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Crystal Powder Statistics. II. Line Profiles in Diffraction Spectra of Identical Crystals and of Gaussian Samples. Crystal Size Distributions

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The average interference function $\langle \mathcal{J}_{hkl}(\Delta S)\rangle$ of a powder sample containing perfect crystals at a reciprocal distance ΔS from the peak is evaluated both for the case of identical parallelepiped crystals and for a Gaussian sample [probability of thickness d along a given crystal direction $= C_1 \exp(-C_2 d^2)$]. In the latter case $\langle \mathcal{J}_{hkl}(\Delta S)\rangle$ decreases as $1/\Delta S^2$ for large ΔS, by analogy with the Bernoullian model [Allegra, Bassi & Meille (1978). *Acta Cryst.* A**34**, 652–655] although with a smaller amplitude, for a fixed integrated intensity and half-peak width. It is shown that the Gaussian interference function, or line profile, cannot be given by any real sample, at least if its crystals neither contain holes nor have concave surfaces. Number and weight probability distributions are calculated both for the Bernoullian and for the Gaussian crystal-size statistics. As expected from the calculated line profiles, the Bernoullian statistics correspond to a larger weight percentage of crystals smaller than the average.

Introduction

In a previous paper (Allegra, Bassi & Meille, 1978) it was shown that the diffraction line profiles of Bernoullian polycrystalline samples of parallelepiped-shaped perfect crystals are represented by Cauchy, or Lorentzian, distributions, provided the average number of unit cells is larger than about 10 along each parallelepiped edge and neglecting the effects of crystal strains. In the present paper we will proceed along similar lines, *i.e.* we will obtain the diffraction lines of powder samples of parallelepiped perfect crystals obeying well-defined statistical distributions. The subject may be divided into three different sections. First, the line profiles of a sample containing identical crystals will be evaluated, under the above-stated assumptions that the number of unit cells along each crystal edge is larger than 10 and that the particle strains are ignored. Second, the case of a sample with parallelepiped crystals obeying independent simple Gaussian distributions along the three edges will be investigated, with the same assumptions. Third, the number and weight distributions of polycrystalline samples will be evaluated as a function of the *volume* of the crystals, for both the Bernoullian and the Gaussian cases.

Mathematical treatment

(*a*) *The line profile for a collection of identical parallelepiped crystals*

The well-known expression for the intensity diffracted by a parallelepiped crystal at the reciprocal coordinates (x^*,y^*,z^*) is

$$I(x^*,y^*,z^*) = |F^2(x^*,y^*,z^*)| \frac{\sin^2(\pi N_1 x^*/a^*)}{\sin^2(\pi x^*/a^*)} \times \frac{\sin^2(\pi N_2 y^*/b^*)}{\sin^2(\pi y^*/b^*)} \cdot \frac{\sin^2(\pi N_3 z^*/c^*)}{\sin^2(\pi z^*/c^*)}, \tag{1}$$

where the crystal edges are taken as parallel to the unit-cell axes $(\mathbf{a},\mathbf{b},\mathbf{c})$, $(N_1 a,N_2 b,N_3 c)$ being the corresponding edge lengths. The reciprocal-cell axes are $(\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*)$, and the corresponding reciprocal-vector components are (x^*,y^*,z^*). We shall take N_1,N_2,N_3 to be at least of order 10, so that $\sin^2(x \pm n\pi)$ in the denominator of equation (1) may be approximately replaced by x^2 in those regions of reciprocal space where the intensity is appreciably different from zero. For the same reason we shall assume $|F^2(x^*,y^*,z^*)|$ to have a constant value in the vicinity of a reciprocal-lattice point (h,k,l), with $h = x^*/a^*$; $k = y^*/b^*$, $l = z^*/c^*$ (integers). With these assumptions, we shall obtain in the following the integrated interference function $\mathcal{J} = I/|F^2|$ around any reciprocal-lattice point (h,k,l) as a function of the reciprocal-vector difference $\Delta S = S - S(hkl)$, where $S = |\mathbf{S}| = 2\sin\theta/\lambda$. Analogously, $\Delta x^* = x^* - ha^*$, $y^* = y^* - kb^*$, $\Delta z^* = z^* - lc^*$; for the above, together with ΔS, they will be treated as infinitesimal quantities.

It was shown in a previous paper (Allegra, Bassi & Meille, 1978) that

$$\Delta x^* = A\Delta S - B\Delta y^* - C\Delta z^*, \tag{2}$$

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with

$$A = S_0/q_1;\quad B = q_2/q_1;\quad C = q_3/q_1;\quad S_0 \equiv S(h,k,l);$$

$$q_1 = ha^* + kb^*\cos\gamma^* + lc^*\cos\beta^*;$$

$$q_2 = ha^*\cos\gamma^* + kb^* + lc^*\cos\alpha^*;$$

$$q_3 = ha^*\cos\beta^* + kb^*\cos\alpha^* + lc^*, \qquad (2')$$

α^*, β^* and γ^* being the reciprocal-cell angles. With the above substitution, the interference function may be written in terms of ΔS, Δy^* and Δz^*

$$\mathscr{I}^0_{hkl}(\Delta S,\Delta y^*,\Delta z^*) = \frac{I(x^*,y^*,z^*)}{|F^2(h,kl)|} \simeq \frac{\sin^2[\pi N_1(A\Delta S - B\Delta y^* - C\Delta z^*)/a^*]}{[\pi(A\Delta S - B\Delta y^* - C\Delta z^*)/a^*]^2} \times \frac{\sin^2[\pi N_2\Delta y^*/b^*]}{[\pi\Delta y^*/b^*]^2}\cdot\frac{\sin^2[\pi N_3\Delta z^*/c^*]}{[\pi\Delta z^*/c^*]^2}. \qquad (3)$$

We are interested in obtaining the integral of $\mathscr{I}^0_{hkl}$ over the sphere S = constant, which represents the value of the integral line profile *versus* S. This may also be regarded as the line profile of a collection of many disorderly oriented identical crystals, apart from a constant factor. Since $\mathscr{I}^0_{hkl}$ falls to zero very rapidly with increasing values of $|\Delta y^*|$ and $|\Delta z^*|$, the sphere may be replaced by the plane normal to the $\mathbf{S}(hkl)$ vector; for the same reason, the integration along Δy^* and Δz^* may be performed from $-\infty$ to $+\infty$. Consequently, the integral is given by [Allegra *et al.*, 1978, equations (10) and (15)]:

$$\mathscr{I}_{hkl}(\Delta S) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathscr{I}^0_{hkl}(\Delta S,\Delta y^*,\Delta z^*).|A|R^*\,\mathrm{d}\Delta y^*\,\mathrm{d}\Delta z^*, \qquad (4)$$

where

$$R^* = \sqrt{(1-\cos^2\alpha^* - \cos^2\beta^* - \cos^2\gamma^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*)}. \qquad (4')$$

Combining equations (3) and (4), we may write

$$\mathscr{I}_{hkl}(\Delta S) \equiv \Phi(u,v,w,X) = K\iint_{-\infty}^{+\infty}\frac{\sin^2[u(X-Y-Z)]}{(X-Y-Z)^2} \times \frac{\sin^2(vY)}{Y^2}\cdot\frac{\sin^2(wZ)}{Z^2}\,\mathrm{d}Y\,\mathrm{d}Z, \qquad (5)$$

where

$$X = \frac{\pi}{a^*}A\Delta S;\quad Y = \frac{\pi}{a^*}B\Delta y^*;\quad Z = \frac{\pi}{a^*}C\Delta z^*;$$

$$u = N_1;\quad v = \frac{a^*}{b^*}\frac{N_2}{|B|};\quad w = \frac{a^*}{c^*}\frac{N_3}{|C|};$$

$$K = \frac{1}{\pi^2}|A|BCR^*\left(\frac{b^*c^*}{a^*}\right)^2. \qquad (5')$$

From equation (5) the following relationship may be derived

$$\Psi(u,v,w,X) = \frac{1}{K}\frac{\partial^3\Phi}{\partial u\,\partial v\,\partial w} = \iint_{-\infty}^{+\infty}\frac{\sin[2u(X-Y-Z)]}{X-Y-Z}\cdot\frac{\sin(2vY)}{Y} \times \frac{\sin(2wZ)}{Z}\,\mathrm{d}Y\,\mathrm{d}Z, \qquad (6)$$

which shows that Ψ, *as a function of* X, is the convolution of three functions of the type $(\sin ax)/x$. The Fourier transform of Ψ with respect to X is therefore the product of the three corresponding transforms. Each of these is a 'step' function extending from $(-a)$ to $(+a)$ along the transformed axis, as may be seen in the following

$$F(x) = \frac{1}{2\pi}\int_{-a}^{+a} e^{-itx}\,\mathrm{d}t = \frac{1}{\pi}\frac{\sin ax}{x}; \qquad (7)$$

$$f(t) = \int_{-\infty}^{+\infty} F(x)e^{+itx}\,\mathrm{d}x = \begin{cases} +1 & \text{between } (-a) \text{ and } (+a) \\ 0 & \text{elsewhere.} \end{cases} \qquad (7')$$

According to the above, the Fourier transform of $\Psi(X)$, say $\psi(t)$, is a step function with the value π^3 between the extremes $(-2k)$ and $(+2k)$ (k being the smallest among u, v and w), zero otherwise. As a result of the antitransformation of $\psi(t)$ to $\Psi(X)$ we have:

$$\Psi(u,v,w,X) = \pi^2\frac{\sin(2kX)}{X} \qquad (8)$$

(k = smallest among u,v,w).

With the help of equations (5) and (6) and assuming that k coincides with w, for example, the line-profile function is now readily obtained:

$$\mathscr{I}_{hkl}(\Delta S) = K\int_0^u\int_0^v\int_0^w \Psi(u,v,w,X)\,\mathrm{d}u\,\mathrm{d}v\,\mathrm{d}w = \pi^2 Kuv\frac{\sin^2(wX)}{X^2} = \frac{S_0}{|q_3|}\frac{N_1N_2}{c^*V}\frac{\sin^2\left(N_3\dfrac{\pi}{c^*}\dfrac{S_0\Delta S}{q_3}\right)}{\left(\dfrac{\pi}{c^*}\dfrac{S_0\Delta S}{q_3}\right)^2}, \qquad (9)$$

where S_0 stands for $S(hkl)$.

In the above, use has been made of the property that Φ vanishes if any among the (u,v,w) parameters has zero value. The last result in equation (9) is obtained after the substitutions given in equations (2′) and (5′) and remembering that V (volume of the unit cell) = $1/(a^*b^*c^*R^*)$. Furthermore, the substitutions x^* =

ha^*, $y^* = kb^*$, $z^* = lc^*$ have been performed. After multiplication by the same factor, the three parameters (u,v,w) may be expressed in an equivalent, more symmetrical form [see equations (2′) and (5′)]:

$$\bar u = \frac{N_1}{a^*|q_1|}\,; \quad \bar v = \frac{N_2}{b^*|q_2|}\,; \quad \bar w = \frac{N_3}{c^*|q_3|}\,. \tag{10}$$

With the above substitutions equation (9) reduces to

$$\mathcal{J}_{hkl}(\Delta S) = \frac{NS_0}{V}\,.\,\bar w\,.\,\frac{\sin^2(\pi\bar w S_0 \Delta S)}{(\pi \bar w S_0 \Delta S)^2}\,, \tag{11}$$

where $N = N_1N_2N_3$ is the total number of unit cells within the crystal. If either $\bar u$ or $\bar v$ is smaller than $\bar w$, it should appear in equation (11) instead of $\bar w$. Consequently, the change of the line profiles in reciprocal space does not show any discontinuity [remember that $\bar u$, $\bar v$ and $\bar w$ depend on h,k,l through equations (2′)]. The most characteristic features of the line profile may be summarized as follows:

$$\text{Peak height} = \lim_{\Delta S \to 0} \mathcal{J}_{hkl}(\Delta S) = \left(\frac{N}{V}\right) S(hkl)\, \bar w(hkl),$$

Full width at half peak height

$$= W_{1/2,hkl} = \frac{0{\cdot}8858}{S\,(hkl)\,.\,\bar w\,(hkl)}\,,$$

$$\text{Integral value} = \int_{-\infty}^{+\infty} \mathcal{J}_{hkl}(\Delta S)\,\mathrm{d}\Delta S = \frac{N}{V}\,. \tag{12}$$

We may now state the following general result: For an assemblage of identical crystals having any parallelepiped shape, provided only that each edge comprises more than about 10 unit cells, the integral interference function, or line profile, is expressed as $A\sin^2(B\Delta S)/(B\Delta S)^2$ for any reflection, although in general A and B have different values for different reflections. As expected, the full width at half height is inversely proportional to the peak height. As is intuitively reasonable, for given values of the reciprocal-space parameters, the B value is mostly influenced by the lowest among the three numbers (N_1,N_2,N_3) characterizing the crystal size. In particular, upon comparison of equation (11) with (1), it is easy to see that the effective (average) thickness of the crystal is given by $\bar w S_0$, *i.e.* it is dictated by the value of N_3 if $\bar w \le (\bar u,\bar v)$. As could have been predicted, the line shape is identical for all the higher orders of one reflection (*i.e.* same ratios h/k, k/l).

(*b*) *The line profile for a polycrystalline sample obeying simple Gaussian statistics*

Let us suppose that the probability of existence $P(N_1,N_2,N_3)$ of a parallelepiped crystal having edge lengths (N_1a,N_2b,N_3c) is

$$P(N_1,N_2,N_3) = 8\alpha\beta\gamma/\pi^{3/2} \exp\left(-\alpha^2N_1^2 - \beta^2N_2^2 - \gamma^2N_3^2\right), \tag{13}$$

where the parameters (α,β,γ) are related to the *average* numbers $(\langle N_1\rangle, \langle N_2\rangle, \langle N_3\rangle)$ by the relation

$$\langle N_1\rangle = 1/(\alpha\pi^{1/2}); \quad \text{(similarly for } \langle N_2\rangle \text{ and } \langle N_3\rangle\text{)}. \tag{14}$$

The above expression represents the simplest Gaussian probability distribution, where it is assumed that the three probabilities along **a**, **b** and **c** are independent. It may be physically conceived as related to a mechanism of crystal growth where each crystal may increase or decrease in size along each direction in steps involving either gain or loss of one two-dimensional layer extending along the other two dimensions. The probabilities per unit time of both gain and loss are equal and independent of crystal size, although being different for the three directions. If all the crystals nucleate at the same time, the parameters (α,β,γ) are fully determined by the corresponding gain-or-loss probabilities as well as by the total time of growth.

From equations (10), (11) and (13), the average contribution to the interference function by the crystals with edge numbers comprised between $\{N_i\}$ and $\{N_i + \mathrm{d}N_i\}$ is, assuming $\bar w \le (\bar u,\bar v)$ and denoting as ν_0 the total number of crystals,

$$\begin{aligned}\mathrm{d}^3\langle \mathcal{J}^{(3)}_{hkl}(\Delta S)\rangle &= \nu_0 . P(N_1N_2,N_3) \\ &\qquad \times \mathcal{J}_{hkl}(\Delta S)\,\mathrm{d}N_1\,\mathrm{d}N_2\,\mathrm{d}N_3 \\ &= \frac{8\nu_0\alpha\beta\gamma}{\pi^{3/2}}.\exp\left(-\alpha^2N_1^2 - \beta^2N_2^2 - \gamma^2N_3^2\right).\frac{N_1N_2S_0}{Vc^*|q_3|} \\ &\quad \times \frac{\sin^2\left(\dfrac{\pi N_3}{c^*|q_3|}S_0\Delta S\right)}{\left(\dfrac{\pi}{c^*|q_3|}S_0\Delta S\right)^2}\,\mathrm{d}N_1\,\mathrm{d}N_2\,\mathrm{d}N_3.\end{aligned} \tag{15}$$

Since $\bar w \le (\bar u,\bar v)$, we have from equations (10)

$$N_1 \ge N_3\frac{a^*|q_1|}{c^*|q_3|} = H_1; \quad N_2 \ge N_3\frac{b^*|q_2|}{c^*|q_3|} = H_2, \tag{16}$$

and, considering $\{N_i\}$ as continuous variables, we may integrate equation (15) over both N_1 and N_2 from H_1 and H_2, respectively, to infinity, obtaining

$$\begin{aligned}&\frac{2\nu_0\gamma}{\alpha\beta\pi^{3/2}}\exp\left[-\left(\alpha^2\frac{a^{*2}q_1^2}{c^{*2}q_3^2} + \beta^2\frac{b^{*2}q_2^2}{c^{*2}q_3^2} + \gamma^2\right)N_3^2\right] \\ &\quad \times \frac{S_0}{Vc^*|q_3|}.\frac{\sin^2\left(\dfrac{\pi N_3}{c^*|q_3|}S_0\Delta S\right)}{\left(\dfrac{\pi}{c^*|q_3|}S_0\Delta S\right)^2}\mathrm{d}N_3,\end{aligned} \tag{17}$$

which may be further integrated over N_3 from zero to infinity:

$$\langle \mathscr{I}^{(3)}_{hkl}(\Delta S)\rangle = \frac{\nu_0}{2\pi}\frac{S_0}{V\alpha\beta\gamma}\frac{(\gamma c^* q_3)^2}{Z} \times \frac{1-\exp\left[-\left(\dfrac{\pi S_0 \Delta S}{Z}\right)^2\right]}{(\pi S_0 \Delta S)} \tag{18}$$

where

$$Z = \sqrt{[(\alpha a^* q_1)^2 + (\beta b^* q_2)^2 + (\gamma c^* q_3)^2]}. \tag{18$'$}$$

So far we have obtained the average contribution to the interference function from the crystals obeying the condition $\bar{w} \le (\bar{u},\bar{v})$, or, equivalently, satisfying equations (16). The corresponding contributions arising from $\bar{u} \le (\bar{v},\bar{w})$ [*i.e.* $\langle \mathscr{I}^{(1)}_{hkl}(\Delta S)\rangle$] and from $\bar{v} \le (\bar{u},\bar{w})$ [$\langle \mathscr{I}^{(2)}_{hkl}(\Delta S)\rangle$] are immediately derived by putting $(\alpha a^* q_1)^2$ and $(\beta b^* q_2)^2$, respectively, instead of $(\gamma c^* q_3)^2$ in equation (18). Finally, the average interference function is

$$\langle \mathscr{I}_{hkl}(\Delta S)\rangle = \sum_{i=1}^{3} \langle \mathscr{I}^{(i)}_{hkl}(\Delta S\rangle$$

$$= \frac{\mathscr{N}\sqrt{\pi}}{2}\cdot\frac{S_0 Z}{V}\cdot\frac{1-\exp\left[-\left(\dfrac{\pi S_0 \Delta S}{Z}\right)^2\right]}{(\pi S\,\Delta S)^2}, \tag{19}$$

where the total number $\mathscr{N}$ of the diffracting unit cells has been introduced as [see equation (14)]

$$\mathscr{N} = \nu_0\langle N\rangle = \nu_0\langle N_1\rangle\langle N_2\rangle\langle N_3\rangle = \frac{\nu_0}{\alpha\beta\gamma\pi^{3/2}}. \tag{20}$$

This parameter appears to be more significant than ν_0 inasmuch as it is proportional to the total amount of diffracting matter. Before proceeding to discuss the characteristic features of the above line profile, let us observe that (for $a > 0$)

$$\int_{-\infty}^{+\infty} \frac{1-\exp(-ax^2)}{x^2}\,\mathrm{d}x = \int_0^a \left[\int_{-\infty}^{+\infty} \exp(-a'x^2)\,\mathrm{d}x\right]\mathrm{d}a' = 2\sqrt{(a\pi)}. \tag{21}$$

Consequently, we have [*cf.* equations (12) and (21) of Allegra *et al.* (1978)]

$$\left.\begin{aligned} &\text{Peak height} = \lim_{\Delta S \to 0} \langle \mathscr{I}_{hkl}(\Delta S)\rangle = \frac{\mathscr{N}\sqrt{\pi}}{2}\frac{S_0}{VZ} \\ &\text{Full width at half-peak height} = W_{1/2,\,hkl} = \frac{2\cdot5248\ldots Z}{\pi S_0} \\ &\text{Integral value} = \int_{-\infty}^{+\infty} \langle \mathscr{I}_{hkl}(\Delta S)\rangle\,\mathrm{d}\Delta S = \frac{\mathscr{N}}{V}. \end{aligned}\right\} \tag{22}$$

As expected, the product of the peak height and the full half-peak width is still proportional to $\mathscr{N}/V$, *i.e.* the integral value (Warren, 1969). It is interesting to compare the present result with the interference function obtained on the assumption of a Bernoullian distribution of crystal sizes [see Allegra *et al.*, 1978, equation (19)]. While in the latter case the interference function behaves like a Lorentzian curve, *i.e.* $1/(1 + x^2)$, where $x = \Delta S \times$ (constant value for given h,k,l), in the present case it behaves as $A[1-\exp(-Bx^2)]/x^2$. Adjusting A and B so that both the total area and the half-peak width are identical in the two cases, the two functions are compared in Fig. 1, where the Gaussian curve $y = \exp(-Cx^2)$ is also reported with the same normalization. While the first two profiles show an obvious similarity inasmuch as they decrease as $1/x^2$ for large x, although with different scale factors, the Gaussian curve drops to essentially zero values (*i.e.* less than 1% of the peak height) for $x > 2\cdot5$. As will be quantitatively discussed below, the smaller 'tail' values of the profile obtained with the Gaussian compared with the Bernoullian crystal-size distribution are related to a lower percentage of small-size crystals in the former case. Obviously, a still lower percentage of such crystals would be required to obtain a Gaussian curve as the resulting line profile; however, it will be shown in the next section that this hypothesis appears to be physically implausible.

In the Bernoullian case it was shown that, at least for rectangular parallelepiped crystals, a reflection characterized by an **S** vector not coinciding with the reciprocal axes x^*,y^*,z^* tends to have a larger width than those along the axes [Allegra *et al.*, 1978, equations (24)]. This is not generally true for the Gaussian size distribution; referring for simplicity to the cubic case (*i.e.* $\alpha = \beta = \gamma$, $a^* = b^* = c^* = 1/a$, $\cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$), the half-peak width is independent of (h,k,l); *i.e.* [*cf.* equations (22), (18′) and (2′)]

$$W_{1/2,\,hkl} = \frac{2\cdot5248\ldots\alpha}{\pi}\,\frac{}{a}. \tag{23}$$

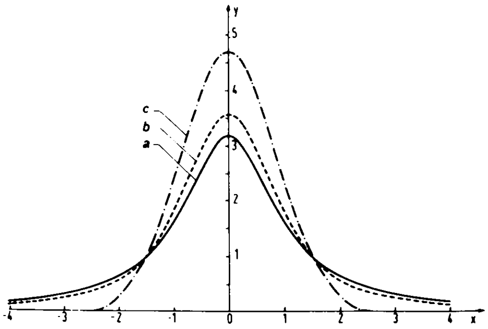

Fig. 1. Plots of (*a*) a Lorentzian function $A_1/(1 + x^2)$; (*b*) a function of the type $A_2[1 - \exp(-B_2x^2)]/x^2$; (*c*) a Gaussian function $A_3\exp(-B_3x^2)$. The coefficients A_i and B_i are adjusted so that for the three cases the integral from $-\infty$ to $+\infty$ is equal to unity and the half-peak half-width is also unity.

(c) *Implausibility of Gaussian size-broadened line profiles*

It was pointed out by Stokes & Wilson (1944), Bertaut (1949) and Warren (1955) that the size effect upon any reflection of a crystalline powder sample may be described as being due to the independent diffraction of unit-cell columns perpendicular to the diffracting planes. Remembering this result, we assume for simplicity $\cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$, and consider $00l$-type reflections. After integration over x^* from $-\frac{1}{2}a^*$ to $+\frac{1}{2}a^*$ and over y^* from $-\frac{1}{2}b^*$ to $+\frac{1}{2}b^*$, the interference function of a column of N_3 unit cells extending along **c** is given by [*cf.* equations (1) and (3), where $x^* = y^* = 0, z^* = lc^* + \Delta S$]

$$\mathcal{J}_{N_3}(\Delta S) = a^* b^* \frac{\sin^2(\pi N_3 \Delta S/c^*)}{(\pi\Delta S/c^*)^2}. \qquad (24)$$

The overall interference function is

$$\langle \mathcal{J}_{00l}(\Delta S)\rangle = \frac{\mathcal{N}}{\langle N_3\rangle} \sum_{N_3=1}^{\infty} P(N_3)\,\mathcal{J}_{N_3}(\Delta S), \qquad (25)$$

where $\langle N_3\rangle$ is the average number of unit cells within the columns along **c** and, consequently, $\mathcal{N}/\langle N_3\rangle$ is the total number of columns, while $P(N_3)$ is the probability of finding a column containing just N_3 unit cells. We will obtain $P(N_3)$ with the assumption that $\langle \mathcal{J}_{00l}(\Delta S)\rangle$ is Gaussian, *i.e.*

$$\langle \mathcal{J}_{00l}(\Delta S)\rangle = CK\exp(-K^2\Delta S^2), \qquad (26)$$

where $C = \mathcal{N}/V\sqrt{\pi}$ [*cf.*, for example, equations (22)].

For simplicity we shall make the substitutions

$$\Delta S = y;\quad N_3 = x;\quad \frac{\pi}{c^*} = \psi;$$

$$P(N_3) = f(x);\quad \sin^2\beta = \frac{1-\cos 2\beta}{2};$$

$$\frac{\mathcal{N}}{\langle N_3\rangle} a^* b^* = \sigma, \qquad (27)$$

so that, combining equations (25) and (26) and changing the sum into an integral,

$$2\psi^2 y^2 CK\exp(-K^2y^2) = \sigma \int_0^{\infty} f(x)(1-\cos 2\psi xy)\,\mathrm{d}x. \qquad (28)$$

Remembering that $\int_0^\infty f(x)\,\mathrm{d}x = 1$, expanding $f(x)$ on the negative side of the x axis with the assumption $f(-x) = f(x)$ after the substitution $\cos(2\psi xy) = \frac{1}{2}[\exp(2i\psi xy) + \exp(-2i\psi xy)]$, equation (28) reduces to

$$\frac{1}{2}\int_{-\infty}^{+\infty} f(x)\exp(2i\psi xy)\,\mathrm{d}x = 1 - \frac{2C}{\sigma}K\psi^2y^2\exp(-K^2y^2). \qquad (29)$$

The function $f(x)$ may now be obtained after a Fourier antitransformation, *i.e.*

$$\tfrac{1}{2}f(x) = \delta(x) - \frac{2C}{\pi\sigma}K\psi^3 \int_{-\infty}^{+c} y^2\exp(-K^2y^2 - 2i\psi xy)\,\mathrm{d}y, \qquad (30)$$

where $\delta(x)$ is the Dirac delta function. The integral on the right-hand side may be computed by standard methods and we finally obtain, remembering equations (27) and $V^{-1} = a^*b^*c^*$,

$$P(N_3) = 2\delta(N_3) + 2\langle N_3\rangle\left(\frac{\pi}{c^*K}\right)^2 \times \left[2\left(\frac{\pi N_3}{c^*K}\right)^2 - 1\right]\exp\left[-\left(\frac{\pi N_3}{c^*K}\right)^2\right]. \qquad (31)$$

In agreement with the starting assumption, the second member turns out to be an even function of N_3; it may be checked that the term following $2\delta(N_3)$ has a zero average value, *i.e.* its integral over N_3 from zero to infinity is zero.

Obviously, the above result is physically absurd. In fact, even apart from the unphysical δ function, the next term is negative for small N_3 values, becomes zero for $\bar{N}_3 = c^*K/\pi\sqrt{2}$, and then becomes positive. As an example, for $K = 100/c^*$, which means $\langle\Delta S^2\rangle^{1/2} \simeq c^*/140$ [see equation (26)], this term is negative up to $\bar{N}_3 = 22$, then it reaches its positive maximum for $N_3 \simeq 40$, the negative value for small N_3 being about twice as large as the maximum itself.

There is only one possibility that the above result is wrong, namely if the crystal contains holes and/or its surface is not convex, all its unit cells being perfectly coherent otherwise (Fig. 2). In fact, equation (24) is only valid if any column containing N_3 unit cells is *continuous*, *i.e.* if it is not given by $N_3 - k$ cells, say, then any number of 'empty' cells, then k cells again with the same alignment (see Fig. 2). On the assumption that we had to deal with such an improbable crystal, a Gaussian size-dependent interference function

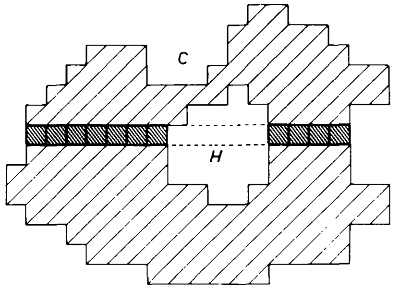

Fig. 2. Sketch showing a crystal with a hole (H) and a surface concavity (C). A row of unit cells (darker regions) is interrupted by the hole.

could perhaps be obtained. Incidentally, Warren's (1969) formula

$$\frac{\mathrm{d}^2\mathscr{A}^S_{N_3}}{\mathrm{d}N_3^2}=P(N_3),$$

where $\mathscr{A}^S_{N_3}$ is the total number of *pairs* of N_3th neighbouring unit cells within the columns, would also fail for a hole-containing crystal ($\mathscr{A}^S_{N_3}$ may be obtained from a Fourier analysis of the size-broadened diffraction profile).

(*d*) *Statistical distribution of crystal sizes for the Bernoullian and Gaussian cases*

A conclusion analogous to that drawn by Allegra *et al.* (1978) may be reported here; *i.e.* if the majority of the (perfect) crystals belonging to the diffracting sample have a parallelepiped shape and if their observed line profiles, after correction for the effect of strain, are all similar to that reported in Fig. 1 (curve *b*), their statistical distribution may probably be reduced to equation (13). In such a case, the line profiles of all the reflections should be interpreted in terms of the three statistical parameters (α,β,γ) according to the general equation (19).

In view of the peculiar simplicity of the Bernoullian and Gaussian crystal-size distributions, we have thought it useful to calculate some related statistical properties. In particular, we have directed our attention to the *number* and the *weight* probability distributions of the crystals as a function of their volume, as the most representative and potentially useful statistics of the polycrystalline samples. Our starting point is represented by the probability distributions of crystals having given edge lengths (N_1a,N_2b,N_3c) in the two cases, *i.e.*

$$\left.\begin{aligned}P_B(x,y,z)&=\alpha\beta\gamma\exp[-(\alpha x+\beta y+\gamma z)]\\P_G(x,y,z)&=\frac{8\alpha\beta\gamma}{\pi^{3/2}}\exp[-(\alpha^2x^2+\beta^2y^2+\gamma^2z^2)],\end{aligned}\right\}\quad(32)$$

that are identical to equation (1) of Allegra *et al.* (1978), and equation (13) of the present paper, the symbols B and G standing for Bernoullian and Gaussian, and (N_1,N_2,N_3) being substituted by the continuous variables (x,y,z). Both distributions are normalized inasmuch as their integral over x, y and z from zero to infinity is unity. For either case we have:

$$\left.\begin{aligned}\frac{\mathrm{d}\nu}{\mathrm{d}v}&=\frac{1}{V}\frac{\mathrm{d}\nu}{\mathrm{d}N}=\frac{\nu_0}{V}\iiint_0^\infty P(x,y,z)\\&\qquad\times\delta(xyz-N)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\\\frac{\mathrm{d}w}{\mathrm{d}v}&=\frac{WN}{V}\frac{\mathrm{d}\nu}{\mathrm{d}N}=\frac{WN\nu_0}{V}\iiint_0^\infty P(x,y,z)\\&\qquad\times\delta(xyz-N)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z,\end{aligned}\right\}\quad(33)$$

where: $N=N_1N_2N_3$ is the total number of unit cells for the general crystal; V is the unit-cell volume; $v=NV$ is the volume of a crystal; W is the weight per unit cell; and NW is the weight of a crystal; $\nu(v)$ and $w(v)$ are the total number and weight of the crystals with volume $\leq v$, while ν_0 is the total crystal number; $\delta(x)$ is the Dirac δ function.

It is apparent that $\mathrm{d}\nu/\mathrm{d}v$ and $\mathrm{d}w/\mathrm{d}v$ are the number and the total weight, respectively, of the crystals with volume comprised between v and $v+\mathrm{d}v$, both divided by $\mathrm{d}v$. For simplicity we shall deal in the following with the related functions $F(N)=(V/\nu_0)(\mathrm{d}\nu/\mathrm{d}v)$ and $G(N)=NF(N)=(V/W\nu_0)(\mathrm{d}w/\mathrm{d}v)$, while a suffix B or G will specify whether the Bernoullian or the Gaussian case is treated. It is not difficult to see that $F(N)$ and $G(N)/\langle N\rangle$ are the *number* and *weight* probability densities, respectively, of crystals containing N unit cells.

First we need a suitable representation of the δ function. Introducing the identity

$$\delta(xyz-N)=\frac{1}{N}\,\delta\left[\ln\left(\frac{xyz}{N}\right)\right]\qquad(34)$$

and adopting the usual Fourier representation for $\delta(x)$, we obtain

$$F_B(N)=\frac{\beta\gamma}{2\pi N}\int_{-\infty}^{+\infty}e^{i\omega\ln N}\left[\int_0^\infty\mathrm{d}x\,e^{-\alpha x}x^{i\omega}\right]\times\left[\int_0^\infty\mathrm{d}y\,e^{\beta y}y^{i\omega}\right]\left[\int_0^\infty\mathrm{d}z\,e^{-\gamma z}z^{i\omega}\right]\mathrm{d}\omega,\qquad(35)$$

that is:

$$F_B(B)=\frac{1}{2\pi N}\int_{-\infty}^{+\infty}e^{-i\omega s}[\Gamma(i\omega+1)]^3\,\mathrm{d}\omega,\qquad(36)$$

where Γ denotes the gamma function, and

$$s=\ln(N\alpha\beta\gamma),\qquad(37)$$

while $\alpha\beta\gamma$ is $\langle N\rangle^{-1}$ (Allegra *et al.*, 1978). For all real values of s, the above integral converges rather quickly, since (Abramowitz & Stegun, 1965, ch. 6)

$$|\Gamma(i\omega+1)|^2=\frac{\pi\omega}{\sinh(\pi\omega)},\qquad(38)$$

so that a numerical evaluation of equation (36) does not pose serious difficulties provided the proper argument is added to $\Gamma(1+i\omega)$, *i.e.*

$$\arg\Gamma(1+i\omega)=\sum_{n=0}^{\infty}\left[\frac{\omega}{1+n}-\operatorname{atan}\left(\frac{\omega}{1+n}\right)\right]-\omega\gamma,\qquad(39)$$

where γ is the Euler–Mascheroni constant. The extension of equation (36) to d-dimensional crystals is

$$F_B(N)=\frac{1}{2\pi N}\left[\prod_{i=1}^{d}\alpha_i\right]\int_{-\infty}^{\infty}e^{-i\omega s}\,[\Gamma(i\omega+1)]^d\,\mathrm{d}\omega, \quad (40)$$

where

$$s=\ln\left(N\prod_{i=1}^{d}\alpha_i\right), \quad (41)$$

and $\alpha_1, \alpha_2, \ldots \alpha_i \ldots$ stand for $(\alpha,\beta,\gamma,\ldots)$. The case $d=1$ is trivial, and gives

$$F_B(N)=\alpha e^{-\alpha N}. \quad (42)$$

However, equation (40) shows that this case is the most critical from the point of view of the convergence. Therefore, the above simple solution for $d=1$ provides a useful check on the numerical accuracy of integration.

For $d=3$, introducing the function $Q(s)$, defined as

$$Q(s)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{-i\omega s}\,[\Gamma(i\omega+1)]^3\,\mathrm{d}\omega, \quad (43)$$

equation (36) reads

$$F_B(N)=N^{-1}\,Q(s), \quad (36')$$

and from the definition $G(N)=NF(N)$

$$G_B(N)=Q(s);\quad [s=\ln(N\alpha\beta\gamma)]. \quad (44)$$

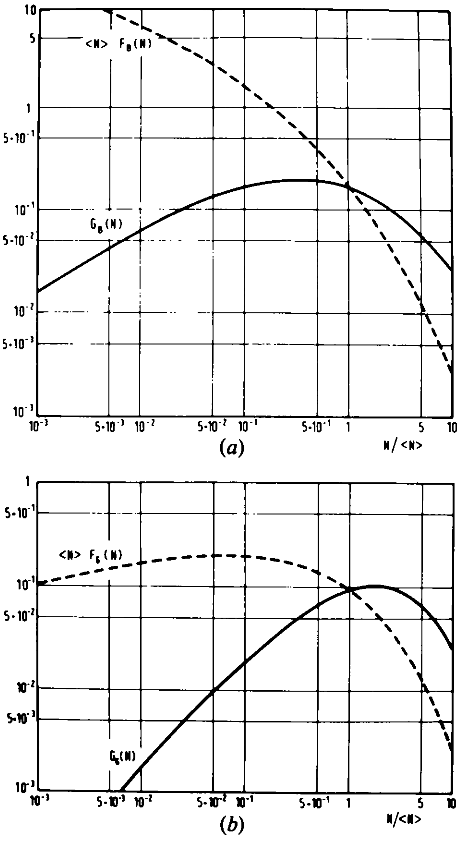

Fig. 3. Logarithmic plots of $\langle N\rangle.F(N)$ and of $G(N)$ *vs* $N/\langle N\rangle$ for both the (*a*) Bernoullian and (*b*) Gaussian crystal-size distributions. $\langle N\rangle$ is the average number of unit cells per crystal; $F(N)$ and $G(N)/\langle N\rangle$ respectively are the number and the weight probability distributions of the crystals comprising N unit cells (see text).

Both $F_B(N)/(\alpha\beta\gamma)=[F_B(N).\langle N\rangle]$ and $G_B(N)$ are reported in Fig. 3(*a*) as functions of the reduced variable $N\alpha\beta\gamma=N/\langle N\rangle$. Since $\int_0^\infty F(N)\,\mathrm{d}N=1$, and $\int_0^\infty G(N)\,\mathrm{d}N=\langle N\rangle$, it is apparent that the integrals of both functions over the reduced variable are unity. At $N=0$, F_B diverges, whereas G_B vanishes with an infinite slope. In the complex ω plane the poles of the integrand in equation (43) are $\omega_n=ni$, with integral positive n. For negative s (*i.e.* for $N\alpha\beta\gamma<1$), the integral can be converted into a sum of residues. If $N\alpha\beta\gamma\ll 1$ (*i.e.* for $s\to-\infty$), only the pole at $\omega=i$ can be considered. In this limit we obtain therefore

$$G_B(N)=Q\ln(N\alpha\beta\gamma)\sim(N\alpha\beta\gamma)\left[3(2C_2^2-C_3)-3C_2\ln\left(\frac{1}{N\alpha\beta\gamma}\right)+\tfrac{1}{2}\ln^2\left(\frac{1}{N\alpha\beta\gamma}\right)\right], \quad (45)$$

where C_2 and C_3 correspond to the series development of $1/\Gamma(Z)$:

$$1/\Gamma(Z)=Z+\sum_{2}^{\infty}C_nZ^n,$$

as given by Abramowitz & Stegun (1965, ch. 6). In particular, $C_2=0{\cdot}5772\ldots$ and $C_3=-0{\cdot}6559\ldots$ Equation (45) is correct up to terms of order $(N\alpha\beta\gamma)\ln^2(1/N\alpha\beta\gamma)$. $F_B/(\alpha\beta\gamma)$ diverges as $\frac{1}{2}\ln^2(1/N\alpha\beta\gamma)$ near $N=0$. In spite of numerous attempts no simple asymptotic formula for $Q(s)$ has been found for large positive s (*i.e.* for $N\alpha\beta\gamma\gg 1$). However, numerical integration suggests that in this limit

$$F_B(N)/(\alpha\beta\gamma)\sim\exp(-N\alpha\beta\gamma). \quad (46)$$

As for the Gaussian probability distribution $P_G(x,y,z)$ [equation (32)], application of the techniques developed for the previous case yields

$$F_G(N)=\frac{1}{2N\pi^{5/2}}\int_{-\infty}^{+\infty}e^{-i\omega\ln(N\alpha\beta\gamma)}\,\Gamma^3\left(\frac{i\omega+1}{2}\right)\mathrm{d}\omega. \quad (47)$$

Shifting the integration path to the horizontal line $Im(\omega)=-\frac{1}{2}$, we easily obtain

$$F_G(N)=\frac{1}{N\pi^{5/2}}\,(N\alpha\beta\gamma)^{-1/2}\times\int_{-\infty}^{+\infty}e^{-2i\omega\ln(N\alpha\beta\gamma)}\,\Gamma^3(i\omega+1)\,\mathrm{d}\omega, \quad (48)$$

which can also be written

$$F_G(N)=\frac{2}{N\pi^{3/2}}\,(N\alpha\beta\gamma)^{-1/2}\,Q[2\ln(N\alpha\beta\gamma)]. \quad (49)$$

From equation (49) we immediately obtain the distribution function $G_G(N)$:

$$G_G(N) = NF_G(N). \tag{50}$$

In Fig. 3(*b*), $F_G/(\alpha\beta\gamma\pi^{3/2}) = (F_G.\langle N\rangle)$ and G_G are reported as functions of the reduced variable $N\alpha\beta\gamma\pi^{3/2} = N/\langle N\rangle$. Asymptotic expressions derived from equation (45) and valid at small N (*i.e.* $N\alpha\beta\gamma \ll 1$) are

$$G_G(N) \sim \frac{2}{\pi^{3/2}}(N\alpha\beta\gamma)^{3/2}\left[3(2C_2^2 - C_3) - 6C_2 \ln\left(\frac{1}{N\alpha\beta\gamma}\right) + 2\ln^2\left(\frac{1}{N\alpha\beta\gamma}\right)\right]; \tag{51}$$

$$\frac{F_G(N)}{(\alpha,\beta,\gamma)} = G_G(N)/(N\alpha\beta\gamma). \tag{52}$$

As for the Bernoullian distribution, no simple asymptotic formulas valid for large N have been obtained. However, if the conjectured expression (46) is correct, we obtain

$$G_G(N) \sim \frac{2}{\pi^{3/2}}(N\alpha\beta\gamma)^{3/2}\exp[-(N\alpha\beta\gamma)^2], \tag{53}$$

and

$$F_G(N)/(\alpha\beta\gamma) \sim \frac{2}{\pi^{3/2}}(N\alpha\beta\gamma)^{1/2}\exp[-(N\alpha\beta\gamma)^2] \tag{54}$$

at $(N\alpha\beta\gamma) \gg 1$.

Concluding remarks

It is sometimes observed that the Cauchy distribution $y = A/(1 + K^2\Delta S^2)$ produces too high values in the tail regions compared with experimental size-broadened line profiles, contrary to the Gaussian distribution $y = A'\exp(-K'^2\Delta S^2)$ that vanishes too quickly (see, for example, Hall, Veeraraghavan, Rubin and Winchell, 1977).

We have proved that the Gaussian distribution cannot be produced by any crystalline powder sample, at least if the (otherwise perfect) crystals neither contain holes nor have concave surfaces. In a previous paper (Allegra *et al.*, 1978) we showed that a sample of Bernoullian crystals [probability of thickness d along a given direction $= C_1\exp(-C_2 d)$] gives Cauchy line profiles. In this paper, investigation of the diffracted intensity by a Gaussian sample {probability of thickness d along a given direction $= C_1\exp[-\exp(C_2 d^2)]$} leads to an interference function of the type $y = A[1 - \exp(-B\Delta S^2)]/\Delta S^2$, which is somehow intermediate between the Cauchy and the Gaussian extremes (see Fig. 1). Consequently, the Gaussian crystal-size distribution may probably be assumed to be a better model for many real samples – the more so because it may be associated with a relatively simple model of crystal growth. However, it should be stressed that the line profiles for both the Bernoullian and the Gaussian crystal-size distributions tend to decrease as $1/\Delta S^2$ for a large reciprocal distance ΔS from the maximum. As expected from the calculated line profiles, the results reported in Figs. 3 and 4 show that there is a larger proportion of small crystals in the Bernoullian than in the Gaussian sample (the respective weight fractions of crystals having a volume smaller than the average are about 6 and 18%, as calculated from Fig. 4). Our results also show that the probability density $F(N)$ tends to infinity for $N \to 0$ in the Bernoullian case, contrary to the Gaussian (remember that N is proportional to the crystal volume), which also appears to favour the Gaussian hypothesis.

Finally, we wish to point out that the exact mathematical expression [see equation (11)] of the interference function for a collection of identical parallelepiped crystals (provided their size exceeds some lower limit) may allow the average interference function for powder samples obeying a variety of size statistics to be obtained. It was only because of the peculiar simplicity of the Bernoullian statistics that one of us was able to obtain the corresponding interference function without making use of equation (11) (Allegra *et al.*, 1978).

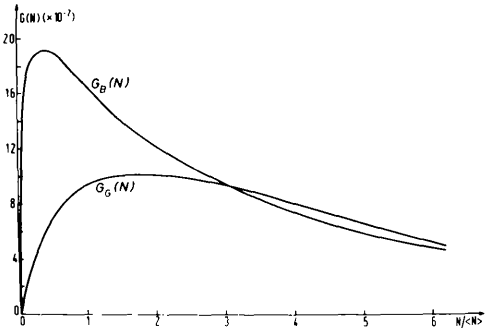

Fig. 4. Plot of $G(N)$ *vs* $N/\langle N\rangle$ for both the Bernoullian (G_B) and Gaussian (G_G) distributions, showing that in the former case there is a larger weight fraction crystallizing below the average size $N/\langle N\rangle = 1$ (*cf.* Fig. 3).

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