J. Appl. Cryst. (1978). **11**, 10–14

A Rapid Method for Analysing the Breadths of Diffraction and Spectral Lines using the Voigt Function

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(*Received* 28 *July* 1977; *accepted* 16 *August* 1977)

The Voigt function provides a rapid and easily applied method for interpreting the breadths of diffraction profiles in terms of specimen defects and for studying absorption or emission spectra. In the past, approximate methods have usually involved the assumption that the constituent profiles are either Cauchy (Lorentzian) or Gaussian, but a better representation of the experimental data is given by the convolution of these functions. The method is illustrated by analysis of the Cu $K\alpha$ emission profile and of crystallite-size broadening in nickel powder.

1. Introduction

Experimental line profiles in diffractometry and spectroscopy are the convolution of the wavelength spectrum with various functions arising from instrumental factors and specimen defects. The process of deconvolution in any detailed study of diffraction broadening is normally carried out by the Fourier technique (Stokes, 1948) or the variance method (Tournarie, 1956; Wilson, 1962, 1963), but in many applications a rapid, if less accurate, measure of diffraction or spectral breadth is adequate for practical purposes. This entails ascribing some closed function to the constituent profiles, and Ruland (1968) has considered in detail the breadths of several curves of interest in diffractometry. However, the earliest functions to be used, and the ones still widely employed in this field, are the Cauchy (Lorentzian) and Gaussian.

If the wavelength spectrum consists of a single line and geometrical effects are small, the instrumental profile is approximately Cauchy, whereas the profile arising from lattice strain is more nearly Gaussian. The broadening from mistakes or small crystallites depends on the nature of the imperfections, the shape of the crystallites and the distribution of size. In these cases neither function is necessarily a good approximation to the broadened line and there is evidence that a better representation is obtained from the convolution of one or more Cauchy and Gaussian functions, as is shown below. The curve formed in this way is known as the Voigt function, of which the Cauchy and Gaussian curves are limiting cases.

It is convenient to describe a symmetrical line profile, irrespective of whether or not it may be defined by a simple mathematical expression, in terms of three parameters. These are (i) the peak height, $I(0)$, (ii) the area, A, and (iii) the full width at half the maximum intensity (the half-width), $2w$; (i) and (ii) may be combined to give the integral breadth, β, where

$$\beta = A/I(0)\,, \tag{1}$$

which is a measure of breadth frequently used in diffractometry. All three parameters are thus included in the ratio $2w/\beta$ and any symmetrical line profile is characterized by this ratio, for which the name *form factor* is proposed. For example, the ratio has values of 0·63662 for all Cauchy functions and 0·93949 for Gaussian functions, with intermediate values for Voigt functions (§2). Following a summary of the properties of Cauchy and Gaussian functions, the Voigt function is discussed in detail. In §3 a method is described whereby the widths of the constituent profiles can easily be obtained from the ratio $2w/\beta$ for a Voigt function and examples of applications of the method are given in §4.

2. The Voigt function

The Voigt function $I(x)$ will be represented as the convolution of m Cauchy and n Gaussian functions, each having the same origin. Subscripts c and g refer to the Cauchy and Gaussian components respectively.

Convolution of m Cauchy functions

The convolution of m Cauchy functions of the form

$$I_{ci}(x) = I_{ci}(0)\,\frac{w_{ci}^2}{w_{ci}^2 + x^2}\,, \tag{2}$$

of area $A_{ci} = \pi w_{ci} I_{ci}(0)$ and integral breadth

$$\beta_{ci} = \pi w_{ci}\,, \tag{3}$$

is also a Cauchy function, given by

$$I_c(x) = I_c(0)\,\frac{w_c^2}{w_c^2 + x^2}\,, \tag{4}$$

where

$$2w_c = \frac{2}{\pi}\,\beta_c = 2\sum_{i=1}^{m} w_{ci}\,, \tag{5}$$

$$A_c = \prod_{i=1}^{m} A_{ci} = \pi^m \prod_{i=1}^{m} w_{ci} I_{ci}(0)\,, \tag{6}$$

and

$$I_c(0)=\frac{A_c}{\pi w_c}. \quad (7)$$

From equation (3) the form factor $2w/\beta$ for a Cauchy function is $2/\pi$ $(=0{\cdot}63662)$.

Convolution of n Gaussian functions

The convolution of n Gaussian functions of the form

$$I_{gi}(x)=I_{gi}(0)\exp(-\pi x^2/\beta_{gi}^2), \quad (8)$$

of area $A_{gi}=I_{gi}(0)\beta_{gi}$ and half-width

$$2w_{gi}=2\beta_{gi}(\log_e 2)^{1/2}/\pi^{1/2}, \quad (9)$$

is the Gaussian function given by

$$I_g(x)=I_g(0)\exp(-\pi x^2/\beta_g^2), \quad (10)$$

where

$$\beta_g^2=\frac{\pi}{4\log_e 2}(2w_g)^2=\sum_{i=1}^{n}\beta_{gi}^2, \quad (11)$$

$$A_g=\prod_{i=1}^{n}A_{gi}=\prod_{i=1}^{n}\beta_{gi}I_{gi}(0), \quad (12)$$

and

$$I_g(0)=A_g/\beta_g. \quad (13)$$

From equation (9) the form factor for a Gaussian function is $2(\log_e 2)^{1/2}/\pi^{1/2}$ $(=0{\cdot}93949)$.

Convolution of m Cauchy and n Gaussian functions

The convolution of m Cauchy and n Gaussian functions is the Voigt function

$$I(x)=\int_{-\infty}^{\infty}I_c(u)I_g(x-u)\mathrm{d}u, \quad (14)$$

where $I_c(x)$ and $I_g(x)$ are given by equations (4) and (10). The Fourier transforms of $I_c(x)$ and $I_g(x)$ are

$$F_c(t)=\beta_c I_c(0)\exp(-2\beta_c t) \quad (15)$$

and

$$F_g(t)=\beta_g I_g(0)\exp(-\pi\beta_g^2 t^2), \quad (16)$$

and the transform of $I(x)$ is

$$F(t)=F_c(t)F_g(t)=\beta_c\beta_g I_c(0)I_g(0)\exp-(2\beta_c t+\pi\beta_g^2 t^2). \quad (17)$$

Since $I_c(x)$ and $I_g(x)$ are even functions, the inverse transform of (17) is also an even function and

$$I(x)=\mathrm{Re}\{2\beta_c\beta_g I_c(0)I_g(0)\int_0^{\infty}\exp-[(2\beta_c-i2\pi x)t+\pi\beta_g^2t^2]\mathrm{d}t\}$$
$$=\mathrm{Re}\{\beta_c I_c(0)I_g(0)\exp[k^2(1-iy)^2]\operatorname{erfc}[k(1-iy)]\}, \quad (18)$$

where k is a factor proportional to the ratio of the Cauchy and Gaussian integral breadths, given by

$$k=\beta_c/\pi^{1/2}\beta_g \quad (19)$$

and

$$y=\pi x/\beta_c. \quad (20)$$

Now $\operatorname{erfc}(a-ib)=\exp(b^2-a^2)\exp(i2ab)\omega[b+ia]$, where $\omega[b+ia]$ is the complex error function, defined as

$$\omega(z)=\exp(-z^2)\left[1+\frac{i2}{\pi^{1/2}}\int_0^z\exp(t^2)\mathrm{d}t\right]. \quad (21)$$

[The complex error function can be obtained from standard tables, such as are given in Abramowitz & Stegun (1965), for example.]

Equation (18) thus reduces to

$$I(x)=\mathrm{Re}\left\{\beta_c I_c(0)I_g(0)\omega\left[\frac{\pi^{1/2}x}{\beta_g}+ik\right]\right\}, \quad (22)$$

giving an explicit equation for a Voigt profile in terms of the parameters defining the constituent Cauchy and Gaussian curves. From equation (17)

$$A=F(0)=\beta_c\beta_g I_c(0)I_g(0), \quad (23)$$

and from equation (22)

$$I(0)=\beta_c I_c(0)I_g(0)\omega[ik]=\beta_c I_c(0)I_g(0)\exp(k^2)\operatorname{erfc}(k). \quad (24)$$

The integral breadth, from equations (23) and (24), is then

$$\beta=\frac{\beta_g\exp(-k^2)}{1-\operatorname{erfc}(k)}, \quad (25)$$

as has been found by Schoening (1965) using a more

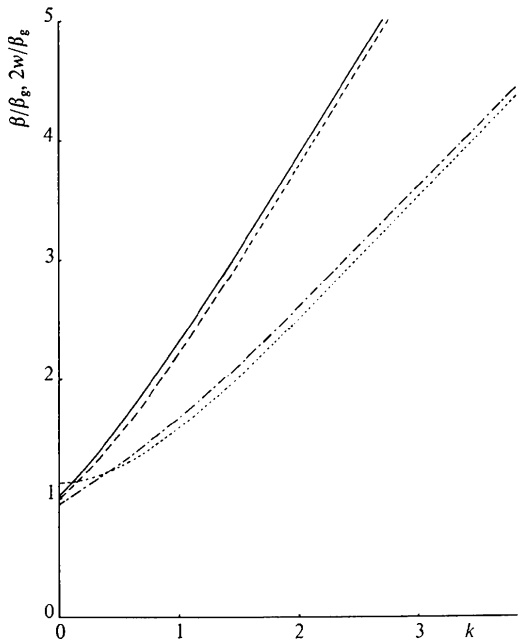

Fig. 1. Voigt function: variation of β/β_g and $2w/\beta_g$ with k. ———— β/β_g from (25); — — — — β/β_g from Halder & Wagner's approximation (26); — - — - — $2w/\beta_g$ from (27); - - - - - - - - $2w/\beta_g$ from Posener's approximation (28).

direct method. Halder & Wagner (1966) have also shown that an approximate value of the integral breadth is given by

$$\beta^2 \sim \beta_c \beta + \beta_g^2 . \tag{26}$$

The full width at half height of the Voigt function, $2w$, is obtained from

$$\mathrm{Re}\left\{\omega\left[\frac{\pi^{1/2}w}{\beta_g} + ik\right]\right\} = \tfrac{1}{2}\omega[ik] = \beta_g/2\beta , \tag{27}$$

which approximates to (Posener, 1959)

$$(2w)^2 \sim \frac{4\beta_g^2}{\pi}(1+k^2) \sim \frac{(2w_g)^2}{\log_e 2} + (2w_c)^2 . \tag{28}$$

The dimensionless quantities β/β_g (equation 25) and $2w/\beta_g$ (equation 27) are plotted as functions of k in Fig. 1. The corresponding approximate values from equations (26) and (28) are also included to give an indication of the magnitude of the errors introduced by these approximations.

3. Numerical analysis of Voigt curves

A Voigt curve can be generated from equation (22) for any combination of Cauchy and Gaussian functions, provided their peak heights and areas are known. (If only one is known, the other may be obtained from the half-width or integral breadth, as indicated in §2.) An example of this is given in Fig. 2, where the convolution of Cauchy and Gaussian curves having unit area and peak height is compared with the constituent profiles. The parameters defining the three curves are listed in Table 1. In this particular case, where $k = 1/\pi^{1/2}$ and $\beta_g = \beta_c$, the tail of the Voigt curve rapidly approaches the roughly inverse-square tail of the Cauchy component. This result is true generally, but it occurs at greater values of x if k is small (a dominant Gaussian component). The use of equations (26) and (28) in this example cause β and $2w$ to be underestimated by 5 and 2% respectively.

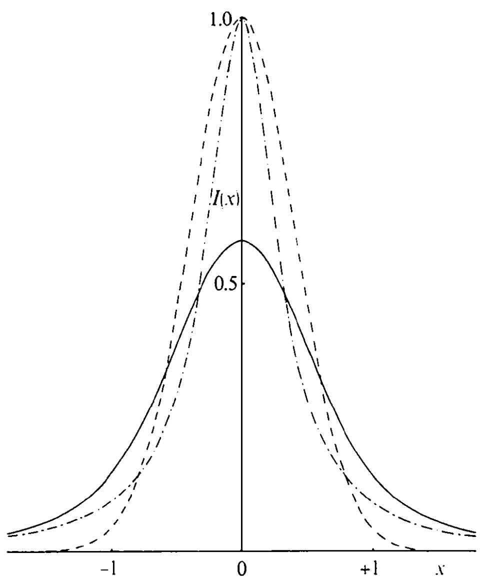

Fig. 2. Synthesis of Voigt curve from Cauchy and Gaussian curves with unit area and maximum value. ----- $I_c(x) = (1+\pi^2x^2)^{-1}$; ---- $I_g(x) = \exp -(\pi x^2)$; —— $I(x) = \mathrm{Re}\,\{\omega[\pi^{1/2}x + i/\pi^{1/2}]\}$.

Table 1. *Synthesis of Voigt curve from Cauchy and Gaussian functions: parameters defining curve and its constituent profiles for* $I_c(0) = I_g(0) = A_c = A_g = 1$

	Cauchy	Voigt	Gaussian
$2w$	0·6366	1·3270	0·9395
$2w$ from (28)	–	1·296	–
β	1	1·7117	1
β from (26)	–	1·618	–
$2w/\beta$	0·6366	0·7792	0·9395
A	1	1	1
$I(0)$	1	0·5842	1

Equation (22) can also be used to obtain a comparison between a theoretical or experimental profile and the equivalent Voigt function. For this purpose it is customary to match the ratio $2w/\beta$ and area of each curve, the widths of the constituent functions for insertion in equation (22) being found by the method given below. This procedure has been carried out by Langford & Wilson (1978, Figs. 1 and 2) for the line profiles arising from spherical and tetrahedral crystallites.

In the majority of practical applications the reverse procedure is usually required. That is, the parameters defining the constituent profiles are to be obtained from a broadened line. If the latter is assumed to be a Voigt curve, equation (27) can in principle be solved to find k and hence β_g and β_c for measured values of $2w$ and β. This cannot readily be carried out analytically, but numerical or graphical methods are sufficiently accurate for most purposes. For any value of k, β_g/β can be calculated from equation (25) or obtained directly from tabulated values of the complex error function for which the argument is purely imaginary (equation 27). The corresponding values of $\pi^{1/2}w/\beta_g$ and hence $2w/\beta$ are then obtained by interpolation from the same tables, using the condition that the real part of $\omega[\pi^{1/2}w/\beta_g + ik]$ is equal to $\beta_g/2\beta$. $2w/\beta$, k and β_g/β are listed in Table 2 for $0{\cdot}0 \le k \le 3{\cdot}9$ and are plotted as functions of k in Fig. 3. The values of β_g/β in Table 2 are correct to four places of decimals, but the tabulated values of $2w/\beta$, found using the method of bivariate linear interpolation, are subject to a maximum error of about 0·5%. It can be seen from Table 2 that the Voigt function reduces to a Gaussian for $k = 0$ ($2w/\beta = 2w_g/\beta_g = 0{\cdot}93949$) and tends to a Cauchy curve as k approaches infinity ($2w/\beta \rightarrow 2w_c/\beta_c = 0{\cdot}63665$). For $k = 3{\cdot}9$, β_c is about seven times greater than β_g and $2w/\beta$ is about 1·5% greater than $2w_c/\beta_c$.

The recommended procedure for estimating the breadths of defect functions or spectral lines whose form is assumed to be Voigt is as follows:

(i) The half-width and integral breadth are obtained from the broadened profile to give the form factor

$2w/\beta$. The background level and area of the line must be obtained with care, since a small error in β can result in significant errors in β_c or β_g, particularly if k is large. Even for $k=1$, if the area is underestimated by 5%, then β_c and β_g are overestimated by about 15%. If a digital output of intensity is available, the area is given by a direct summation, and for output on a chart recorder, a planimeter can be used to find the area of the broadened line. When a correction for instrumental effects has been made by means of the Fourier method (Stokes, 1948), the integral breadth of the corrected function is given by

$$\beta = 2\sigma / \sum_n A_n \,, \tag{29}$$

Table 2. *Voigt function*: $2w/\beta$, $k(=\beta_c/\pi^{1/2}\beta_g)$ *and* β_g/β

For $2w/\beta = 2/\pi = 0{\cdot}63662$, $k=\infty$ and $\beta_g/\beta = 0$.

$2w/\beta$	k	β_g/β	$2w/\beta$	k	β_g/β
0·9395	0·0	1·0000	0·6682	2·0	0·2554
0·8977	0·1	0·8965	0·6658	2·1	0·2451
0·8628	0·2	0·8090	0·6636	2·2	0·2356
0·8326	0·3	0·7346	0·6617	2·3	0·2267
0·8079	0·4	0·6708	0·6600	2·4	0·2185
0·7866	0·5	0·6157	0·6585	2·5	0·2108
0·7681	0·6	0·5678	0·6570	2·6	0·2036
0·7530	0·7	0·5259	0·6557	2·7	0·1969
0·7397	0·8	0·4891	0·6546	2·8	0·1905
0·7282	0·9	0·4565	0·6535	2·9	0·1846
0·7184	1·0	0·4276	0·6525	3·0	0·1790
0·7099	1·1	0·4017	0·6516	3·1	0·1737
0·7026	1·2	0·3785	0·6507	3·2	0·1687
0·6961	1·3	0·3576	0·6499	3·3	0·1640
0·6903	1·4	0·3387	0·6492	3·4	0·1595
0·6854	1·5	0·3216	0·6486	3·5	0·1553
0·6812	1·6	0·3060	0·6480	3·6	0·1513
0·6774	1·7	0·2917	0·6474	3·7	0·1474
0·6740	1·8	0·2786	0·6469	3·8	0·1438
0·6709	1·9	0·2665	0·6464	3·9	0·1403

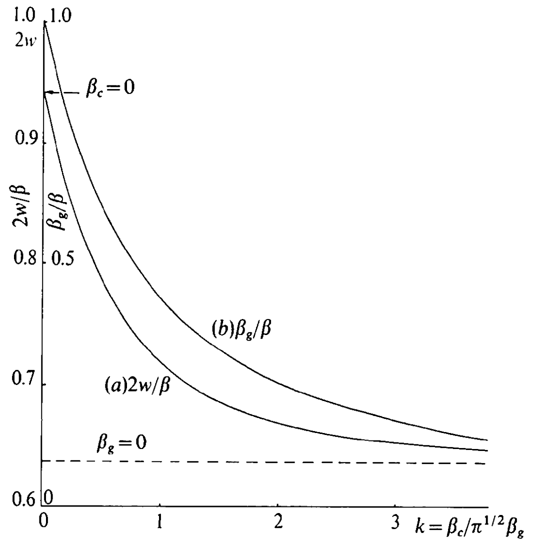

Fig. 3. Analysis of Voigt functions: graphical separation of β_c and β_g.

where the intensity is recorded over the range $\pm\sigma$ and A_n is the Fourier coefficient of the nth harmonic. The half-width is then obtained graphically from a reconstruction of the corrected profile by using the inverse transformation.

(ii) The breadths of the constituent profiles are then obtained and, if necessary, corrected for instrumental broadening. If $2w/\beta$ is in the region of 0·637, the profile is Cauchy and the breadth can be corrected in the usual way from equation (5). If it is in the region of 0·939, the profile is Gaussian and equation (11) is used. For intermediate values of $2w/\beta$, k is found from Table 2 or Fig. 3, curve (*a*), and the corresponding value of β_g is obtained from the same table or Fig. 3, curve (*b*). β_c is then given by equation (19) and, if required, $2w_c$ and $2w_g$ can be obtained from equations (3) and (9). These quantities can then be corrected by using the corresponding breadths of an instrumental function with equations (5) and (11). If $2w/\beta$ lies outside the above limits, a rare occurrence in practice, then the broadened profile cannot be represented by a Voigt function.

(iii) If the total breadth of the defect function or spectral distribution is required, rather than its constituent Cauchy and Gaussian components, β_c and β_g (or $2w_c$ and $2w_g$) are then combined by using the reverse of the procedure outlined in (ii). However, the magnitudes of the components may result from several causes whose separation is required. In the particular case of defect broadening from a powder sample, for example, small-crystallite broadening or mistake broadening varies inversely as $\cos\theta$, where θ is the Bragg angle, and the broadening due to small lattice strains varies as $\tan\theta$. Thus the intercept of a plot of $\beta_c \cos\theta$ as a function of $\sin\theta$ yields the Cauchy component due to crystallite size or mistakes and the slope gives the strain component. Similarly, a plot of $\beta_g^2 \cos^2\theta$ against $\sin^2\theta$ gives the corresponding Gaussian components. These can be combined to give the individual breadths of the defect function from which the average apparent crystallite or domain size and the strain can be evaluated (Langford, 1968*a*; 1971).

4. Typical applications

(*a*) Cu *Kα spectral line*

With the 333 peak from a silicon crystal used to analyse unfiltered Cu K radiation, the half-width of the α_1 line was found to be $0{\cdot}573 \pm 3 \times 10^{-3}$ Å and the integral breadth was $0{\cdot}914 \pm 3 \times 10^{-3}$ Å, giving $2w/\beta = 0{\cdot}628 \pm 5$. This value is close to, but slightly less than the theoretical ratio for a pure Cauchy curve. The small discrepancy mainly arises from the presence of the $K\alpha$ satellite group superimposed on the short-wavelength tail of the $K\alpha_1$ line. This increases the total intensity and hence the integral breadth by a small amount.

(*b*) *Small-crystallite broadening*

The application of the Voigt analysis to crystallite-size broadening may be illustrated by means of the 200

Table 3. *Voigt analysis of small-crystallite broadening of the* 200 *line for submicron nickel powder*

Cu $K\alpha$ radiation, $\theta = 26{\cdot}39°$

(*a*) Half-widths, integral breadths [°(2θ)], *etc.*

1. Annealed 6 μm nickel powder. 2. Submicron nickel powder. 3. As 2, corrected for instrumental broadening.

	1	2	3
β	0·243	0·637	0·541
$2w$	0·220	0·490	0·408
$2w/\beta$	0·905	0·769	0·755
k	0·083	0·595	0·690
β_g	0·222	0·363	0·287
β_c	0·032	0·383	0·351

(*b*) Apparent crystallite size ε (Å)

	Gaussian	Voigt	Cauchy
$\varepsilon_w = \lambda/2w \cos\theta$	226	242	366
$\varepsilon_\beta = \lambda/\beta \cos\theta$	167	183	251

line for a sample of submicron nickel powder (Langford, 1968*b*). A correction for instrumental effects was made by using the corresponding line for annealed nickel in which the crystallite size was greater than 6 μm. The observed breadths using Cu $K\alpha$ radiation ($\theta = 26{\cdot}39°$) are given in columns 1 and 2 of Table 3(*a*). The form factor and corresponding values of k, β_c and β_g are also listed. β_c and β_g for the defect function, obtained from equations (5) and (11), are given in column 3. These could be included with values from other lines in a study of their variation as some function of θ or, as shown here, they can be combined by means of Table 2 to give the apparent size based on the 200 line.

In Table 3(*b*) the sizes based on the half-widths and integral breadths, if the curves are assumed to be Voigt, can be compared with the corresponding estimates of size based on assumed Cauchy and Gaussian profiles. In this particular example the Gaussian estimates are 7–10% low and those based on Cauchy curves are about 40–50% high. This result is predicted by the form factor for the crystallite-size curve [Table 3(*a*), column 3], which is fairly close to the Gaussian limit. It should perhaps be emphasized that the difference between the half-width and integral breadth arises from the different definitions of apparent size in each case; to obtain the true size, these values must be multiplied by the appropriate Scherrer constant (Langford & Wilson, 1978).

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