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Exact Random-Walk Models in Crystallographic Statistics. II. The Bicentric Distribution for the Space Group $P\bar{1}$

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Abstract

An exact probability density function for the magnitude of the normalized structure factor $|E|$ has been derived for the space group $P\bar{1}$, taking account of the presence of one non-crystallographic center of symmetry. The function is based on the exact solution of the corresponding random-walk model and its expansion into a Fourier series. The above result is compared with simulated semi-cumulative distributions based on hypothetical structures and very good agreement is obtained for the equal-atom case, as well as for a heterogeneous asymmetric subunit containing fourteen carbon atoms and one uranium atom. The new exact bicentric probability density functions of $|E|$, for the space group $P\bar{1}$, reduce to the well known asymptotic expressions that are valid for equal-atom structures and a large number of atoms in the asymmetric unit of the space group.

Introduction

Effects of non-crystallographic symmetry on distributions of diffracted intensity have long since been recognized and investigated. Major attention has been devoted to the presence of one or more non-crystallographic centers in centrosymmetric (Lipson & Woolfson, 1952; Rogers & Wilson, 1953) and non-centrosymmetric (Srinivasan & Parthasarathy, 1976) crystals composed of equal atoms, and similar approximations based on the central limit theorem were also derived for the presence of non-crystallographic translational symmetry (hyperparallelism; Rogers & Wilson, 1953).

The best known, among these 'anomalous' distributions, is that due to the presence of one non-crystallographic center of symmetry, *i.e.* the bicentric distribution. An approximate generalization of this distribution to centrosymmetric space groups, and any atomic composition of the asymmetric unit, has recently been given by Ghosh & Nigam (1983) as a three-term expansion, with coefficients depending on definite integrals that can be tabulated. Another route to such generalizations has been outlined by Shmueli & Wilson (1982, 1983) and explicit polynomials, orthogonal to the Rogers-Wilson (1953) bicentric probability density function (p.d.f.) have been obtained. Such approximate generalizations may prove useful for not too large departures from the asymptotic bicentric p.d.f., but their convergence behavior is obviously space-group dependent and may give rise to difficulties in space groups of low symmetry (see, *e.g.*, Shmueli, 1982*a*).

An exact solution to this problem, at least for the important case of the space group $P\bar{1}$, can be given in the form of a p.d.f. based on a Fourier expansion of the exact solution to the problem of random walk (Barakat, 1974; Weiss & Kiefer, 1983; Kiefer & Weiss, 1984). Such p.d.f.'s have recently been applied with success to effects of atomic heterogeneity on departures from the widely used Wilson (1949) distributions (Shmueli, Weiss, Kiefer & Wilson, 1984).

The aims of the present paper are (i) to derive an exact probability density function for the magnitude of the normalized structure factor, which accounts for the presence of a non-crystallographic center in the asymmetric unit of $P\bar{1}$ for an arbitrary atomic composition, and (ii) to demonstrate the probable

usefulness of this p.d.f. by its comparison with simulated distributions, arising from equal-atom as well as highly heterogeneous asymmetric units. It is also shown that the exact p.d.f. proposed in this paper approaches the Rogers–Wilson bicentric p.d.f. in the limit of a large number of equal atoms.

The bicentric p.d.f. for $P\bar{1}$

Let the asymmetric unit of $P\bar{1}$ consist of two identical subunits, which are related by a center of symmetry and assume that all the atoms, as well as the additional center, are located in general Wyckoff positions of the space group. The equivalent atomic positions with respect to the non-crystallographic center at, say, \mathbf{d} can be labeled as \mathbf{r}_j and $\mathbf{r}_{j+N/4}$, and it is readily seen that

$$\mathbf{r}_{j+N/4} = -\mathbf{r}_j + 2\mathbf{d}. \quad (1)$$

The structure factor for the above arrangement can thus be written as

$$\begin{aligned} F(\mathbf{h}) &= 2 \sum_{j=1}^{N/4} f_j [\cos 2\pi\mathbf{h} \cdot \mathbf{r}_j + \cos 2\pi\mathbf{h} \cdot (2\mathbf{d} - \mathbf{r}_j)] \\ &= 4 \sum_{j=1}^{N/4} f_j \cos(2\pi\mathbf{h} \cdot \mathbf{d}) \cos[2\pi\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{d})]. \end{aligned} \quad (2)$$

Since all the positions are general, and under the assumption that a large set of F 's is available, the scalar products $\mathbf{h} \cdot \mathbf{r}_j$ and $\mathbf{h} \cdot \mathbf{d}$ can be taken as uniform in the $[0, 1]$ range, and the structure-factor equation (2) can be rewritten for statistical purposes as

$$F = 4 \sum_{j=1}^{N/4} f_j \cos \varphi \cos(\theta_j - \varphi), \quad (3)$$

where $\theta_j = 2\pi\mathbf{h} \cdot \mathbf{r}_j$ and $\varphi = 2\pi\mathbf{h} \cdot \mathbf{d}$ are random variables, taken as uniform in the $[0, 2\pi]$ range (cf. Shmueli *et al.*, 1984).

The analogy of F , represented as a vector polygon in the complex plane, with the picture of randomly oriented contiguous steps in the plane has been pointed out by Hauptman & Karle (1952) and by Wilson (1952), in connection with their early studies of structure-factor statistics. In the present case, a step in this random walk corresponds to four times the atomic scattering factor and the trigonometric expression in (3) is identified with a function that determines the projection of such a step onto the real axis. The required p.d.f. of F thus corresponds to that of the random walk, projected onto this direction, and can be determined from the relevant characteristic function as outlined, for example, by Weiss & Kiefer (1983).

The characteristic function of the structure factor (3) is given by

$$C(\omega_1) = \left\langle \exp \left[4i\omega_1 \sum_{j=1}^{N/4} f_j \cos \varphi \cos(\theta_j - \varphi) \right] \right\rangle. \quad (4)$$

The integration in the right-hand side of (4) is performed first on the variables $\theta_1, \dots, \theta_{N/4}$ and subsequently on φ . After some calculation one obtains

$$C(\omega_1) = \left\langle \prod_{j=1}^{N/4} J_0(4\omega_1 f_j \cos \varphi) \right\rangle_{\varphi} \quad (5)$$

$$= \frac{2}{\pi} \int_0^{\pi/2} \left[\prod_{j=1}^{N/4} J_0(4\omega_1 f_j \cos \varphi) \right] d\varphi, \quad (6)$$

where $J_0(x)$ is the Bessel function of the first kind of order zero (see, e.g., Abramowitz & Stegun, 1972).

Since the structure factor can differ from zero only in the interval $[-S_1, S_1]$, where $S_1 = \sum_{j=1}^{N/4} f_j$, and the corresponding p.d.f. for F is analogous to that of the projected random walk, we obtain it as the Fourier series

$$P(F) = \frac{1}{2S_1} \left[1 + 2 \sum_{m=1}^{\infty} C_m \cos(\pi m F / S_1) \right] \quad (7)$$

(see Weiss & Kiefer, 1983; Shmueli *et al.*, 1984), where, in the present case,

$$C_m = \frac{2}{\pi} \int_0^{\pi/2} \left[\prod_{j=1}^{N/4} J_0 \left(\frac{4\pi m f_j}{S_1} \cos \varphi \right) \right] d\varphi \equiv C \left(\frac{\pi m}{S_1} \right). \quad (8)$$

Observing that $P(F) = P(-F)$, we obtain the p.d.f. of $|F|$ by doubling the right-hand side of (7). Noting that

$$P(|E|) = \left(\sum_{j=1}^N f_j^2 \right)^{1/2} P(|F|) \quad (9)$$

(e.g. Shmueli & Wilson, 1981), we can finally express the p.d.f. of the normalized structure amplitude $|E|$ as

$$P(|E|) = \alpha \left[1 + 2 \sum_{m=1}^{\infty} C_m \cos(\pi m \alpha |E|) \right], \quad (10)$$

where

$$\alpha = \left(\sum_{j=1}^N f_j^2 \right)^{1/2} / \sum_{j=1}^N f_j \quad (11)$$

and the Fourier coefficients C_m are defined by (8). The functional form of (10), apart from the problem-dependent Fourier coefficients, is the same as that given by Shmueli *et al.* (1984) for the p.d.f. of $|E|$ in the space group $P\bar{1}$, in the absence of non-crystallographic symmetry.

It is interesting to note that one can readily derive the Rogers–Wilson (1953) distribution from (10) by assuming that all the atoms are of the same kind and the number of atoms in the unit cell is large. This calculation is given in Appendix A, where the corresponding reduction of the exact p.d.f. of $|E|$ for $P\bar{1}$, in the absence of non-crystallographic symmetry (Shmueli *et al.*, 1984), is also indicated.

In order to evaluate the p.d.f. in (10), the integrals in (8) (i.e. the Fourier coefficients) must be computed numerically. Since the integrand in (8) is a rather slowly varying function, any method of numerical integration appears to be adequate. We have tried the trapezoidal rule and Gaussian integration with nearly identical results. It is interesting to point out that, for large values of m , the Fourier coefficients turn out to be nearly proportional to $1/m$ and use can be made of closed expressions for sums of the type $\sum_k \cos(ky)/k$ (e.g. Gradshteyn & Ryzhik, 1980), in attaining precise results. The computations shown in the next section were carried out using a twelve-point Gaussian integration, with the $[0, \pi/2]$ interval subdivided into four parts. The use of 40 terms in (10) appears to be more than adequate for the purpose of comparison of theoretical with simulated semi-cumulative distributions (i.e. histograms) and has to be increased if the residual small oscillations, due to series-termination errors, are to be smoothed out. It must be pointed out, however, that the series-termination errors are independent of the heterogeneity of the asymmetric unit and their elimination is of aesthetic rather than practical importance.

Simulated distributions

The results obtained in the previous section have been applied to representative cases of a bicentric $P\bar{1}$ structure: (i) the equal-atom case, and (ii) an outstandingly heavy atom being present in the asymmetric subunit of the bicentric arrangement. For each case, 3000 magnitudes of $|E|$ have been simulated using (3) and were grouped into thirty equal ranges in the interval $0 < |E| < 3$, as described elsewhere (Shmueli, 1982*b*; Shmueli *et al.*, 1984). The resulting histograms represent cumulative distribution of the simulated $|E|$ values, and are compared in Fig. 1 with the asymptotic p.d.f. for the equal-atom case (Rogers & Wilson, 1953) and with (10), which takes into account any given atomic composition of the asymmetric subunit.

Both theoretical p.d.f.'s agree very well with the equal-atom histogram (Fig. 1*a*), as expected. The approximate coalescence of both theoretical p.d.f.'s is also not surprising in view of their equivalence in the equal-atom case and in the limit of large N (see Appendix).

Fig. 1*b* shows the result obtained for an asymmetric subunit of $P\bar{1}$, corresponding to the composition $C_{14}U$. The main effects of the heavy atom are a decreased origin peak, an enhanced probability for the occurrence of $|E|$ values in the intermediate range and a faster decrease of the probability for high $|E|$ values—when compared to the equal-atom case.

The discrepancies between the theoretical and simulated distributions are due to fluctuations that are inherent in a simulation by computer-generated random numbers, and in actual comparisons they are

expected to arise from the effects of finite sampling (cf. Shmueli *et al.*, 1984).

As in the absence of non-crystallographic symmetry (e.g. Shmueli & Wilson, 1981; Shmueli *et al.*, 1984), the presence of the heavy atom makes the distribution appear less 'centric'. However, whereas in the absence of non-crystallographic symmetry the distribution acquires definite 'acentric' features (e.g. Shmueli *et al.*, 1984), in the present case (Fig. 1*b*) the effect of the heavy atom on the departure from the Rogers-Wilson (1953) statistics is appreciably less prominent.

A quantitative comparison of the histograms with the two relevant theoretical p.d.f.'s is given in Table 1, in terms of χ^2 and R discrepancy criteria (cf. Shmueli *et al.*, 1984).

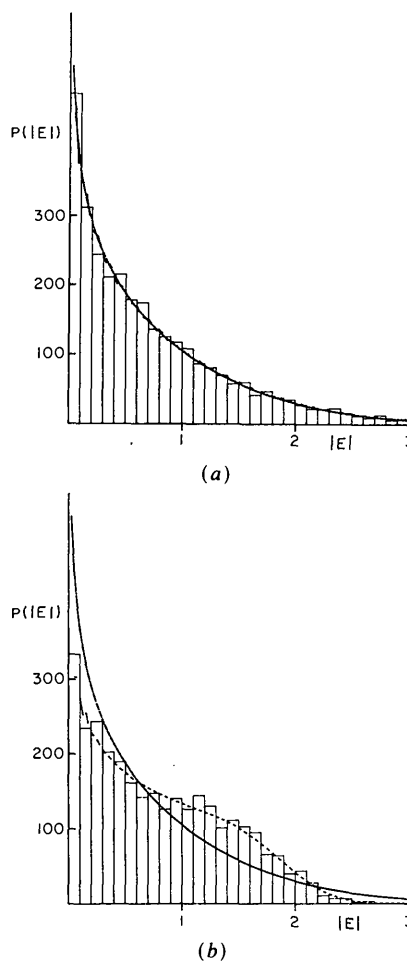


Fig. 1. Simulated and theoretical distributions of $|E|$. The theoretical p.d.f.'s given in the figure are scaled to the histograms. The solid lines denote the asymptotic bicentric p.d.f. (Rogers & Wilson, 1953) and the dashed lines correspond to the random-walk p.d.f., given by equation (10). The height of each rectangle equals the number of $|E|$ values that lie within the corresponding histogram channel. (a) The equal-atom case, with 15 atoms in the asymmetric subunit of $P\bar{1}$ ($N=60$). (b) A $C_{14}U$ asymmetric subunit in $P\bar{1}$ ($N=60$).

Table 1. *Discrepancy measures for comparison of simulated distributions with asymptotic and exact p.d.f.'s*

The assumed composition of the asymmetric subunit is $C_m X_p$, and the indicator of heterogeneity is denoted by $\rho = Z_X/Z_C$, where Z is the atomic number.

Discrepancy measures: R and χ^2 are defined by equations (20) and (21) of Shmueli *et al.* (1984). The subscripts on R and χ^2 are 10 or $\bar{1}$, according as the histogram is compared with equation (10) or the asymptotic bicentric p.d.f. (Rogers & Wilson, 1953), respectively. The effective number of channels that participated in the calculation of χ^2 is denoted by k_{10} or $K_{\bar{1}}$, the subscripts having the same meaning as for R and χ^2 above.

Simulated bicentric $P\bar{1}$ distributions:

m	p	ρ	χ_{10}^2	k_{10}	$\chi_{\bar{1}}^2$	$k_{\bar{1}}$	R_{10}	$R_{\bar{1}}$
14	1	1	17.8	30	17.0	30	0.067	0.068
14	1	15 $\frac{1}{3}$	27.1	26	381.6	30	0.086	0.274

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APPENDIX A

If we assume that all the atoms are of the same kind, the p.d.f.'s of $|E|$ for the space group $P\bar{1}$ have the form

$$P^{(k)}(|E|) = \frac{1}{N^{1/2}} \left[1 + 2 \sum_{m=1}^{\infty} C_m^{(k)} \cos(\pi m |E| / N^{1/2}) \right], \quad (A1)$$

where

$$C_m^{(1)} = J_0^{N/2}(2\pi m / N), \quad (A2)$$

in the absence of non-crystallographic symmetry (Shmueli *et al.*, 1984), and

$$C_m^{(2)} = \frac{2}{\pi} \int_0^{\pi/2} J_0^{N/4}[(4\pi m / N) \cos \varphi] d\varphi, \quad (A3)$$

in the bicentric $P\bar{1}$ case, discussed in the text.

In the limit of large N we can approximate the Bessel function in (A3) by

$$J_0[(4\pi m / N) \cos \varphi] \approx 1 - (4\pi^2 m^2 / N^2) \cos^2 \varphi \quad (A4)$$

so that

$$C_m^{(2)} \approx \frac{2}{\pi} \int_0^{\pi/2} \exp\{(N/4) \times \ln[1 - (4\pi^2 m^2 / N^2) \cos^2 \varphi]\} d\varphi \quad (A5)$$

$$\approx \frac{2}{\pi} \int_0^{\pi/2} \exp[-(\pi^2 m^2 / N) \cos^2 \varphi] d\varphi, \quad (A6)$$

where the corresponding expansion of the logarithm led from (A5) to (A6). Making use of the identity $\cos^2 \varphi = (1 + \cos 2\varphi)/2$, and of known integral representations of Bessel functions (*e.g.* Abramowitz & Stegun, 1972), we obtain

$$C_m^{(2)} \approx \exp(-\pi^2 m^2 / 2N) I_0(\pi^2 m^2 / 2N), \quad (A7)$$

where $I_0(x)$ is a Bessel function.

If we substitute (A7) in (A8) and approximate the sum by an integral by replacing the discrete $m/N^{1/2}$ by a continuous variable $y = m/N^{1/2}$, (A1) becomes (for $k=2$)

$$P^{(2)}(|E|) \approx 2 \int_0^{\infty} \exp(-\pi^2 y^2 / 2) I_0(\pi^2 y^2 / 2) \times \cos(\pi |E| y) dy. \quad (A8)$$

From the known definite integral

$$\int_0^{\infty} x^{-1/2} \exp(-x) I_0(x) \cos(4ax^{1/2}) dx = 1/(2\pi)^{1/2} \exp(-a^2) K_0(a^2), \quad (A9)$$

(Gradshteyn & Ryzhik, 1980), (A1) becomes, for $k=2$,

$$P^{(2)}(|E|) \approx \frac{1}{\pi^{3/2}} \exp(-|E|^2 / 8) K_0(|E|^2 / 8), \quad (A10)$$

where $K_0(x)$ is a Bessel function. Equation (A10) is just the central limit theorem approximation derived by Rogers & Wilson (1953) for the bicentric distribution.

It can also be shown by similar methods that (A1), with the Fourier coefficient given by (A2), reduces in the limit of large N to

$$P^{(1)}(|E|) \approx \left(\frac{2}{\pi}\right)^{1/2} \exp(-|E|^2 / 2), \quad (A11)$$

which is the well known Wilson (1949) p.d.f. of $|E|$ for the centrosymmetric case, in the absence of non-crystallographic symmetry.

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Symmetries in Texture Analysis

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Abstract

It is shown that a comprehensive symmetry description in polycrystalline bodies needs black-white point groups rather than the usual (one-colour) groups that are sufficient for single crystals.

1. Introduction

Crystalline solids such as metals, ceramics or natural rocks usually exhibit a polycrystalline structure, *i.e.* they consist of small crystallites of the same crystal structure but with different orientations of their crystallographic axes. The orientation distribution of the crystallites is called the *texture* of the materials. If all crystal orientations are equally frequent, the material is then said to be macroscopically isotropic, *i.e.* its properties are the same in all directions. If, however, different orientations are present with different relative frequencies, the anisotropies of the crystallites will, in general, not cancel each other and the material will be macroscopically anisotropic, *i.e.* its physical properties will be different when measured in different sample directions. In the latter case, symmetries may be observed in the directional dependence of the properties according to the specific features of the orientation distribution function. This type of symmetry has been called *sample symmetry* and it should be kept distinct from crystal symmetry. The sample symmetry in rolled metal sheets, for example, is determined by the symmetry of the production process, *i.e.* the geometry of the roll gap by which the material

has been shaped. This is an orthorhombic symmetry and the same *type* of symmetry is found in materials with different crystal structure and crystal symmetry, *e.g.* in cubic, hexagonal, tetragonal metals. (The details of the orientation distribution of the crystallites are, of course, different in these cases whereas the type of sample symmetry is the same.)

The purpose of this paper is to show that sample symmetries in polycrystalline materials can arise in two different ways, either by one-to-one relations between individual crystal orientations (conventional symmetry operations) or by certain integral relations taken over a continuous manifold of orientations (non-conventional symmetry operations). The non-conventional symmetry operations can occur in addition to the conventional ones, thus requiring an extension of the conventional point-symmetry groups for polycrystals (Bunge, Esling & Muller, 1980). The most efficient description of this extension is that of black-white groups considered for the first time by Heesch (1930), Shubnikov (1951) and Niggli & Wondratschek (1960).

It should be mentioned that black-white symmetries have been considered in connection with textures by Shubnikov (1958), Shubnikov, Sheludev, Konstantinova & Silvestrova (1958), Shubnikov & Belov (1964), but in a completely different sense. In these cases crystals having an additional black-white property were considered, whereas in the present paper the black-white notation is being used in order to describe certain properties of the orientation distribution of single-coloured crystals. A comprehensive