

An Alternative Approach to the Quantitative Determination of Grain Size Distribution in X-ray Diffraction*

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Abstract

An alternative approach is introduced to determine the grain size distribution directly from the shape of the line profile in X-ray diffraction from a crystalline powder.

1. Introduction

In a crystalline powder, small crystals are oriented in random directions. The diffraction of X-rays from the powder gives a set of rings (Debye–Scherrer lines) corresponding to reflection from the (hkl) planes of the structure. If each crystal is perfect, then the broadening of the line profiles (after correcting for instrumental effects), reflects the finite size of the crystals in the powder. The intensity in a Debye–Scherrer line profile can be written as (Bertaut, 1950; Guinier, 1963)

$$I(x) = \sum_{N=1}^{\infty} g(N) \frac{\sin^2 Nx/2}{N(x/2)^2}. \quad (1)$$

In this equation, $x = sd_{hkl}$, where d_{hkl} is the distance between (hkl) planes and $s = |S - G|$ is the deviation parameter defined by

$$s = \frac{4\pi}{\lambda} (\sin \theta - \sin \theta_{hkl}),$$

where θ_{hkl} is the Bragg angle and λ is the wavelength of the X-rays. Bertaut's (1950) theorem of X-ray diffraction from a crystalline powder states that 'The profile of the (hkl) line is the same as that of the diffraction pattern for a set of parallel and incoherent segments whose lengths are distributed like the diameters of the grains normal to the reflecting plane (hkl) ' (Guinier, 1963). In other words each term in (1) is the intensity function equivalent to the scattering of a plane wave from a segment of a straight line of length Nd_{hkl} . In (1) $g(N)$ is the volume distribution function of that portion of the grain (or grains, if they have different sizes) that

has the length Nd_{hkl} normal to the (hkl) plane. The volume distribution function $g(N)$ is directly related to the crystal size distribution and the crystal shape $g(N)$ is normalized such that

$$\sum_{N=1}^{\infty} g(N) = 1. \quad (2)$$

It has been stated that $g(N)$, the volume distribution function, cannot be obtained directly from (1) (Guinier, 1963). Bertaut (1950) has shown that $g(N)$ can be obtained, however from the second derivative of the Fourier transform of the intensity $I(x)$.

Numerous applications of his method have appeared in the literature (Sashital, Cohen, Burwell & Butt, 1977). The usual procedure, after taking the data, is to take their Fourier transform, remove the instrumental contribution by the Stokes method (Guinier, 1963), and plot the second derivative of the resulting function to obtain the volume distribution function, $g(N)$. Bertaut's method assumes the kinematic approximation and therefore is limited, for accurate results, to grain sizes of roughly less than 100 lattice constants. This particle size range is especially useful in catalysis, thin-film growth, and some metallurgical phenomena.

In this paper, we show that a direct inversion of (1) is possible. We believe this leads to an easier and more direct determination of the volume distribution function $g(N)$. Our treatment, just as Bertaut's, is based on kinematic theory. In the next section we shall present the mathematical derivation of $g(N)$ in terms of the intensity function $I(x)$. Some model calculations are given in the following section.

II. Derivation of $g(N)$

Equation (1) can be rewritten as

$$\begin{aligned} I(x) \left(\frac{x}{2}\right)^2 &= \sum_{N=1}^{\infty} \frac{g(N)}{N} \sin^2 N \frac{x}{2} \\ &= \frac{1}{2} \sum_{N=1}^{\infty} \frac{g(N)}{N} (1 - \cos Nx). \end{aligned} \quad (3)$$

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Defining

$$G(x) = -\frac{x^2}{2} I(x),$$

we have, from (3),

$$G(x) = A_0 + \sum_{N=1}^{\infty} A_N \cos Nx, \quad (4)$$

where

$$A_0 = -\sum_{N=1}^{\infty} \frac{g(N)}{N} = \text{constant},$$

and

$$A_N = \frac{g(N)}{N}.$$

Equation (4) states that the A_N are the coefficients of a Fourier cosine series of the function $G(x)$. Therefore, the inversion gives

$$A_N = \frac{g(N)}{N} = \frac{1}{\pi} \int_{-\pi}^{\pi} G(x) \cos Nx \, dx,$$

or

$$g(N) = \frac{N}{\pi} \int_{-\pi}^{\pi} G(x) \cos Nx \, dx, \quad (5)$$

for $N \neq 0$. The intensity is normalized such that

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} G(x) \, dx = A_0. \quad (6)$$

Equation (5) is the basic result of this paper. It allows determination of the volume distribution function $g(N)$ directly from $G(x)$, which contains the intensity function $I(x)$. It should be remarked again that $I(x)$ assumes the instrumental broadening has been removed from the measured profile. This can be done in the standard way (Stokes method; Guinier, 1963) or by an iterative deconvolution of the instrumental profile.

III. Model calculations

We now present model calculations of the distribution function $g(N)$ for a given intensity function, $I(x)$.

Figs. 1 and 2 show the distribution function $g(N)$ evaluated for a Gaussian intensity distribution of the form $I(x) \propto \exp(-a^2 x^2)$, where a^2 has been taken to be 2 and 300 respectively. If we take $\lambda = 1 \text{ \AA}$ and $d_{hkl} = 3 \text{ \AA}$, $I(x) \propto \exp(-2x^2)$ and $I(x) \propto \exp(-300x^2)$ correspond to first-order diffracted beams with angular width of $\Delta(2\theta) \simeq 2$ and $\Delta(2\theta) \simeq 0.15^\circ$. The solid curve in the figures represents the distribution function $g(N)$

obtained from a noise-free intensity profile. The same result is obtained with Bertaut's (1950) method. The dashed curve gives $g(N)$ obtained from an intensity profile to which $\pm 2\%$ random noise has been added.

In all cases it is assumed that instrumental broadening has been removed by deconvolution. For the curves in Fig. 1, the integral in (5) was taken over the entire Brillouin zone, *i.e.* from $-\pi$ to π . The size distribution is well reproduced for the noisy data. Fig. 2 represents the size distribution for a much narrower intensity profile. For the noise-free data, the integral is again over

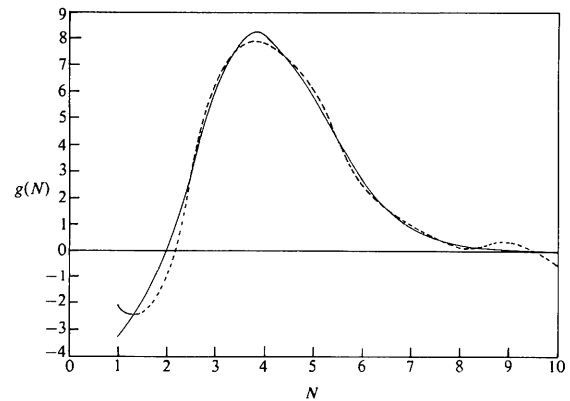


Fig. 1. The volume distribution function $g(N)$ calculated from a Gaussian intensity profile $I(x) \propto \exp(-2x^2)$. N is the number of lattice constants. For $\lambda = 1 \text{ \AA}$ and $d_{hkl} = 3 \text{ \AA}$, this intensity profile corresponds to a first-order diffracted beam with physical width $\Delta(2\theta) = 2^\circ$. Solid curve: exact result, for intensity profile without noise; dashed curve: for intensity profile to which $\pm 2\%$ random noise has been added. The maximum in the curve is related to the average grain size normal to the (hkl) plane. The fact that $g(N)$ has negative values for small N indicates that a Gaussian function does not represent a realistic intensity distribution.

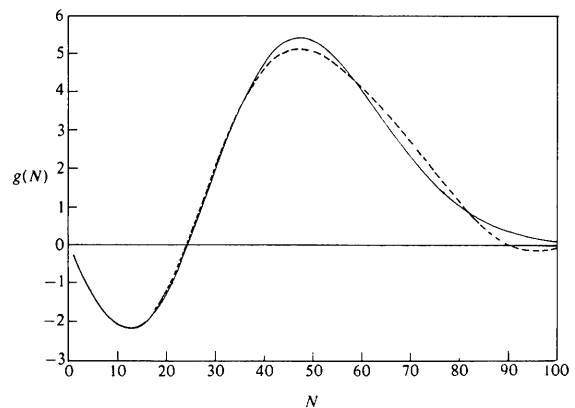


Fig. 2. The volume distribution function $g(N)$ calculated from a Gaussian intensity profile $I(x) \propto \exp(-300x^2)$, corresponding to a much smaller angular width, $\Delta(2\theta) = 0.15^\circ$, for the same conditions as in Fig. 1. Solid curve: exact result, for intensity profile without noise; dashed curve: for intensity profile to which $\pm 2\%$ random noise has been added. The maximum in the curve is related to the average grain size normal to the (hkl) plane.

the whole Brillouin zone. However, for the curve with $\pm 2\%$ noise, the noise dominates the signal in the wings. Therefore, the integral in (5) was chosen from -0.15 to $+0.15$, the region of significant intensity in the peak. The size distribution is again reproduced for the noisy data.

We next consider a Lorentzian intensity function of the form $I(x) = 1/(1 + b^2x^2)$ and a double-square-type intensity function of the form $I(x) = 1/(1 + b^2x^2)^2$. The volume distribution functions $g(N)$ for these intensity functions are shown for $\lambda = 1 \text{ \AA}$, $d_{hkl} = 3 \text{ \AA}$ in

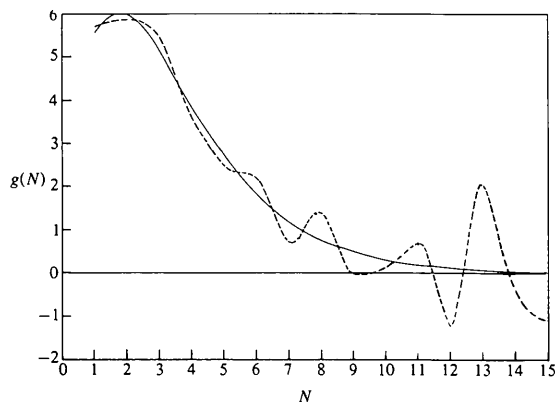


Fig. 3. The volume distribution function $g(N)$ calculated from a Lorentzian intensity profile $1/(1 + 3x^2)$. Solid curve: exact result, for intensity profile without noise; dashed curve: with $\pm 2\%$ random noise added. The maximum in the curve is related to the average grain size normal to the (hkl) plane.

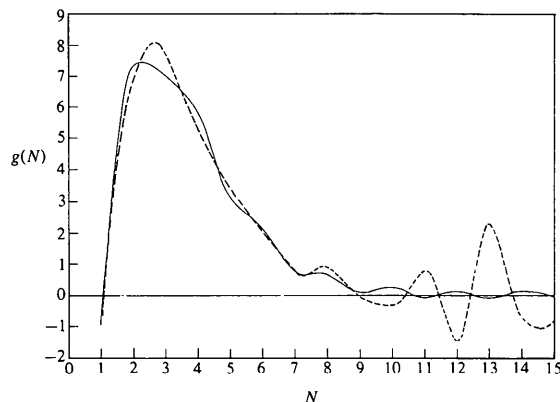


Fig. 4. The volume distribution function $g(N)$ calculated from a double-square type intensity profile $1/(1 + x^2)^2$. Solid curve: exact result, for intensity profile without noise; dashed curve: with $\pm 2\%$ random noise added. The maximum in the curve is related to the average grain size normal to the (hkl) plane.

Figs. 3 and 4 respectively. The corresponding angular widths for a first-order diffraction maximum are about 2° for both profiles. The integrals to determine $g(N)$ are in all cases over the whole Brillouin zone.

In general, it is not possible to determine the size of the crystals from the volume distribution function $g(N)$. However, if one knows *a priori* the shape of the crystals, it is possible to calculate the true size distribution of the crystals (for the particular shape under consideration) from $g(N)$. This is well known, (Guinier, 1963), and is independent of the method by which $g(N)$ is obtained. Thus the method presented here can be used to determine size distributions of particles whose shape is known.

IV. Conclusions

We have shown that, in X-ray diffraction from a crystalline powder, the volume distribution function $g(N)$, which describes the portion of the grains that have the length Nd_{hkl} normal to the (hkl) plane, is the set of Fourier coefficients of a function $G(x)$ that contains the intensity distribution $I(x)$. Therefore $g(N)$ can be obtained by direct Fourier inversion of the function $G(x)$. Model calculations of $g(N)$ for both Gaussian and Lorentzian intensity functions have been presented.

The derivation of our result is simple and physically transparent. Moreover, this method can be generalized to two- and three-dimensional problems. The two-dimensional analog of this theory can be used, for example, to determine straightforwardly the two-dimensional island size distribution in an adsorbed overlayer or the superionic cluster size distribution in a superionic conductor. An application in three dimensions would be the determination of the size distribution of precipitated phases in a solid solution growing with the 'Widmanstätten structure'.

References

- BERTAUT, F. (1950). *Acta Cryst.* **3**, 14–15.
 GUINIER, A. (1963). *X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies*. ch. 5. San Francisco: Freeman.
 SASHITAL, S. R., COHEN, J. B., BURWELL, R. L. & BUTT, J. B. (1977). *J. Catal.* **50**, 479–493, and references therein.