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Exact Random-Walk Models in Crystallographic Statistics. VI. P.D.F.'s of $|E|$ for All Plane Groups and Most Space Groups*

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Abstract

An exact calculation of the probability density function (p.d.f.) of $|E|$, the magnitude of the normalized structure factor, can be developed in terms of Fourier and Fourier-Bessel series whose coefficients can be expressed in terms of the characteristic function. This article provides the formulae for atomic contributions to such characteristic functions. The results presented in this study are applicable to all the plane groups and to 206 three-dimensional space groups. Only the space groups isomorphous to the cubic point groups 432, $\bar{4}3m$ and $m\bar{3}m$ were omitted due to the complexity of the resulting expressions and the small deviations of the corresponding densities from the central-limit-theorem approximation, which have been observed in simulations for extreme atomic heterogeneities. Representative derivations illustrating the problems and techniques of their solution are provided. All the theoretical results have been computed numerically and compared with simulated distributions. Some results of these computations are illustrated in the accompanying paper, Part VII of this series [Rabinovich, Shmueli, Stein, Shashua & Weiss (1991). *Acta Cryst.* A47, 336-340].

Introduction

The existing probability density functions (p.d.f.'s) and other statistics of the magnitude $|E|$ of the normalized structure factor, which depend on the atomic composition and the space-group symmetry, can be classified in two groups. The older one comprises approximate Gram-Charlier and Edgeworth expansions (*e.g.* Shmueli & Wilson, 1981; Shmueli, 1982), based on exact moments of the structure factor (Wilson, 1978; Shmueli & Kaldor, 1981, 1983) and ideal centric and acentric p.d.f.'s (Wilson, 1949). More recent developments, which led to exact representations of the p.d.f.'s and in many cases allow for feasible numerical calculations, are the Fourier and Fourier-Bessel series for the p.d.f.'s of $|E|$ (*e.g.* Shmueli, Weiss, Kiefer & Wilson, 1984; Shmueli & Weiss, 1987, 1988). However, while the approximate expressions are available for all the three-dimensional space groups, the latter exact formulations have been worked out for a small number of space groups of low symmetry only. While it is true that deviations from the popular central-limit-theorem approximation are greatest for the lowest symmetries, the presence of very significant deviations in space groups of higher symmetry has been established from an examination of the properties of exact moments (Shmueli & Wilson, 1981) as well as from recent simulations. These considerations suggest the utility of having expressions for the characteristic functions for all the space groups. Moreover, statistics of projection data have been limited to the relevant moments of normalized intensity (Foster & Hargreaves, 1963) and, in a more comprehensive study, to moments of trigonometric structure factors (Shmueli & Kaldor, 1983). The corresponding Fourier or Fourier-Bessel series for the p.d.f.'s of the plane groups have not been calculated. It is desirable to do so since these formulations can cope with departures from ideal behaviour that are inaccessible to treatment by the older approximate methods. The study of plane groups also appeared most useful to us as it enables one to discriminate between several non-centrosymmetric space groups with equivalent three-dimensional statistics by making use of projection data.

The purpose of this paper is to present the results obtained for the characteristic functions for all the plane groups and the three-dimensional space groups except those based on the three highest cubic point groups. The next section summarizes the general expressions for the p.d.f.'s and refers the reader to the tables of characteristic functions for the symmetries treated here. Some representative derivations are presented in Appendices *A*, *B* and *C*.

* Part V: Shmueli, Rabinovich & Weiss (1990).

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Results

The normalized structure factor is given, in general, by

$$E(\mathbf{h}) = \sum_j n_j[\xi_j(\mathbf{h}) + i\eta_j(\mathbf{h})] = A + iB, \quad (1)$$

where ξ and η are symmetry-dependent trigonometric structure factors. On making the assumption that atomic contributions to the structure factor are independent, one can express the characteristic function of $E(\mathbf{h})$ as

$$C(\omega_1, \omega_2) = \langle \exp[i(\omega_1 A + \omega_2 B)] \rangle = \prod_j \langle \exp\{i[\omega_1 \xi_j(\mathbf{h}) + \omega_2 \eta_j(\mathbf{h})]\} \rangle. \quad (2)$$

The average in (2) is evaluated under the assumption that the arguments of the trigonometric functions involved are uniformly distributed in the interval $[0, 2\pi]$. The present derivation is confined to the case of all the atoms being located in general positions and to general reflections. Anomalous-scattering effects are neglected and we will assume that no non-crystallographic symmetry affects the p.d.f.'s.

Shmueli & Weiss (1987) have shown that the Fourier coefficients of the p.d.f. of $|E|$ are just values of the characteristic function at points related to summation indices and that the p.d.f. takes the form

$$p(|E|) = \tfrac{1}{2}\pi\alpha^2|E| \sum_u \sum_v C(\pi\alpha u, \pi\alpha v) \times J_0[\pi\alpha|E|(u^2+v^2)^{1/2}] \quad (3)$$

for non-centrosymmetric space groups and

$$p(|E|) = \alpha\left\{1 + 2\sum_{u=1}^{\infty} C(\pi\alpha u)\cos(\pi u\alpha|E|)\right\} \quad (4)$$

for the centrosymmetric ones, where the transform variables ω_1 and ω_2 of the characteristic function have been replaced by their Fourier-series equivalents $\pi\alpha u$ and $\pi\alpha v$ respectively. Symmetry-dependent numerical coefficients are omitted from (3) and (4). The quantity α in (3) and (4) is the reciprocal of the maximum value of $|E|$ and is given by

$$\alpha^{-1} = \sum_{j=1}^{N} n_j \quad \text{and} \quad n_j = f_j/\Sigma^{1/2}, \quad \text{with } \Sigma = \sum_{j=1}^{N} f_j^2, \quad (5)$$

where f_j is an atomic scattering factor. If the Fourier coefficient depends on $(u^2+v^2)^{1/2}$ rather than on u and v separately, it is possible to write the p.d.f. for non-centrosymmetric space groups as a single Fourier-Bessel series rather than the double Fourier series (3) (Shmueli & Weiss, 1987). The Fourier-Bessel p.d.f. is given by

$$p(|E|) = 2\alpha^2|E| \sum_{u=1}^{\infty} D_u J_0(\alpha\gamma_u|E|), \quad (6)$$

with

$$D_u = [J_1^2(\gamma_u)]^{-1} C(\alpha\gamma_u), \quad (7)$$

where $J_1(x)$ is the Bessel function of the first kind, of the first order, γ_u is the uth root of the equation $J_0(x) = 0$ [the uth zero of $J_0(x)$] and $C(\alpha\gamma_u)$ is the value of the characteristic function corresponding to the uth term of the series.

All that is needed in order to derive the Fourier or Fourier-Bessel p.d.f. of $|E|$ for a given space group is the corresponding characteristic function, and the latter requires one's ability to obtain a manageable expression for the average in (2). The calculation of these averages is straightforward in most space groups of low symmetry (see *e.g.* Appendix *A* of Shmueli & Weiss, 1987) but may become somewhat involved in cases of higher symmetry. One class of problems that we tackle is of a strictly computational nature, *e.g.* how to transform a given expression into one with more favourable convergence properties. We illustrate this in Appendix *A* by the derivation of the characteristic function for the space group *P*4. Another problem to be addressed is that of the dependence of the arguments of the trigonometric functions that make up the trigonometric structure factor. This problem occurs in most groups of the hexagonal family and the question is how should this dependence be treated. Appendix *B* illustrates this issue by presenting two methods for deriving the characteristic function for the plane group *p*3: a direct one and one obtained using the Dirac delta distribution. It appears that the above direct method is preferable for cases of low algebraic complexity [such as, for example, our study of the three-phase invariant (Shmueli, Rabinovich & Weiss, 1989)] and the δ-function approach is advantageous when more complex expressions are to be analyzed. A routine application of the δ function to our work is illustrated by the derivation in Appendix *C*.

Atomic characteristic functions for the 17 plane groups are given in Table 1 and those for the 206 space groups - collected in 69 classes - are shown in Table 2. The present subdivision of the space groups is the same as that used by Shmueli & Kaldor (1981, 1983) in their study of moments of the trigonometric structure factors. The functions are given in the tables in terms of Bessel functions or related functions explicitly defined in the caption to Table 1 and the footnote that accompanies Table 2. All of the atomic characteristic functions shown in Table 2 can be reduced to real quantities either because the imaginary parts do not appear in the first place or because they vanish upon integration. The integration ranges shown in the footnote to Table 2 refer to the (relevant) real parts of the atomic contributions only. This is not the case for the last four functions shown in Table 1. The Fourier coefficients for hexagonal plane-group p.d.f.'s can be calculated in terms of the real part of a product of complex atomic contributions. The p.d.f.'s to be employed are chosen in the following manner. If the space group is

Table 1. *Atomic characteristic functions for the 17 plane groups*

The table shows the number, g, of asymmetric units in the unit cell of the plane group indicated and the atomic contributions to characteristic functions of E.

The atomic characteristic functions for the last four plane groups in the table are given in terms of the function

$$P_j(a,\rho)=\sum_{k=-\infty}^{\infty}\exp(3ik\rho)J_k^3(an_j).$$

The atomic characteristic functions are real and even, *i.e.* $C(-\omega_1,\omega_2)=C(\omega_1,-\omega_2)=C(\omega_1,\omega_2)=C(-\omega_1,-\omega_2)$ and $C(-\omega_1)=C(\omega_1)$, except those in the last four lines in the table. The real parts of $P(\omega_1,\omega_2)$ and $P(\omega_1)$ are even while the imaginary ones are odd.

Plane group(s)	g	Atomic characteristic function
$p1$	1	$J_0(\omega n_j)$
$p2$	2	$J_0(2\omega_1 n_j)$
pm, pg	2	$J_0^2(\omega_{n_j})$
cm	4	$J_0^2(2\omega n_j)$
$pmm, pmg, pgg, p4$	4	$J_0^2(2\omega_1 n_j)$
cmm	8	$J_0^2(4\omega_1 n_j)$
$p4m, p4g$	8	$J_0^4(2\omega n_j)$
$p3$	3	$P_j(\omega,\Delta)$
$p3m1, p31m$	6	$P_j^2(\omega,\Delta)$
$p6$	6	$P_j(2\omega_1,\pi/2)$
$p6m$	12	$P_j^2(2\omega_1,\pi/2)$

centrosymmetric (*i.e.* the atomic characteristic function depends only on a single Fourier transform variable, ω_1), (4) is to be used. The p.d.f. of $|E|$ can be computed from (3) for any non-centrosymmetric space group; however, the more expedient Fourier–Bessel series (6) can be used when the atomic characteristic function depends on $\omega\equiv(\omega_1^2+\omega_2^2)^{1/2}$ alone. A convenient algorithm for the computation of the required roots of $J_0(x)$ is given by Shmueli *et al.* (1984). Thus, the double Fourier summation (3) *must* be used only if the atomic characteristic function depends on both ω and $\Delta=\tan^{-1}(\omega_1/\omega_2)$.

Generalizations of the present results, in which effects of dispersion and some kinds of non-crystallographic symmetry are accounted for can be treated along the lines of the work of Shmueli, Rabinovich & Weiss (1990).

All of the p.d.f.'s based on the characteristic functions shown in Table 2, and the hexagonal ones in Table 1, were computed numerically and are compared with the corresponding simulated distribution of $|E|$ and the p.d.f.'s based on Wilson (1949) statistics in the following article (Rabinovich, Shmueli, Stein, Shashua & Weiss, 1991). It will suffice to point out here that all these Fourier and Fourier–Bessel series p.d.f.'s converge well and display significant deviations from the ideal behaviour for many space groups of higher symmetry.

Preliminary examinations of some of the last 24 cubic space groups, which we have not included in

Table 2. *Atomic characteristic functions for the p.d.f. of E, for most three-dimensional space groups.*

The table lists the expressions for the atomic characteristic functions, corresponding to the p.d.f. of E, for all the space groups except those based on the cubic point groups 432, $\bar{4}3m$ and $m\bar{3}m$. The column labelled Space group(s) gives the symbols of space groups or sets of statistically equivalent space groups and the associated point groups; the second column, g, contains the number of asymmetric units in the unit cell for the symmetry indicated; the third column, labelled Atomic characteristic functions lists the expressions for the atomic characteristic functions in symbolic form, explicitly defined in the footnote section of the table. The last column, Remarks, lists the parities of reflection classes, for which different expressions of the atomic characteristic functions are obtained.

Space group(s)	g	Atomic characteristic functions	Remarks
Point group: 1			
$P1$	1	$J_0(\omega n_j)$	
Point group: $\bar{1}$			
$P\bar{1}$	2	$J_0(2\omega_1 n_j)$	
Point groups: 2, m			
All P	2	$J_0^2(\omega n_j)$	
All C	4	$J_0^2(2\omega n_j)$	
Point group: $2/m$			
All P	4	$J_0^2(2\omega_1 n_j)$	
All C	8	$J_0^2(4\omega_1 n_j)$	
Point group: 222			
All P	4	$L_j(\omega,\Delta)^{(a)}$	
All C and I	8	$L_j(2\omega,\Delta)$	
$F222$	16	$L_j(4\omega,\Delta)$	
Point group: $mm2$			
All P	4	$L_j(\omega,0)$	
All A, C and I	8	$L_j(2\omega,0)$	
$Fmm2$	16	$L_j(4\omega,0)$	
$Fdd2$	16	$L_j(4\omega,0)$	$h+k+l=2n$
	16	$L_j(4\omega,\pi/4)$	$h+k+l=2n+1$
Point group: mmm			
All P	8	$L_j(2\omega_1,0)$	
All C and I	16	$L_j(4\omega_1,0)$	
$Fmmm$	32	$L_j(8\omega_1,0)$	
$Fddd$	32	$L_j(8\omega_1,0)$	$h+k+l=2n$
	32	$L_j(8\omega_1,\pi/4)$	$h+k+l=2n+1$
Point group: 4			
$P4$, $P4_2$	4	$L_j(\omega,0)$	
$P4_1^*$	4	$L_j(\omega,0)$	$l=2n$
	4	$L_j(\omega,\pi/4)$	$l=2n+1$
$I4$	8	$L_j(2\omega,0)$	
$I4_1$	8	$L_j(2\omega,0)$	$2h+l=2n$
	8	$L_j(2\omega,\pi/4)$	$2h+l=2n+1$
Point group: $\bar{4}$			
$P\bar{4}$	4	$L_j(\omega,\Delta)$	
$I\bar{4}$	8	$L_j(2\omega,\Delta)$	
Point group: $4/m$			
All P	8	$L_j(2\omega_1,0)$	
$I4/m$	16	$L_j(4\omega_1,0)$	
$I4_1/a$	16	$L_j(4\omega_1,0)$	$l=2n$
	16	$L_j(4\omega_1,\pi/4)$	$l=2n+1$

Table 2 (*cont.*)

Space group(s)	g	Atomic characteristic functions	Remarks
Point group: 422			
$P422$, $P42_12$, $P4_222$ and $P4_22_12$	8	$Q_j^{(1)}(\omega, \Delta)^{(b)}$	
$P4_122$,* $P4_12_12$*	8	$Q_j^{(1)}(\omega, \Delta)$	$l = 2n$
	8	$Q_j^{(2)}(\omega, \Delta)^{(c)}$	$l = 2n+1$
$I422$	16	$Q_j^{(1)}(2\omega, \Delta)$	
$I4_122$	16	$Q_j^{(1)}(2\omega, \Delta)$	$2k+l = 2n$
	16	$Q_j^{(2)}(2\omega, \Delta)$	$2k+l = 2n+1$
Point group: $4mm$			
All P	8	$Q_j^{(1)}(\omega, 0)$	
$I4mm$, $I4cm$	16	$Q_j^{(1)}(2\omega, 0)$	
$I4_1md$, $I4_1cd$	16	$Q_j^{(1)}(2\omega, 0)$	$2k+l = 2n$
	16	$Q_j^{(1)}(2\omega, \pi/4)$	$2k+l = 2n+1$
Point groups: $\bar{4}2m$, $\bar{4}m2$			
All P	8	$Q_j^{(1)}(\omega, \Delta)$	
$I\bar{4}2m$, $I\bar{4}m2$, $I\bar{4}c2$	16	$Q_j^{(1)}(2\omega, \Delta)$	
$I\bar{4}2d$	16	$Q_j^{(1)}(2\omega, \Delta)$	$2h+l = 2n$
	16	$Q_j^{(2)}(2\omega, \Delta)$	$2h+l = 2n+1$
Point group: $4/mmm$			
All P	16	$Q_j^{(1)}(2\omega_1, 0)$	
$I4/mmm$, $I4/mcm$	32	$Q_j^{(1)}(4\omega_1, 0)$	
$I4_1/amd$, $I4_1/acd$	32	$Q_j^{(1)}(4\omega_1, 0)$	$l = 2n$
	32	$Q_j^{(1)}(4\omega_1, \pi/4)$	$l = 2n+1$
Point group: 3			
All P and R	3	$J_0^3(\omega n_j)$	
Point group: $\bar{3}$			
All P and R	6	$J_0^3(2\omega_1 n_j)$	
Point group: 32			
All P and R	6	$T_j(\omega, \Delta)^{(d)}$	
Point group: $3m$			
P3m1, P31m, R3m	6	$T_j(\omega, \pi/2)$	
$P3c1$, $P31c$, $R3c$	6	$T_j(\omega, \pi/2)$	$l = 2n(P)$, h+k+l = 2n(R)
	6	$T_j(\omega, 0)$	$l = 2n+1(P)$, h+k+l = 2n+1(R)
Point group: $\bar{3}m$			
$P\bar{3}m1$, $P\bar{3}1m$, $R\bar{3}m$	12	$T_j(2\omega_1, \pi/2)$	
$P\bar{3}c1$, $P\bar{3}1c$, $R\bar{3}c$	12	$T_j(2\omega_1, \pi/2)$	$l = 2n(P)$, h+k+l = 2n(R)
	12	$T_j(2\omega_1, 0)$	$l = 2n+1(P)$, h+k+l = 2n+1(R)
Point group: 6			
$P6$	6	$H_j^{(1)}(\omega, \pi/2)^{(e)}$	
$P6_1^*$	6	$H_j^{(1)}(\omega, \pi/2)$	$l = 6n$
	6	$H_j^{(2)}(\omega, 0)^{(f)}$	$l = 6n+1, 6n+5$
	6	$H_j^{(2)}(\omega, \pi/2)$	$l = 6n+2, 6n+4$
	6	$H_j^{(1)}(\omega, 0)$	$l = 6n+3$
$P6_2^*$	6	$H_j^{(1)}(\omega, \pi/2)$	$l = 3n$
	6	$H_j^{(2)}(\omega, \pi/2)$	$l = 3n \pm 1$
$P6_3$	6	$H_j^{(1)}(\omega, \pi/2)$	$l = 2n$
	6	$H_j^{(1)}(\omega, 0)$	$l = 2n+1$
Point group: $\bar{6}$			
$P\bar{6}$	6	$\tilde{H}_j^{(1)}(\omega, \Delta)$	
Point group: $6/m$			
$P6/m$	12	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2)$	
$P6_3/m$	12	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(2\omega_1, 0)$	$l = 2n+1$
Point group: 622			
$P622$	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, -\pi/2, \Delta)^{(g)}$	
$P6_122$*	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, -\pi/2, \Delta)$	$l = 6n$
	12	$\tilde{H}_j^{(2)}(\omega, 0, 0, \Delta)^{(h)}$	$l = 6n+1, 6n+5$
	12	$\tilde{H}_j^{(2)}(\omega, \pi/2, \pi/2, \Delta)$	$l = 6n+2, 6n+4$
	12	$\tilde{H}_j^{(1)}(\omega, 0, 0, \Delta)$	$l = 6n+3$
$P6_222$*	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, -\pi/2, \Delta)$	$l = 3n$
	12	$\tilde{H}_j^{(2)}(\omega, \pi/2, \pi/2, \Delta)$	$l = 3n \pm 1$
$P6_322$	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, -\pi/2, \Delta)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(\omega, 0, 0, \Delta)$	$l = 2n+1$
Point group: $6mm$			
$P6mm$	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, \pi/2, 0)$	
$P6cc$	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, -\pi/2, 0)$	$l = 2n+1$
$P6_3cm$, $P6_3mc$	12	$\tilde{H}_j^{(1)}(\omega, \pi/2, \pi/2, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(\omega, 0, 0, 0)$	$l = 2n+1$
Point groups: $\bar{6}2m$, $\bar{6}m2$			
$P\bar{6}2m$, $P\bar{6}m2$	12	$\tilde{H}_j^{(1)}(\omega, \Delta, \Delta, 0)$	
$P\bar{6}2c$, $P\bar{6}c2$	12	$\tilde{H}_j^{(1)}(\omega, \Delta, \Delta, 0)$	$l = 2n$
	12	$\tilde{H}_j^{(1)}(\omega, \Delta+\pi/2, -\Delta-\pi/2, 0)$	$l = 2n+1$
Point group: $6/mmm$			
$P6/mmm$	24	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2, \pi/2, 0)$	
$P6/mcc$	24	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2, -\pi/2, 0)$	$l = 2n+1$
$P6_3/mcm$, $P6_3/mmc$	24	$\tilde{H}_j^{(1)}(2\omega_1, \pi/2, \pi/2, 0)$	$l = 2n$
	24	$\tilde{H}_j^{(1)}(2\omega_1, 0, 0, 0)$	$l = 2n+1$
Point group: 23			
$P23$, $P2_13$	12	$L_j^3(\omega, \Delta)$	
$I23$, $I2_13$	24	$L_j^3(2\omega, \Delta)$	
$F23$	48	$L_j^3(4\omega, \Delta)$	
Point group: $m\bar{3}$			
$Pm\bar{3}$, $Pn\bar{3}$, $Pa\bar{3}$	24	$L_j^3(2\omega_1, 0)$	
$Im\bar{3}$, $Ia\bar{3}$	48	$L_j^3(4\omega_1, 0)$	
$Fm\bar{3}$	96	$L_j^3(8\omega_1, 0)$	
$Fd\bar{3}$	96	$L_j^3(8\omega_1, 0)$	$h+k+l = 2n$
	96	$L_j^3(8\omega_1, \pi/4)$	$h+k+l = 2n+1$

Definitions of atomic characteristic functions

The definitions of all the symbols used in Table 2 are summarized below. The transform variables of the atomic characteristic function are ω_1 for centrosymmetric space groups and $\omega \equiv (\omega_1^2+\omega_2^2)^{1/2}$, $\Delta \equiv \arctan(\omega_1/\omega_2)$ for the non-centrosymmetric ones. The following abbreviations are used in the subsequent definitions of the symbols:

$s_+ = 2an_j \sin(\varphi \pm \rho)$, $c_+ = 2an_j \cos(\varphi \pm \rho)$ and $\sigma_\pm = 2an_j \sin(\varphi \pm 2\pi/3 + \rho)$.

(*a*) $L_l(a, \rho) = \langle J_0(s_+)J_0(s_-)\rangle_\varphi$

$$= \sum_{k=-\infty}^{\infty} \cos(4k\rho) J_k^4(an_j)$$

$$= J_0^4(an_j) + 2\sum_{k=1}^{\infty} \cos(4k\rho) J_k^4(an_j).$$

Table 2 (*cont.*)

Definitions of atomic characteristic functions

(*b*) $Q_j^{(1)}(a,\rho)=\langle J_0^2(s_+)J_0^2(s_-)\rangle_\varphi$.

(*c*) $Q_j^{(2)}(a,\rho)=\langle J_0(c_+)J_0(s_-)J_0(c_+)J_0(c_-)\rangle_\varphi$.

(*d*) $T_j(a,\rho)=\sum_{k=-\infty}^{\infty}\exp(6ik\rho)J_k^6(an_j)$

$=J_0^6(an_j)+2\sum_{k=1}^{\infty}\cos(6k\rho)J_k^6(an_j)$

(*e*) $H_j^{(1)}(a,\mu)=\langle\mathrm{Re}[S_j^{(1)}(\varphi;a,\mu,0)]\rangle_\varphi$.

(*f*) $H_j^{(2)}(a,\mu)=\langle\mathrm{Re}[S_j^{(2)}(\varphi;a,\mu\,0)]\rangle_\varphi$.

(*g*) $\tilde{H}_j^{(1)}(a,\mu_1,\mu_2,\rho)=\langle\mathrm{Re}[S_j^{(1)}(\varphi;a,\mu_1,\rho)S_j^{(1)}(\varphi;a,\mu_2,-\rho)]\rangle_\varphi$.

(*h*) $\tilde{H}_j^{(2)}(a,\mu_1,\mu_2,\rho)=\langle\mathrm{Re}[S_j^{(2)}(\varphi;a,\mu_1,\rho)S_j^{(2)}(\varphi;a,\mu_2,-\rho)]\rangle_\varphi$.

where

$$S_j^{(1)}(\varphi;a,\mu\rho)=\sum_{k=-\infty}^{\infty}\exp(3ik\mu)J_k^3(s_+)$$

and

$$S_j^{(2)}(\varphi;a,\mu,\rho)=\sum_{k=-\infty}^{\infty}\exp(3ik\mu)J_k(s_+)J_k(\sigma_+)J_k(\sigma_-).$$

All the atomic characteristic functions, derived in this work, can be reduced to real quantities. The following symmetry relations hold: $C_j(\omega_1,\omega_2)=C_j(-\omega_1,\omega_2)=C_j(\omega_1,-\omega_2)=C_j(-\omega_1,-\omega_2)$ for the non-centrosymmetric groups, for which double Fourier series have to be computed, and $C_j(\omega_1)=C_j(-\omega_1)$ for the centrosymmetric ones. In most, but not all, cases, $C_j(\omega_1,0)$ and $C_j(0,\omega_2)$ are also equivalent.

The averages appearing in the above summary are, in general, computed as $\langle f(\varphi)\rangle_\varphi=(2/\pi)\int_0^{\pi/2}f(\varphi)\,\mathrm{d}\varphi$, except $H_j^{(2)}$ and $\tilde{H}_j^{(2)}$ which are computed as $(3/\pi)\int_0^{\pi/3}f(\varphi)\,\mathrm{d}\varphi$, where $f(\varphi)$ is any of the atomic functions indicated above.

* And the enantiomorphous space group.

this paper, led to highly unwieldy expressions. Before considering whether their detailed study by the Fourier method is indeed worthwhile we decided to simulate the corresponding distributions of $|E|$ and compare the simulations with the ideal Wilson (1949) p.d.f.'s. The computations were performed for a model asymmetric unit containing 14 C atoms and one U atom, *i.e.* for a strongly heterogeneous composition. The results indicate that the distributions of $|E|$ for most cubic space groups are insensitive to atomic heterogeneity. Even in those few cases where deviations from ideal behaviour are significant they are not likely to give rise to misleading indications of the Wilson (1949) p.d.f.'s when applied to highly heterogeneous cubic crystals with all the atoms in general positions. This is further discussed elsewhere (Rabinovich *et al.*, 1991).

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APPENDIX *A*

Derivation of the characteristic function for the space group *P*4

This derivation illustrates techniques and results used to derive the characteristic functions for some space groups of orthorhombic and tetragonal systems in addition to the cubic ones for which results have been obtained. The normalized structure factor for *P*4 is given by $E=A+iB$, where

$$A=4\sum_{j=1}^{N/4}n_j\cos\varphi_j\cos\lambda_j\cos\mu_j$$

and (*A*.1)

$$B=4\sum_{j=1}^{N/4}n_j\sin\varphi_j\cos\lambda_j\cos\mu_j,$$

where

$$\lambda_j=\pi[(h-k)x_j+(h+k)y_j],$$

$$\mu_j=\pi[(h+k)x_j-(h-k)y_j]\quad\text{and}\quad\varphi_j=2\pi lz_j \quad (A.2)$$

(*International Tables for X-ray Crystallography*, 1965). If we make use of the assumptions outlined earlier the characteristic function, formally defined as $C(\omega_1,\omega_2)=\langle\exp[i(\omega_1A+\omega_2B)]\rangle$, can be written

$$C(\omega,\Delta)=\prod_{j=1}^{N/4}\left\{[1/(2\pi)^3]\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\mathrm{d}\varphi\,\mathrm{d}\lambda\,\mathrm{d}\mu\right.$$
$$\left.\times\exp[4in_j\omega\sin(\varphi+\Delta)\cos\lambda\cos\mu]\right\}, \quad (A.3)$$

where $\omega=(\omega_1^2+\omega_2^2)^{1/2}$ and $\Delta=\tan^{-1}(\omega_1/\omega_2)$. The phase Δ can be eliminated by a change of the φ variable. If we now make use of the integral representation of the Bessel function $J_0(x)$,

$$J_0(x)=(1/2\pi)\int_{-\pi}^{\pi}\exp(ix\sin\beta)\,\mathrm{d}\beta$$

(Gradshteyn & Ryzhik, 1980; 8.411-1) and the known definite integral

$$\int_0^{\pi}J_0(2z\cos x)\cos(2nx)\,\mathrm{d}x=(-1)^n\pi J_0^2(z)$$

(Gradshteyn & Ryzhik, 1980; 6.681-5), we can reduce (*A*.3) to

$$C(\omega)=\prod_{j=1}^{N/4}\left\{(1/2\pi)\int_{-\pi}^{\pi}\mathrm{d}\mu\,J_0^2(2n_j\omega\cos\mu)\right\}$$
$$=\prod_{j=1}^{N/4}\left\{(1/2\pi)\int_{-\pi}^{\pi}\mathrm{d}\mu\,J_0^2(2n_j\omega\sin\mu)\right\}. \quad (A.4)$$

The integral in (*A*.4) can be evaluated numerically but it is possible, and far more efficient, to convert it into a series which converges quickly. This can be

done by means of the expansion

$$J_0(z\sin\beta)=\sum_{k=-\infty}^{\infty}J_k^2(z/2)\exp(ik\beta),\quad (A.5)$$

which is a special case of the addition theorem for Bessel functions (Gradshteyn & Ryzhik, 1980; 8.531-3), as follows

$$\begin{aligned}(1/2\pi)&\int_{-\pi}^{\pi}d\mu\,J_0^2(2n_j\omega\sin\mu)\\&=\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}J_k^2(n_j\omega)J_l^2(n_j\omega)\\&\quad\times\left\{(1/2\pi)\int_{-\pi}^{\pi}\exp[i(k+l)\mu]\,d\mu\right\}\\&=\sum_{k=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}J_k^2(n_j\omega)J_l^2(n_j\omega)\delta_{k,-l},\end{aligned}\quad (A.6)$$

where $\delta_{k,-l}$, the Kronecker delta, equals 0 or 1 according as $k\neq -l$ or $k=-l$, respectively, with the consequence that

$$C(\omega)=\sum_{k=-\infty}^{\infty}J_k^4(n_j\omega)=J_0^4(n_j\omega)+2\sum_{k=1}^{\infty}J_k^4(n_j\omega).\quad (A.7)$$

Only the first few terms of the series in (*A*.7) are required for most practical purposes. An asymptotic approximation to the integral in (*A*.4) also exists (Stoyanov & Farrell, 1987) but its usefulness is limited to large values of the argument, *i.e.* to terms in the Fourier or Fourier-Bessel series with large summation indices. We made no use of it in this study.

APPENDIX *B*

Derivation of the characteristic function for the plane group *p*3

This derivation illustrates much of the methodology used in the derivations of characteristic functions for plane groups and space groups containing a unique threefold or sixfold axis. The normalized structure factor for *p*3 is given by $E=A+iB$, where

$$A=\sum_{j=1}^{N/3}n_j\sum_{k=1}^{3}\cos\mu_{jk}\quad\text{and}\quad B=\sum_{j=1}^{N/3}n_j\sum_{k=1}^{3}\sin\mu_{jk}\quad (B.1)$$

with

$$\mu_{j1}=2\pi(hx_j+ky_j),\quad \mu_{j2}=2\pi(kx_j+iy_j)\quad\text{and}\quad \mu_{j3}=2\pi(ix_j+hy_j),\quad (B.2)$$

where $i=-h-k$ (*International Tables for X-ray Crystallography*, 1965). Note that only two of the μ's can be independent and the remaining one is found from the relation $\mu_{j1}+\mu_{j2}+\mu_{j3}=0$.

If we make use of our earlier assumptions, the characteristic function can be written

$$C(\omega_1,\omega_2)=\langle\exp[i(\omega_1A+\omega_2B)]\rangle\quad (B.3)$$

$$=\prod_{j=1}^{N/3}\left\langle\exp\left\{in_j\sum_{k=1}^{3}(\omega_1\cos\mu_{jk}+\omega_2\sin\mu_{jk}\right\}\right\rangle,\quad (B.4)$$

where use has been made of the assumption of independence of the atomic contributions. If we set $\omega_1=\omega\sin\Delta$ and $\omega_2=\omega\cos\Delta$, so that $\tan\Delta=\omega_1/\omega_2$ and $\omega=(\omega_1^2+\omega_2^2)^{1/2}$, we obtain

$$C(\omega,\Delta)=\prod_{j=1}^{N/3}\left\langle\exp\left\{in_j\omega\sum_{k=1}^{3}(\sin\Delta\cos\mu_{jk}+\cos\Delta\sin\mu_{jk})\right\}\right\rangle\quad (B.5)$$

$$=\prod_{j=1}^{N/3}\left\langle\exp\left\{in_j\omega\sum_{k=1}^{3}\sin(\mu_{jk}+\Delta)\right\}\right\rangle\equiv\prod_{j=1}^{N/3}C_j(\omega,\Delta).\quad (B.6)$$

The assumption of uniform distribution of the atomic phase factors allows us to rewrite the average in (*B*.6) as

$$\begin{aligned}C_j(\omega,\Delta)=[1/(2\pi)^2]\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\exp\{in_j\omega[&\sin(\mu_1+\Delta)\\&+\sin(\mu_2+\Delta)\\&+\sin(-\mu_1-\mu_2+\Delta)]\}\,d\mu_1\,d\mu_2.\end{aligned}\quad (B.7)$$

The integral in (*B*.7) can be computed numerically, but it is possible and much more efficient to convert it into a rapidly converging series. This can be done with the aid of the identity

$$\exp(ix\sin\beta)=\sum_{k=-\infty}^{\infty}J_k(x)\exp(ik\beta)$$

(*e.g.* Gradshteyn & Ryzhik, 1980; 8.511-3), where $J_k(x)$ is a Bessel function of the first kind and of order k. By making use of this identity we can then rewrite (*B*.7) as

$$\begin{aligned}C_j(\omega,\Delta)=&\sum_{k=-\infty}^{\infty}\sum_{m=-\infty}^{\infty}\sum_{n=-\infty}^{\infty}J_k(n_j\omega)\,J_m(n_j\omega)\\&\times J_n(n_j\omega)\exp[i(k+m+n)\Delta]\\&\times[1/(2\pi)^2]\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\exp[i(k-n)\mu_1]\\&\times\exp[i(m-n)\mu_2]\,d\mu_1\,d\mu_2\end{aligned}\quad (B.8)$$

$$=\sum_{k=-\infty}^{\infty}\exp(3ik\Delta)J_k^3(n_j\omega)\quad (B.9)$$

since the integral on the second line of (*B*.8) evaluates to $\delta_{kn}\delta_{mn}$, where δ_{pq} is the Kronecker delta (*cf.* Appendix *A*).

An evaluation of (*B*.6) that preserves symmetry makes use of the periodic Dirac δ distribution, *i.e.* $\delta_h(x)=\sum_{j=-\infty}^{\infty}\delta(x-jh)$ (*e.g.* Bremermann, 1965). When this representation is inserted into (*B*.6), it is transformed into

$$C(\omega,\Delta)=\prod_{j=1}^{N/3}\left\{\left([1/(2\pi)^2]\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\mathrm{d}\mu_1\,\mathrm{d}\mu_2\,\mathrm{d}\mu_3\times\delta_{2\pi}(\mu_1+\mu_2+\mu_3)\times\exp\left[in_j\omega\sum_{k=1}^{3}\sin(\mu_k+\Delta)\right]\right)\right\}. \quad (B.10)$$

A most convenient implementation of the Dirac delta distribution, in the present context, is its Fourier-series representation:

$$\delta_{2\pi}(\mu_1+\mu_2+\mu_3)=(1/2\pi)\sum_{k=-\infty}^{\infty}\exp[-ik(\mu_1+\mu_2+\mu_3)] \quad (B.11)$$

(*e.g.* Bremermann, 1965). If we substitute (*B*.11) into (*B*.10), we obtain

$$C(\omega,\Delta)=\prod_{j=1}^{N/3}\left\{\sum_{k=-\infty}^{\infty}\left[(1/2\pi)\int_{-\pi}^{\pi}\exp[-ik\mu+in_j\omega\sin(\mu+\Delta)]\,\mathrm{d}\mu\right]^3\right\}. \quad (B.12)$$

The summand in (*B*.12) is related to the integral representation of a kth-order Bessel function. A change of variable $\mu'=\mu+\Delta$ leads to $-ik\mu=-ik\mu'+ik\Delta$, $\sin(\mu+\Delta)=\sin\mu'$ and the appearance of the phase factor $\exp(ik\Delta)$. Finally, we find

$$C(\omega,\Delta)=\prod_{j=1}^{N/3}\left\{\sum_{k=-\infty}^{\infty}\exp(3ik\Delta)\left[(1/2\pi)\times\int_{-\pi}^{\pi}\exp(-ik\mu+in_j\omega\sin\mu)\,\mathrm{d}\mu\right]^3\right\} \quad (B.13)$$

$$=\prod_{j=1}^{N/3}\left\{\sum_{k=-\infty}^{\infty}\exp(3ik\Delta)J_k^3(n_j\omega)\right\} \quad (B.14)$$

(*e.g.* Gradshteyn & Ryzhik, 1980; 8.411-1), in agreement with the result obtained by our previous method.

APPENDIX *C*

Derivation of the characteristic function for $P\bar{6}c2$ with $l=2n+1$

We next illustrate the derivation of the characteristic function of the p.d.f. $p(A,B)$, where $E=A+iB$ is the normalized structure factor, for the hexagonal space group $P\bar{6}c2$, for the parity $l=2n+1$. The corresponding real and imaginary parts of E are given by

$$A=-2\sum_{j=1}^{N/12}n_j\sin\varphi_j\sum_{k=1}^{3}(\sin\mu_{jk}+\sin\lambda_{jk}) \quad (C.1)$$

and

$$B=2\sum_{j=1}^{N/12}n_j\sin\varphi_j\sum_{k=1}^{3}(\cos\mu_{jk}-\cos\lambda_{jk}), \quad (C.2)$$

where

$$\mu_{j1}=2\pi(hx_j+ky_j),\quad \mu_{j2}=2\pi(kx_j+iy_j),\quad \mu_{j3}=2\pi(ix_j+hy_j),$$
$$\lambda_{j1}=2\pi(kx_j+hy_j),\quad \lambda_{j2}=2\pi(hx_j+iy_j),\quad \lambda_{j3}=2\pi(ix_j+ky_j)$$

and $\varphi_j=2\pi lz_j$. The form of the trigonometric structure factor given in (*C*.1) and (*C*.2) corresponds to the format in the forthcoming Volume B of *International Tables for Crystallography* (Shmueli, 1991). Each of these angular variables can be regarded as being uniformly distributed on $[0,2\pi]$, but only two of the μ's and two of the λ's are independent since $\sum\mu_k\equiv 0$ and $\sum\lambda_k\equiv 0$. The characteristic function for the required p.d.f., defined as a product of individual atomic contributions, is given by

$$C(\omega_1,\omega_2)=\langle\exp[i(\omega_1A+\omega_2B)]\rangle=\prod_{j=1}^{N/12}C_j(\omega_1,\omega_2), \quad (C.3)$$

where it was assumed that the atomic contributions to the structure factor are independent and the averaging extends over all the angular variables after proper account has been taken of the dependence between the μ's and λ's. If we change to the polar coordinate form $\omega_1=\omega\sin\Delta$ and $\omega_2=\omega\cos\Delta$ and rearrange the trigonometric part of (*C*.3) to the more convenient form

$$\sum_{k=1}^{3}[-\omega_1(\sin\mu_{jk}+\sin\lambda_{jk})+\omega_2(\cos\mu_{jk}-\cos\lambda_{jk})]=\omega\sum_{k=1}^{3}[\cos(\mu_{jk}+\Delta)-\cos(\lambda_{jk}-\Delta)],$$

the atomic characteristic function in (*C*.3) can be transformed to

$$C_j(\omega_1,\omega_2)=[1/(2\pi)^5]\int_{-\pi}^{\pi}\mathrm{d}\varphi\times\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\mathrm{d}\mu_1\,\mathrm{d}\mu_2\,\mathrm{d}\mu_3\,\mathrm{d}\lambda_1\,\mathrm{d}\lambda_2\,\mathrm{d}\lambda_3\times\delta_{2\pi}(\mu_1+\mu_2+\mu_3)\delta_{2\pi}(\lambda_1+\lambda_2+\lambda_3)\times\exp\left\{2in_j\omega\sin\varphi\sum_{k=1}^{3}[\cos(\mu_k+\Delta)-\cos(\lambda_k-\Delta)]\right\}. \quad (C.4)$$

The integral (*C*.4) is now conveniently evaluated with the aid of the Fourier representation of the periodic δ distribution (*e.g.* Bremermann, 1965)

$$\delta_{2\pi}(\alpha) = (1/2\pi) \sum_{k=-\infty}^{\infty} \exp(-ik\mu). \qquad (C.5)$$

Since the α's are equivalent, and so are the β's, we obtain

$$C_j(\omega_1, \omega_2) = (1/2\pi) \int_{-\pi}^{\pi} d\varphi \, \mathcal{P}_j \mathcal{Q}_j, \qquad (C.6)$$

where

$$\begin{aligned}\mathcal{P}_j &= [1/(2\pi)^2] \int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi} d\mu_1\, d\mu_2\, d\mu_3 \\ &\quad \times \delta_{2\pi}(\mu_1+\mu_2+\mu_3) \\ &\quad \times \exp\left[2in_j\omega \sin\varphi \sum_{m=1}^{3} \cos(\mu_{jm}+\Delta)\right] \qquad (C.7) \\ &= \sum_{k=-\infty}^{\infty} \left\{(1/2\pi) \int_{-\pi}^{\pi} \exp[-ik\mu \right. \\ &\quad \left. + 2in_j\omega \sin\varphi \cos(\mu+\Delta)]\, d\mu\right\}^3. \qquad (C.8)\end{aligned}$$

The change of the variable $\mu' = \mu + (\Delta + \pi/2)$ allows us to rewrite this as

$$\begin{aligned}\mathcal{P}_j &= \sum_{k=-\infty}^{\infty} \exp[3ik(\Delta+\pi 2)]\left\{\frac{1}{2\pi}\right. \\ &\quad \left. \times \int_{-\pi}^{\pi} \exp(-ik\mu' + 2in_j\omega \sin\varphi \sin\mu')\, d\mu'\right\}^3, \qquad (C.9)\end{aligned}$$

which can be written, using the integral representation of a kth-order Bessel function $J_k(x)$, as

$$\mathcal{P}_j = \sum_{k=-\infty}^{\infty} \exp[3ik(\Delta+\pi/2)] J_k^3(2n_j\omega \sin\varphi) \qquad (C.10)$$

(*e.g.* Gradshteyn & Ryzhik, 1980, equation 8.411). If we follow the above procedure with the variable change $\lambda' = \lambda - (\Delta + \pi/2)$, we obtain for the quantity $\mathcal{Q}_j$ in (*C*.6)

$$\mathcal{Q}_j = \sum_{l=-\infty}^{\infty} \exp[-3il(\Delta+\pi/2)] J_l^3(2n_j\omega \sin\varphi). \qquad (C.11)$$

The characteristic function for the space group considered is therefore given by (*C*.3), where the atomic characteristic function is computed from (*C*.6) with (*C*.10) and (*C*.11). Since $\mathcal{P}_j$ and $\mathcal{Q}_j$ are complex conjugates, the imaginary part of $\mathcal{P}_j\mathcal{Q}_j$ vanishes, and because of the symmetry of the integrals involved the relevant entry for this space group is computed as

$$\begin{aligned}C_j(\omega_1, \omega_2) &\equiv \tilde{H}_j^{(1)}[\omega, (\Delta+\pi/2), -(\Delta+\pi/2), 0] \\ &= 2/\pi \int_0^{\pi/2} \mathrm{Re}(\mathcal{P}_j\mathcal{Q}_j)\, d\varphi.\end{aligned}$$

References

BREMERMANN, H. (1965). *Distributions, Complex Variables and Fourier Transforms.* Reading: Addison-Wesley.

FOSTER, F. & HARGREAVES, A. (1963). *Acta Cryst.* **16**, 1124-1133.

GRADSHTEYN, I. S. & RYZHIK, I. M. (1980). *Tables of Integrals, Series and Products.* New York: Academic Press.

International Tables for X-ray Crystallography (1965). Vol. I, edited by N. F. M. HENRY & K. LONSDALE. Birmingham: Kynoch Press.

RABINOVICH, S., SHMUELI, U., STEIN, Z., SHASHUA, R. & WEISS, G. H. (1991). *Acta Cryst.* A**47**, 336-340.

SHMUELI, U. (1982). *Acta Cryst.* A**38**, 362-371.

SHMUELI, U. (1991). In *International Tables for Crystallography*, Vol. B, edited by U. SHMUELI, Ch. 1.4. In the press.

SHMUELI, U. & KALDOR, U. (1981). *Acta Cryst.* A**37**, 76-80.

SHMUELI, U. & KALDOR, U. (1983). *Acta Cryst.* A**39**, 619-621.

SHMUELI, U., RABINOVICH, S. & WEISS, G. H. (1989). *Acta Cryst.* A**45**, 361-367.

SHMUELI, U., RABINOVICH, S. & WEISS, G. H. (1990). *Acta Cryst.* A**46**, 241-246.

SHMUELI, U. & WEISS, G.H. (1987). *Acta Cryst.* A**43**, 93-98.

SHMUELI, U. & WEISS, G.H. (1988). *Acta Cryst.* A**44**, 413-417.

SHMUELI, U., WEISS, G. H., KIEFER, J. E. & WILSON, A. J. C. (1984). *Acta Cryst.* A**40**, 651-660.

SHMUELI, U. & WILSON, A. J. C. (1981). *Acta Cryst.* A**37**, 342-353.

STOYANOV, B.J. & FARRELL, R. A. (1987). *Math. Comput.* **49**, 275-279.

WILSON, A.J.C. (1949). *Acta Cryst.* **2**, 318-321.

WILSON, A. J. C. (1978). *Acta Cryst.* A**34**, 986-994.