives of $V(t)$, the volume common to the crystal and its 'ghost' displaced by a distance t parallel to the scattering vector, and of $J(t)-iK(t)$, the mean value of the product FF^* of the structure factors of unit cells separated by the same translation. The expression takes the form of a series that can be carried to any desired degree of approximation; previously only the first two or three terms had been obtained. For particle-size broadening by crystals of certain simple shapes the series terminates, giving an 'exact' expression.

Introduction

The intensities, positions, widths, asymmetries, ... of diffraction maxima in crystallography have been specified by such measures as peak height, peak position, width at half height, ratio of the intercepts of the chord at half height by the perpendicular through the peak, ... and other *ad hoc* constructs. In mathematics, and particularly statistics, however, the use of the moments of the distribution as measures of its properties is more common. Moments have in fact been used as measures of the effect of geometrical aberrations since the work of Spencer (1931), but their use as measures of the properties of diffraction profiles is comparatively recent, since the 'tails' of these profiles approach zero approximately as the inverse square of the distance from the centre of the profile, so that the zeroth moment (integrated intensity) is convergent, the first moment (centroid position) is convergent by reasonable convention, and all other moments diverge. Tournarie (1956 *a*, *b*), however, investigated the manner of divergence of the second moment (variance), and showed that the second moment of a deliberately truncated portion of the powder diffraction maximum was directly proportional to the length of the truncated portion, the proportionality factor being inversely proportional to the mean crystallite size of the specimen. To the degree

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of approximation used by Tournarie the second moments of the diffraction profile, the instrumental aberrations, and the profile of the emission spectrum are simply additive, so that the second moment of the diffraction profile may be obtained from the second moment of the observed profile by direct subtraction of the effects of the experimental arrangement and the emission spectrum, without the necessity of an elaborate 'unfolding' process, as required for other measures of line width. When a higher degree of approximation is required the moments are not strictly additive, but the correction remains a matter of simple arithmetic (Wilson, 1964*a*, 1970; Edwards & Toman, 1970).

Tournarie's result is in fact the first term in a series for the second moment. Wilson (1962*a*, 1962*b*, 1963) generalized his treatment, extending it to strain and mistake broadening in addition to particle-size broadening, and obtaining the second term in the series. Wilson also considered briefly the first moment (centroid displacement), the third moment (skewness), and the zeroth moment (integrated intensity) (Wilson, 1964*b*). Mitra (1964) has discussed the fourth moment. Not all the moments have been obtained to the same degree of accuracy, and the degree of accuracy is in any case somewhat problematical. Wilson (1962*b*), for example, shows that certain terms are zero 'to the degree of approximation employed elsewhere in this paper', a correct but hardly quantitative assessment. The following work was therefore undertaken with the aim of expressing the moments of the diffraction profile as series that can be extended to an indefinite number of terms, so that

(i) any moment can be calculated to any desired degree of approximation and the accuracy of the approximation assessed,

(ii) in particular, a further term can be written in the expression for the asymptotic form of the variance *versus* range curve, and

(iii) in particular, 'exact' expressions can be obtained for the particle-size diffraction-profile moments of crystals of those simple shapes for which the series terminate.

For some moments object (iii) requires one or two more terms than object (ii). The remarkable reproducibility achieved by Langford (1965, 1968*a*, *b*) and Edwards & Toman (1971) in their measurements of the variances of the line profiles of the X-ray diffraction maxima of several specimens of polycrystalline metals has given a further stimulus to obtain better theoretical expressions for the moments as a function of range.

The theoretical expression for the line profile is

$$I(s)=2\int_0^\tau A(t)\cos 2\pi st\,dt-2\int_0^\tau B(t)\sin 2\pi st\,dt \quad (1)$$

in the notation of Wilson (1962*c*). Briefly, and aside from slowly varying factors, $A(t)$ is the product $V(t)J(t)$ and $B(t)$ is the product $V(t)K(t)$, where $V(t)$ is the volume common to a crystal and its 'ghost' displaced a distance t perpendicular to the reflecting planes (Stokes & Wilson, 1942), and $J(t)-iK(t)$ is the mean value of the product of the structure factors FF^* for pairs of cells separated by the same displacement (Wilson, 1943, where, however, J_t was written for the entire complex function). The volume $V(t)$ vanishes for t greater than some value τ, and s is the deviation of the angle of diffraction from its ideal value, expressed in reciprocal-space units. The range of integration over s used in determining the moments of the line profile is deliberately limited to $-\sigma_1$ to $+\sigma_2$, where in practice σ_1 and σ_2 are nearly equal, and the moments are sought as functions of σ_1 and σ_2. In the following $A(0)$, $A'(0)$, $J''(0)$, *etc.* denote the limits of the functions as t approaches zero from positive values, and $A'(\tau)$, $J''(\tau)$, *etc.* denote the limits as t approaches τ from lower values; from their definitions

$$A(\tau)=B(\tau)=B(0)=0\,. \quad (2)$$

The nth moment of the truncated line profile is given by

$$M_n=\int_{-\sigma_1}^{\sigma_2} s^n I(s)\,ds \quad (3)$$

$$=2\int_{-\sigma_1}^{\sigma_2}\int_0^\tau s^n A(t)\cos 2\pi st\,dt\,ds$$

$$-2\int_{-\sigma_1}^{\sigma_2}\int_0^\tau s^n B(t)\sin 2\pi st\,dt\,ds\,. \quad (4)$$

It is convenient to consider the even moments and the odd moments separately, since they involve sines and cosines in a more or less reciprocal fachion. Except where it is otherwise stated, it is assumed that $A(t)$ and $B(t)$ have continuous derivatives in the range $0<t<\tau$.

The even moments

When n is even equation (4) may be written

$$M_n=\frac{(-1)^{n/2}2}{(2\pi)^n}\left\{\int_{-\sigma_1}^{\sigma_2}\int_0^\tau A(t)\left(\frac{d}{dt}\right)^n\cos 2\pi st\,dt\,ds\right.$$

$$\left.-\int_{-\sigma_1}^{\sigma_2}\int_0^\tau B(t)\left(\frac{d}{dt}\right)^n\sin 2\pi st\,dt\,ds\right\} \quad (5)$$

$$=\frac{(-1)^{n/2}2}{(2\pi)^n}\left\{\int_0^\tau A(t)\left(\frac{d}{dt}\right)^n\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}\,dt\right.$$

$$\left.-\int_0^\tau B(t)\left(\frac{d}{dt}\right)^n\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}\,dt\right\}, \quad (6)$$

where first s^n has been manufactured as the nth derivative of the sine or cosine of $2\pi st$ and then the integration with respect to s has been performed. Provided that the necessary derivatives are continuous in the range from 0 to τ, equation (6) can now be integrated by parts n times, giving

$$M_n=2\,(-1)^{n/2}\,(2\pi)^{-n}\,\{P_n+Q_n-R_n-S_n\} \quad (7)$$

where

$$P_n = A(t)\left(\frac{d}{dt}\right)^{n-1}\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}$$
$$-A'(t)\left(\frac{d}{dt}\right)^{n-2}\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}$$
$$+\ldots\ldots$$
$$+(-1)^n A^{n-2}(t)\frac{d}{dt}\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}$$
$$-(-1)^n A^{n-1}(t)\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}\Bigg]_0^\tau, \quad (8)$$

$$Q_n = \int_0^\tau A^n(t)\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}\,dt, \quad (9)$$

$$R_n = B(t)\left(\frac{d}{dt}\right)^{n-1}\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}$$
$$-B'(t)\left(\frac{d}{dt}\right)^{n-2}\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}$$
$$+\ldots\ldots$$
$$+(-1)^n B^{n-2}(t)\frac{d}{dt}\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}$$
$$-(-1)^n B^{n-1}(t)\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}\Bigg]_0^\tau, \quad (10)$$

$$S_n = \int_0^\tau B^n(t)\frac{\cos 2\pi\sigma_1 t-\cos 2\pi\sigma_2 t}{2\pi t}\,dt. \quad (11)$$

For n even, of course, the factors $(-1)^n$ in equations (8) and (10) are positive, but expressions of the same form with n odd are needed later. If the derivatives of $A(t)$ and $B(t)$ are not continuous over the full range 0 to τ, but are piecewise continuous over the ranges 0 to t_1, t_1 to t_2, ..., t_m to τ, the various terms in equation (8) *etc.* must be evaluated for each range and the results summed. If, for example, $P_n\,(t-)$ is the value taken by the expression on the right of equation (8) as t is approached from lower values and $P_n\,(t+)$ is its value as t is approached from higher values, the value of P_n for piecewise continuous derivatives of $A(t)$ is

$$P_n=[P_n(t_1-)-P_n(0+)]+[P_n(t_2-)-P_n(t_1+)] + \ldots +[P_n(\tau-)-P_n(t_m+)]. \quad (12)$$

Parallel expressions can be written for Q_n, R_n, S_n. Fortunately $A(t)$ and $B(t)$ have continuous derivatives over the range 0 to τ in the problems normally considered, though they are not continuous actually at 0 and τ. The non-oscillatory terms in the moments involve only the values for $0+$; these are usually the terms of practical importance. Evaluating the derivatives and inserting the limits in equations (8) and (10) for P_n and R_n can always be done, though it be becomes tedious for large values of n. The first term, involving $(d/dt)^{n-1}$, vanishes at both limits in each case. The integrals in equations (9) and (11) for Q_n and S_n can be expanded in series of inverse powers of σ_1 and σ_2 in two ways. The first is simply to write $A^n(t)$ and $B^n(t)$ as power series in t and integrate term by term. This gives series with the properties that successive terms have finite values for small σ, that the non-oscillatory parts decrease as successive inverse powers of σ, and that only the derivatives at $t=0$ are involved. The oscillatory terms, however, are all of the order of σ^{-1}. The other method is successive integration by parts. The series obtained in this way have terms that are not individually finite for small σ, and involve derivatives of $A(t)$ and $B(t)$ at both $t=0$ and $t=\tau$. Successive terms do, however, genuinely decrease as successive inverse powers of σ; the non-oscillatory parts are the same for both types of series. Which expansion is more convenient will depend on the purpose for which it is wanted, and the two are, of course, identical when they terminate, as for particle-size broadening by simple shapes. The series of the first type are thus

$$Q_n = A^n(0)\int_0^\tau\frac{\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t}{2\pi t}\,dt$$
$$+\frac{A^{n+1}(0)}{2\pi}\int_0^\tau(\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t)\,dt$$
$$+\frac{A^{n+2}(0)}{(2\pi)2!}\int_0^\tau t(\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t)\,dt$$
$$+\frac{A^{n+3}(0)}{(2\pi)3!}\int_0^\tau t^2(\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t)\,dt$$
$$+\frac{A^{n+4}(0)}{(2\pi)4!}\int_0^\tau t^3(\sin 2\pi\sigma_1 t+\sin 2\pi\sigma_2 t)\,dt$$
$$+\ldots\ldots \quad (13)$$
$$=\frac{1}{2\pi}\Bigg\{A^n(0)[\mathrm{Si}\,(2\pi\sigma_1\tau)+\mathrm{Si}\,(2\pi\sigma_2\tau)]$$
$$+A^{n+1}(0)\left[\frac{1-\cos 2\pi\sigma_1\tau}{2\pi\sigma_1}+\frac{1-\cos 2\pi\sigma_2\tau}{2\pi\sigma_2}\right]$$
$$+\frac{A^{n+2}(0)}{2!}\Bigg[\frac{\sin 2\pi\sigma_1\tau-2\pi\sigma_1\tau\cos 2\pi\sigma_1\tau}{(2\pi\sigma_1)^2}$$
$$+\frac{\sin 2\pi\sigma_2\tau-2\pi\sigma_2\tau\cos 2\pi\sigma_2\tau}{(2\pi\sigma_2)^2}\Bigg]$$
$$+\frac{A^{n+3}(0)}{3!}\Bigg[\frac{4\pi\sigma_1\tau\sin 2\pi\sigma_1\tau-(4\pi^2\sigma_1^2\tau^2-2)\cos 2\pi\sigma_1\tau}{(2\pi\sigma_1)^3}$$
$$-\frac{1}{4\pi^3}\left(\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right)$$
$$+\frac{4\pi\sigma_2\tau\sin 2\pi\sigma_2\tau-(4\pi^2\sigma_2^2\tau^2-2)\cos 2\pi\sigma_2\tau}{(2\pi\sigma_2)^3}\Bigg]$$
$$+\frac{A^{n+4}(0)}{4!}$$

$$\times \left[\frac{(12\pi^2\sigma_1^2\tau^2-6)\sin 2\pi\sigma_1\tau-(8\pi^3\sigma_1^3\tau^3-12\pi\sigma_1\tau)\cos 2\pi\sigma_1\tau}{(2\pi\sigma_1)^4}\right.$$
$$\left.+\frac{(12\pi^2\sigma_2^2\tau^2-6)\sin 2\pi\sigma_1\tau-(8\pi^3\sigma_2^3\tau^3-12\pi\sigma_2\tau\cos 2\pi\sigma_2\tau}{(2\pi\sigma_2)^4}\right]+\ldots\Big\}, \quad (14)$$

and similarly

$$S_n=-\frac{1}{2\pi}\Big\{B^n(0)\left[\operatorname{Cin}(2\pi\sigma_1\tau)-\operatorname{Cin}(2\pi\sigma_2\tau)\right]$$
$$+B^{n+1}(0)\left[\frac{-\sin 2\pi\sigma_1\tau}{2\pi\sigma_1}+\frac{\sin 2\pi\sigma_2\tau}{2\pi\sigma_2}\right]$$
$$+\frac{B^{n+2}(0)}{2!}\left[\frac{1-\cos 2\pi\sigma_1\tau-2\pi\sigma_1\tau\sin 2\pi\sigma_1\tau}{(2\pi\sigma_1)^2}\right.$$
$$\left.-\frac{1-\cos 2\pi\sigma_2\tau-2\pi\sigma_2\tau\sin 2\pi\sigma_2\tau}{(2\pi\sigma_2)^2}\right]$$
$$+\frac{B^{n+3}(0)}{3!}$$
$$\times\left[\frac{-4\pi\sigma_1\tau\cos 2\pi\sigma_1\tau-(4\pi^2\sigma_2^2\tau^2-2)\sin 2\pi\sigma_1\tau}{(2\pi\sigma_1)^3}\right.$$
$$\left.+\frac{4\pi\sigma_2\tau\cos 2\pi\sigma_2\tau+(4\pi\sigma_1^2\tau^2-2)\sin 2\pi\sigma_2\tau}{(2\pi\sigma_2)^3}\right]$$
$$+\ldots\Big\}, \quad (15)$$

where Si(z) and Cin(z) are the sine and cosine integrals

$$\operatorname{Si}(z)=\int_0^z \frac{\sin z}{z}\,\mathrm{d}z \quad (16)$$

and

$$\operatorname{Cin}(z)=\int_0^z \frac{1-\cos z}{z}\,\mathrm{d}z\,. \quad (17)$$

They are tabulated and their main properties listed by, for example, Abramowitz & Stegun (1964). The series have been carried far enough to give 'exact' expressions for all moments of particle-size line profiles for crystals of simple shape. In order to obtain the other type of expansion equation (9) is rewritten

$$Q_n=A^n(0)\int_0^\tau \frac{\sin 2\pi\sigma_1 t}{2\pi t}\,\mathrm{d}t+\int_0^\tau \frac{A^n(t)-A^n(0)}{2\pi t}\sin 2\pi\sigma_1 t\,\mathrm{d}t$$
$$+\text{similar terms in } \sigma_2\,. \quad (18)$$

The first integral gives the same sine integral as in equation (14). The second may be integrated by parts, giving

$$Q_n=\frac{1}{2\pi}\Big\{A^n(0)\operatorname{Si}(2\pi\sigma_1\tau)+\frac{A^{n+1}(0)}{2\pi\sigma_1}-\frac{A^{n+3}(0)}{3(2\pi\sigma_1)^3}$$
$$+\frac{A^{n+5}(0)}{5(2\pi\sigma_1)^5}-\ldots$$
$$-\cos 2\pi\sigma_1\tau\left[\frac{A^n(\tau)-A^n(0)}{2\pi\sigma_1\tau}\right.$$
$$-\frac{1}{(2\pi\sigma_1)^3}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^2\frac{A^n(\tau)-A^n(0)}{\tau}$$
$$\left.+\frac{1}{(2\pi\sigma_1)^5}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^4\frac{A^n(\tau)-A^n(0)}{\tau}-\ldots\right]$$
$$+\sin 2\pi\sigma_1\tau\left[\frac{1}{(2\pi\sigma_1)^2}\frac{\mathrm{d}}{\mathrm{d}\tau}\frac{A^n(\tau)-A^n(0)}{\tau}\right.$$
$$-\frac{1}{(2\pi\sigma_1)^4}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^3\frac{A^n(\tau)-A^n(0)}{\tau}$$
$$\left.+\frac{1}{(2\pi\sigma_1)^6}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^5\frac{A^n(\tau)-A^n(0)}{\tau}-\ldots\right]$$
$$+\text{similar terms in } \sigma_2\Big\}, \quad (19)$$

provided that $A(t)$ has continuous derivatives. If it has not, the calculation would start from the analogue of equation (12) instead of from equation (9), and would be correspondingly more complex.

Similarly,

$$S_n=\frac{1}{2\pi}\Big\{-B^n(0)\operatorname{Cin}(2\pi\sigma_1\tau)-\frac{B^{n+2}(0)}{2(2\pi\sigma_1)^2}+\frac{B^{n+4}(0)}{4(2\pi\sigma_1)^4}$$
$$-\frac{B^{n+6}(0)}{6(2\pi\sigma_1)^6}+\ldots$$
$$+\sin 2\pi\sigma_1\tau\left[\frac{B^n(\tau)-B^n(0)}{2\pi\sigma_1\tau}\right.$$
$$-\frac{1}{(2\pi\sigma_1\tau)^3}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^2\frac{B^n(\tau)-B^n(0)}{\tau}$$
$$\left.+\frac{1}{(2\pi\sigma_1\tau)^5}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^4\frac{B^n(\tau)-B^n(0)}{\tau}-\ldots\right]$$
$$+\cos 2\pi\sigma_1\tau\left[\frac{1}{(2\pi\sigma_1\tau)^2}\frac{\mathrm{d}}{\mathrm{d}\tau}\frac{B^n(\tau)-B^n(0)}{\tau}\right.$$
$$-\frac{1}{(2\pi\sigma_1)^4}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^3\frac{B^n(\tau)-B^n(0)}{\tau}$$
$$+\frac{1}{(2\pi\sigma_1)^6}\left(\frac{\mathrm{d}}{\mathrm{d}\tau}\right)^5\frac{B^n(\tau)-B^n(0)}{\tau}$$
$$\left.-\ldots\right]-\text{similar terms in } \sigma_2\Big\}. \quad (20)$$

Any even nth moment can now be written down from equation (7), equations (8), (14) or (19), (10) and (15) or (20) providing the necessary values of P_n, Q_n, R_n and S_n. Many of the terms oscillate with period $\sigma_1\tau$ or $\sigma_2\tau$ and small amplitude, and these oscillations are not ordinarily observable experimentally. The non-oscillatory terms are therefore those of greater interest, and they are readily picked out of the relevant general equations. For P_n and R_n they arise from the derivatives that do not vanish at the lower limit, and are thus

$$P_n = A'(0)\,\frac{(-1)^{(n-2)/2}(2\pi)^{n-2}}{n-1}\,[\sigma_1^{n-1}+\sigma_2^{n-1}]$$
$$+A'''(0)\,\frac{(-1)^{(n-4)/2}(2\pi)^{n-4}}{n-3}\,[\sigma_1^{n-3}+\sigma_2^{n-3}]$$
$$+\ \ldots\ldots$$
$$+A^{n-1}(0)[\sigma_1+\sigma_2]\,, \tag{21}$$

no even powers of σ appearing, and

$$R_n = B''(0)\,\frac{(-1)^{n/2}(2\pi)^{n-3}}{n-2}\,[\sigma_1^{n-2}-\sigma_2^{n-2}]$$
$$+B^{\text{iv}}(0)\,\frac{(-1)^{(n-2)/2}(2\pi)^{n-5}}{n-4}\,[\sigma_1^{n-4}-\sigma_2^{n-4}]$$
$$+\ \ldots\ +\ B^{n-2}(0)\,\frac{2\pi}{2}\,[\sigma_1^2-\sigma_2^2]\,, \tag{22}$$

no odd powers of σ appearing. The sine and cosine integrals in equations (14,) (15), (19) and (20) oscillate, but from their properties the sum of the two sine integrals oscillates about π and the difference of the cosine integrals oscillates about the logarithm of the range ratio.

The non-oscillatory parts are thus

$$Q_n = \tfrac{1}{2}A^n(0) + \frac{1}{(2\pi)^2}\,A^{n+1}(0)\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right]$$
$$-\frac{1}{3(2\pi)^4}\,A^{n+3}(0)\left[\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right]+\ \ldots \tag{23}$$

and

$$S_n = -\frac{1}{2\pi}\,B^n(0)\log(\sigma_1/\sigma_2) - \frac{1}{2(2\pi)^3}$$
$$\times\ B^{n+2}(0)\left[\frac{1}{\sigma_1^2}-\frac{1}{\sigma_2^2}\right]+\ \ldots . \tag{24}$$

Further terms are easily supplied from equations (19) and (20) if required. The even moments of greatest interest are the zeroth, second and fourth. For the zeroth moment equation (7) gives

$$M_0 = A(0) + \frac{1}{2\pi^2}\,A'(0)\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right]$$
$$+\frac{1}{8\pi^3}\,B''(0)\left[\frac{1}{\sigma_1^2}-\frac{1}{\sigma_2^2}\right]$$
$$-\frac{1}{24\pi^4}\,A'''(0)\left[\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right]+\ \ldots . \tag{25}$$

The first two terms are those derived by Wilson (1964*b*); the other two are new. For the second moment equation (7) gives

$$M_2 = -\frac{1}{2\pi^2}\,A'(0)[\sigma_1+\sigma_2] - \frac{1}{4\pi^2}\,A''(0)$$
$$-\frac{1}{4\pi^3}\,B''(0)\log(\sigma_1/\sigma_2) - \frac{1}{8\pi^4}\,A'''(0)$$
$$\times\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right] - \frac{1}{32\pi^5}\,B^{\text{iv}}(0)\left[\frac{1}{\sigma_1^2}-\frac{1}{\sigma_2^2}\right]$$
$$+\frac{1}{96\pi^6}\,A^{\text{v}}(0)\left[\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right]+\ \ldots . \tag{26}$$

The first term is that derived by Tournarie (1956*a*, *b*), the second was added by Wilson (1962*a*, *b*), and the rest are new. For the fourth moment equation (7) gives

$$M_4 = -\frac{1}{6\pi^2}\,A'(0)[\sigma_1^3+\sigma_2^3] - \frac{1}{8\pi^3}\,B''(0)[\sigma_1^2-\sigma_2^2]$$
$$+\frac{1}{8\pi^4}\,A'''(0)[\sigma_1+\sigma_2] + \frac{1}{16\pi^4}\,A^{\text{iv}}(0)$$
$$+\frac{1}{16\pi^5}\,B^{\text{iv}}(0)\log(\sigma_1/\sigma_2)$$
$$+\frac{1}{32\pi^6}\,A^{\text{v}}(0)\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right]+\ \ldots . \tag{27}$$

The terms in A', A''', and A^{iv} are those found by Mitra (1964); the rest are new.

The odd moments

When n is odd the transformation of equation (4) by turning s into $\mathrm{d}/\mathrm{d}t$ takes a slightly different form, so that the sines and cosines are interchanged and some of the signs are different. The equivalent of equation (6) becomes

$$M_n = \frac{(-1)^{(n-1)/2}2}{(2\pi)^n}$$
$$\times\left\{\int_0^\tau A(t)\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)^n \frac{\cos 2\pi\sigma_1 t - \cos 2\pi\sigma_2 t}{2\pi t}\,\mathrm{d}t\right.$$
$$\left.+\int_0^\tau B(t)\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)^n \frac{\sin 2\pi\sigma_1 t + \sin 2\pi\sigma_2 t}{2\pi t}\,\mathrm{d}t\right\}. \tag{28}$$

Let us denote by P'_n, Q'_n, R'_n, S'_n the result of interchanging A and B in equations (8) to (20). Then the general expression for the nth odd moment, the equivalent of equation (7), is

$$M_n = \frac{(-1)^{(n-1)/2}2}{(2\pi)^n}\,\{R'_n - S'_n + P'_n - Q'_n\}\,, \tag{29}$$

and by its use any odd moment can be expressed to any desired degree of approximation. As for the even moments, the oscillatory terms are not normally observable. With the interchange of A and B equations (23) and (24) give the correct values of Q'_n and S'_n, but in equations (8) and (10) it is the alternate set of terms that lead to a non-oscillatory contribution at the lower limit, so that

$$P'_n = B''(0)\,\frac{(-1)^{(n-1)/2}(2\pi)^{n-2}}{2\pi(n-2)}\,[\sigma_1^{n-2}+\sigma_2^{n-2}]$$
$$+B^{\text{iv}}(0)\,\frac{(-1)^{(n-3)/2}(2\pi)^{n-4}}{2\pi(n-4)}\,[\sigma_1^{n-4}+\sigma_2^{n-4}]$$

$$+ \ldots\ldots$$
$$+B^{n-3}(0)\, \frac{(-1)^2(2\pi)^3}{(2\pi)3}\, [\sigma_1^3+\sigma_2^3]$$
$$+B^{n-1}(0)\, \frac{(-1)(2\pi)}{2\pi}\, [\sigma_1+\sigma_2] \tag{30}$$

and

$$R'_n=A'(0)\, \frac{(-1)^{(n-1)/2}(2\pi)^{n-1}}{2\pi(n-1)}\, [\sigma_1^{n-1}-\sigma_2^{n-1}]$$
$$+A'''(0)\frac{(-1)^{(n-3)/2}(2\pi)^{n-3}}{2\pi(n-3)}\, [\sigma_1^{n-3}-\sigma_2^{n-3}]$$
$$+ \ldots\ldots$$
$$+A^{n-4}(0)\frac{(-1)^2(2\pi)^4}{(2\pi)4}\, [\sigma_1^4-\sigma_2^4]$$
$$+A^{n-2}(0)\, \frac{(-1)(2\pi)^2}{(2\pi)2}\, [\sigma_1^2-\sigma_2^2]\,. \tag{31}$$

The non-oscillatory part of any odd moment can now be written down from equation (20), but only the first and third have been found of interest so far. The first moment is

$$M_1=-\frac{1}{2\pi}B'(0)+\frac{1}{2\pi^2}A'(0)\log(\sigma_1/\sigma_2)$$
$$-\frac{1}{4\pi^3}B''(0)\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right]+\frac{1}{16\pi^4}A'''(0)$$
$$\times\left[\frac{1}{\sigma_1^2}-\frac{1}{\sigma_2^2}\right]+\frac{1}{48\pi^5}B^{\mathrm{iv}}(0)\left[\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right]+\ldots. \tag{32}$$

Only the first of these terms was given by Wilson (1962*b*). The third moment is

$$M_3=\frac{1}{4\pi^2}A'(0)[\sigma_1^2-\sigma_2^2]+\frac{1}{4\pi^3}B''(0)[\sigma_1+\sigma_2]$$
$$+\frac{1}{8\pi^3}B'''(0)-\frac{1}{8\pi^4}A'''(0)\log(\sigma_1/\sigma_2)$$
$$+\frac{1}{16\pi^5}B^{\mathrm{iv}}(0)\left[\frac{1}{\sigma_1}+\frac{1}{\sigma_2}\right]-\frac{1}{64\pi^6}A^{\mathrm{v}}(0)$$
$$\times\left[\frac{1}{\sigma_1^2}-\frac{1}{\sigma_2^2}\right]-\frac{1}{192\pi^7}B^{\mathrm{vi}}(0)\left[\frac{1}{\sigma_1^3}+\frac{1}{\sigma_2^3}\right]+\ldots. \tag{33}$$

Wilson (1962*b*) gave the second and third of these terms with, however, an error of 2π in the coefficient of $B''(0)$ in his equation (21). This error is carried forward into his equation (23) and Mitra's (1964) equation (2). Wilson's equation (23) for the skewness should be corrected to

$$\gamma_1=\left[\frac{-A(0)}{2(\sigma_1+\sigma_2)\{A'(0)\}^3}\right]^{1/2}B''(0)\,. \tag{34}$$

Discussion

The first draft of this paper was prepared in 1968. Although only a preliminary abstract has been published previously (Wilson, 1969), it has formed the background to the use of further terms in the asymptotic variance–range relation in recent Birmingham work (Edwards & Toman, 1970, 1971; Edwards & Langford, 1971; Wilson, 1970). Non-additivity of the diffraction-profile and emission-profile contributions to the variance–range intercept casts some doubt on the application to nickel made in the final sentence of the paper by Wilson (1968), though his general argument is not affected.

For particle-size broadening $B(t)\equiv 0$, and the various equations above simplify considerably, especially for those particle shapes for which $A(t)$ is a polynomial (Stokes & Wilson, 1942). 'Exact' expressions for the particle-size moments in such cases will be treated elsewhere.

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