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The Probability Distribution of X-ray Intensities. V. A Note on some Hypersymmetric Distributions

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The parallel repetition of a motif modulates the Fourier transform of the motif by the transform of the repetition arrangement, thus increasing the dispersion of the resultant transform. Several arrangements are considered in which the repetition involves the introduction of non-crystallographic symmetry. Statistical criteria are evaluated for the recognition of each of the resulting distributions and some comments are offered on the correlation of the statistical evidence for parallelism with that given by inspection of the reciprocal lattice or by the Patterson function.

1. Introduction

1·1

It was pointed out in § 2·4 of the first paper of this series (Wilson, 1949) that pseudosymmetry can give rise to abnormal intensity distributions, but it seemed desirable to test the usefulness of the two usual distributions before embarking on a detailed study of pseudosymmetry. The discovery of the hypercentric distribution by Lipson & Woolfson (1952) suggests that this caution was unwarranted, and that a treatment of distributions corresponding to the more probable types of pseudosymmetry would be useful.

1·2

The hypercentric intensity distribution arises when two molecules, each with a non-crystallographic centre of symmetry, occupy general positions in a centrosymmetric space group. They are then necessarily parallel and their Fourier transform is modulated by a sinusoidal fringe system which increases the dispersion beyond that of the centric distribution. An obvious extension is (*a*) that each centrosymmetric molecule should consist of two centrosymmetric parts related by a further non-crystallographic centre of symmetry, as in Fig. 1. (Dibiphenylene ethylene provides an approximation to such a molecule, but the arrangement of molecules is complex (Fenimore, 1948).) The modulation pattern is then the product of two sinusoidal fringe systems which, in general, are unrelated in both spacing and orientation. This extension is generalized in § 2, and will be termed hypercentrosymmetry.

Other parallel arrangements have been considered and are discussed in §§ 2, 3, 4. They are

(*b*) *n*-fold repetition of a motif by a group of multiplicative translations (Fig. 2), which will be termed hyperparallelism,

(*c*) *n*-fold repetition of a motif at regular intervals along a straight line, for which the modulation pattern consists of one set of parallel fringes with a profile of the form $\sin n\psi/\sin\psi$,

(*d*) many repetitions of a motif at random in a centrosymmetric or a non-centrosymmetric space group, for which the modulation pattern is irregular with a centric or acentric distribution respectively.

1·3

It is obvious that the arrangements (*a*)–(*d*) above do not exhaust the possibilities for even parallel pseudosymmetry, but they are probably sufficient to show the general effects of non-crystallographic parallelism on the ordinary acentric and centric distributions. So far as is known (§ 5·1), *crystallographic* symmetry can result in only one or the other of these two distributions, however many symmetry elements are present, but unfortunately the effect of additional *non-crystallographic* symmetry is not dependent merely on whether the space group of the crystal is centrosymmetric or not. A preliminary investigation suggests that the effect of additional non-crystallographic symmetry must be considered separately for at least each crystal class. The distributions derived in this note cannot, therefore, be applied uncritically to cases other than (i) the space groups $P1$ and $P\bar{1}$, and (ii) projections without crystallographic symmetry or with a crystallographic centre of symmetry only.

1·4

Although the higher types of hypercentrosymmetric distribution can be generalized readily from that of Lipson & Woolfson, a unified treatment has been adopted here in which, so far as applicable, the notations of Wilson (1949) and Cramér (1946, chap. 15) are used. In addition the structure factor for a single *motif*, which is not necessarily the crystallographic asymmetric unit, is denoted by

$$M \exp(i\mu) = \sum_{j=1}^{m} f_j \exp(2\pi i \mathbf{s}.\mathbf{r}_j)\,,$$

the structure factor of the repetition *arrangement* (referred to the same origin) is denoted by

$$A \exp(i\alpha) = \sum_{j=1}^{n} \exp(2\pi i \mathbf{s}.\mathbf{d}_j) ,$$

and that for the whole unit cell by $F \exp(i\varphi)$, which, for all the cases discussed here, may be written as

$$F \exp(i\varphi) = MA \exp i(\mu+\alpha) . \quad (1)$$

With the structure factor for a non-centrosymmetric motif written in the form $M = x+iy$, the joint probability of x lying between x and $x+dx$, y lying between y and $y+dy$, is (Wilson, 1949)

$$(1)P(x, y)dxdy = (\pi\Sigma_M)^{-1} \exp\{-(x^2+y^2)/\Sigma_M\}dxdy , \quad (2)$$

where $\Sigma_M = \sum_{j=1}^{m} (f_j)^2$ for all atoms in the motif. This can also be written as

$$(1)P(M, \mu)dMd\mu = (\pi\Sigma_M)^{-1} \exp(-M^2/\Sigma_M)MdMd\mu \quad (3)$$

or

$$(1)P(M)dM = (2/\Sigma_M) \exp(-M^2/\Sigma_M)MdM , \quad (3a)$$

since μ has a uniform probability in the range 0 to 2π. If, on the other hand, the motif is centrosymmetric, its structure factor is real when referred to its centre as origin, and the corresponding distribution of the modulus is

$$(\bar{1})P(M)dM = (2/\pi\Sigma_M)^{\frac{1}{2}} \exp(-M^2/2\Sigma_M)dM . \quad (4)$$

Three criteria already published for the recognition of a distribution type are

(*a*) the cumulative probability $N(z) = \int_0^z P(z)dz$, where $z = |F|^2/\Sigma = I/\langle I\rangle$ (Howells, Phillips & Rogers, 1950),

(*b*) the test ratio $\varrho = \langle|F|\rangle^2/\langle|F|^2\rangle$ (Wilson, 1949), and

(*c*) the specific variance $v = V/\Sigma^2 = \langle(I-\langle I\rangle)^2\rangle/\Sigma^2$ (Wilson, 1951). These will be evaluated for each of the cases considered and, for this purpose, some of the moments of the distribution functions are required. The mth absolute moment is

$$\nu_m = \int_0^\infty F^m P(F)dF \quad (5)$$

(since in the present notation F is already a modulus), and the corresponding central moment is

$$\mu_m = \nu_m \text{ for } m \text{ even,}$$
$$= 0 \quad \text{for } m \text{ odd.}$$

In particular ν_2 is always equal to Σ (Wilson, 1942), a consequence of the conservation of the diffracted energy.

In terms of these, the second and third criteria become

$$\varrho = \nu_1^2/\Sigma = \nu_1^2/\nu_2 \quad (6)$$

and

$$v = V/\Sigma^2 = \langle F^4\rangle/\Sigma^2-1 = \nu_4/\nu_2^2-1 . \quad (7)$$

2. Hypersymmetry

2·1. *Hypercentrosymmetry*

The Lipson–Woolfson case is generalized as follows. Consider a crystallographic asymmetric unit built up from 2^{n-2} centrosymmetric motifs which are related by a sequence of $n-1$ centres of symmetry at vectorial positions $\mathbf{d}_2, \ldots, \mathbf{d}_n$, none of which coincide with a

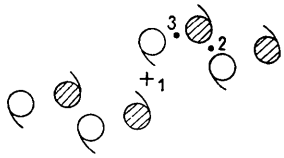

Fig. 1. Hypersymmetric arrangement with $n = 3$. The crystallographic centre of symmetry (1) is indicated by a cross, the non-crystallographic local centres (2, 3) are indicated by dots; $\mathbf{d}_2$ is the vector from 1 to 2 and $\mathbf{d}_3$ the vector from 2 to 3.

crystallographic symmetry centre (see Fig. 1, where $n = 3$). The asymmetric unit is duplicated by the crystallographic centre of symmetry at $\mathbf{d}_1 = 0$. If the unit cell contains only these two units

$$A = |2^{n-1} \cos\psi_2 \cos\psi_3 \ldots \cos\psi_n| , \quad (8)$$

where

$$\psi_j = 2\pi\mathbf{s}.\mathbf{d}_j ,$$

$$M = |2\sum_{j=1}^{\frac{1}{2}m} f_j \cos\theta_j| , \quad (9)$$

where

$$\theta_j = 2\pi\mathbf{s}.\mathbf{r}_j ,$$

and

$$\Sigma = 2^{n-1}\Sigma_M . \quad (10)$$

Hence, for all points in reciprocal space defined by the combination $\psi_2, \psi_3, \ldots \psi_n$, we have from equation (4)

$$[P_n(F)dF]_{\psi_2\ldots\psi_n} = (2^n/\pi\Sigma)^{\frac{1}{2}} \frac{\exp[-F^2/2^n\Sigma \cos^2\psi_2\ldots\cos^2\psi_n]}{2^{n-1}\cos\psi_2\ldots\cos\psi_n} dF \quad (11)$$

and, since each ψ_j has uniform probability in the range 0 to 2π, this gives for all reciprocal space

$$P_n(F)dF = (2^n/\Sigma\pi^{2n-1})^{\frac{1}{2}} \times \int_0^{\frac{1}{2}\pi}\ldots\int_0^{\frac{1}{2}\pi} \exp[-F^2 \sec^2\psi_2\ldots\sec^2\psi_n/2^n\Sigma] \times \sec\psi_2\ldots\sec\psi_n d\psi_2\ldots d\psi_n dF . \quad (12)$$

There does not seem to be any simple analytic expression for $P_n(F)$, though P_1 reduces to the ordinary centric distribution and P_2 can be expressed in terms of the zero-order Bessel function of the third kind, K_0 (Watson, 1922, p. 78):

$$P_2(F)dF = (4/\pi^3\Sigma)^{\frac{1}{2}} \times \int_0^{\frac{1}{2}\pi} \exp\{-F^2 \sec^2\psi/4\Sigma\} \sec\psi d\psi dF , \quad (13)$$

which becomes, with the substitution $\sec\psi = \cosh\theta$,

$$P_2(F) = (\pi^3\Sigma)^{-\frac{1}{2}} \exp(-F^2/8\Sigma) \times \int_0^{\infty} \exp\{-F^2 \cosh 2\theta/8\Sigma\} d(2\theta) \quad (14)$$

$$= (\pi^3\Sigma)^{-\frac{1}{2}} \exp(-F^2/8\Sigma) K_0(F^2/8\Sigma)\,, \quad (15)$$

by equation (5), p. 172, Watson (1922). The function K_0 has an infinity at the origin; it is rather interesting that $P_0(F)$ is zero, $P_1(F)$ is finite and $P_2(F)$ and higher members of the sequence are infinite for $F=0$.

2·2. *Hyperparallelism*

Consider a non-centrosymmetric space group and an asymmetric unit containing 2^n parallel non-centro-

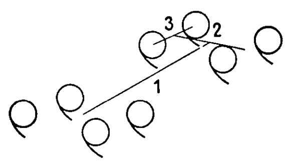

Fig. 2. Hyperparallel arrangement with $n = 3$. The displacements relating parallel motifs are indicated by the lines marked 1, 2, 3; their lengths are $\mathbf{d}_1$, $\mathbf{d}_2$, $\mathbf{d}_3$.

symmetric motifs related by a chain of n displacements ($\mathbf{d}_1$ to $\mathbf{d}_n$), as in Fig. 2 for $n = 3$. This gives

$$A = |2^n \cos\psi_1 \cos\psi_2 \ldots \cos\psi_n|\,, \quad (16)$$

where, in this case,

$$\psi_j = \pi \mathbf{s}.\mathbf{d}_j\,,$$

and

$$\Sigma = 2^n \Sigma_M\,. \quad (17)$$

Then, by equation (3*a*),

$$P_n(F)dF = (2F\,dF/\pi^n\Sigma) \int_0^{\frac{1}{2}\pi} \ldots \int_0^{\frac{1}{2}\pi} \exp\{-F^2 \sec^2\psi_1 \ldots \sec^2\psi_n/2^n\Sigma\} \times \sec^2\psi_1 \ldots \sec^2\psi_n d\psi_1 \ldots d\psi_n\,. \quad (18)$$

There is an obvious resemblance between this and equation (12), which can be increased to formal identity in the following way. Consider one-half of the centrosymmetric motif of § 2·1, for which, in an obviously analogous notation,

$$M' \exp(i\mu) = \sum_{j=1}^{\frac{1}{2}m} f_j \exp(i\theta_j)\,, \quad (19)$$

$$A' = |2^n \cos\mu \cos\psi_2 \ldots \cos\psi_n| \quad (20)$$

and

$$\Sigma = 2^n \Sigma_{M'}\,. \quad (21)$$

Then, from equation (3),

$$P_n(F)dF = (2FdF/\pi^n\Sigma) \times \int_0^{\frac{1}{2}\pi} \ldots \int_0^{\frac{1}{2}\pi} \exp\{-F^2 \sec^2\mu \sec^2\psi_2 \ldots \sec^2\psi_n/2^n\Sigma\} \times \sec^2\mu \sec^2\psi_2 \ldots \sec^2\psi_n d\mu d\psi_2 \ldots d\psi_n\,, \quad (22)$$

which is formally identical with equation (18), as it is irrelevant whether the first integration variable is called ψ_1 or μ.

This formal identity introduces a valuable economy into the subsequent work. Any case of hypersymmetry for which A takes the form $|2^n \prod_{j=1}^{n} \cos\psi_j|$ will then be covered by a general treatment, irrespective of the particular physical significance attached to each ψ_j. Thus, where the cell contains only one or two asymmetric units (in the crystallographic sense), the results to be obtained for $n = 0, 1, 2, \ldots$ represent with equal validity the sequences acentric, centric, bicentric (= hypercentric, Lipson & Woolfson), ..., or alternatively aparallel = acentric, parallel, biparallel, ...

2·2·1.—One rather disturbing consequence of this is that two parallel non-centrosymmetric motifs related by a non-crystallographic translation in a non-centrosymmetric space group give the same (centric) distribution as when they are in centrosymmetric antiparallelism. Equation (18) becomes

$$P(F) = (2F/\pi\Sigma) \int_0^{\frac{1}{2}\pi} \exp(-F^2 \sec^2\psi/2\Sigma) d\psi\,, \quad (23)$$

whence, with the substitution $t = \tan\psi$,

$$P(F) = (2F/\pi\Sigma) \exp(-F^2/2\Sigma) \int_0^{\infty} \exp(-F^2t^2/2\Sigma) dt \quad (24)$$

$$= (2/\pi\Sigma)^{\frac{1}{2}} \exp(-F^2/2\Sigma)\,, \quad (25)$$

which is the centric distribution (equation (4)). This conclusion is discussed in § 5·2·1 below.

2·3. *Criteria for hypersymmetry*

2·3·1. *The* $N(z)$ *test*.—Equation (12) can be written in terms of z as

$$P(z)dz = 2^{\frac{1}{2}n-1}\pi^{-n+\frac{1}{2}} \int_0^{\frac{1}{2}\pi} \ldots \int_0^{\frac{1}{2}\pi} z^{-\frac{1}{2}} \exp\{-z \sec^2\psi_2 \ldots \sec^2\psi_n/2^n\} \times \sec\psi_2 \ldots \sec\psi_n d\psi_2 \ldots d\psi_n dz\,, \quad (26)$$

whence

$$N(z) = (2/\pi)^{n-1} \times \int_0^{\frac{1}{2}\pi} \ldots \int_0^{\frac{1}{2}\pi} \operatorname{erf}[(z/2^n)^{\frac{1}{2}} \sec\psi_2 \ldots \sec\psi_n] d\psi_2 \ldots d\psi_n\,. \quad (27)$$

It is easy to show directly from equation (18) that for the acentric distribution (when $\psi_1 \equiv \psi_2 \equiv \ldots \equiv 0$)

$$N_0(z) = 1 - \exp(-z)\,. \quad (28)$$

The above equation gives

$$N_1(z) = \operatorname{erf}(z/2)^{\frac{1}{2}} \quad (29)$$

and

Table 1(*a*). *Statistical data for the first few hypersymmetric distributions*

n	0	1	2	3
	Acentric or aparallel	Centric or parallel	Bicentric or biparallel	Tricentric or triparallel
z	$N_0(z)$	$N_1(z)$	$N_2(z)$	$N_3(z)$
0·00	0·0000	0·0000	0·0000	0·000
0·05	0·0488	0·1774	$0{\cdot}292_3$	0·386
0·1	0·0952	0·2481	$0{\cdot}368_0$	0·460
0·2	0·1813	0·3453	$0{\cdot}463_2$	0·548
0·3	0·2592	0·4187	$0{\cdot}526_1$	0·605
0·4	0·3297	0·4738	$0{\cdot}573_6$	0·647
0·5	0·3935	0·5205	$0{\cdot}611_7$	0·680
0·6	0·4512	0·5614	$0{\cdot}643_5$	0·705
0·7	0·5034	0·5972	$0{\cdot}670_5$	0·727
0·8	0·5507	0·6289	$0{\cdot}693_9$	0·746
0·9	0·5934	0·6572	$0{\cdot}714_7$	0·762
1·0	0·6321	0·6833	$0{\cdot}733_2$	0·776
1·2	0·6988	0·7267	$0{\cdot}764_2$	0·800
1·4	0·7534	0·7633	$0{\cdot}791_0$	0·820
1·6	0·7981	0·7940	$0{\cdot}813_1$	0·837
2·0	0·8647	0·8427	$0{\cdot}848_5$	0·863
2·4	0·9093	0·8786	$0{\cdot}875_2$	0·884
2·8	0·9392	0·9058	$0{\cdot}896_2$	0·900
ϱ_n	$\frac{\pi}{4} = 0{\cdot}785$	$\frac{2}{\pi} = 0{\cdot}637$	$\frac{16}{\pi^3} = 0{\cdot}516$	$\frac{2^7}{\pi^5} = 0{\cdot}418$
v_n	1	2	$3\frac{1}{2}$	$5\frac{3}{4}$

Table 1(*b*)

n	4	5	6	7
ϱ_n	0·339	0·275	0·223	0·180
v_n	9·125	14·19	21·78	33·17

$$N_2(z) = 2\pi^{-1}\int_0^{\frac{1}{2}\pi} \operatorname{erf}\,[\tfrac{1}{2}z^{\frac{1}{2}}\sec\psi]\,d\psi\,, \qquad (30)$$

which is easily proved to be equivalent to Lipson & Woolfson's expression, and is better suited to numerical integration than equation (15). Table 1(*a*) and Fig. 3

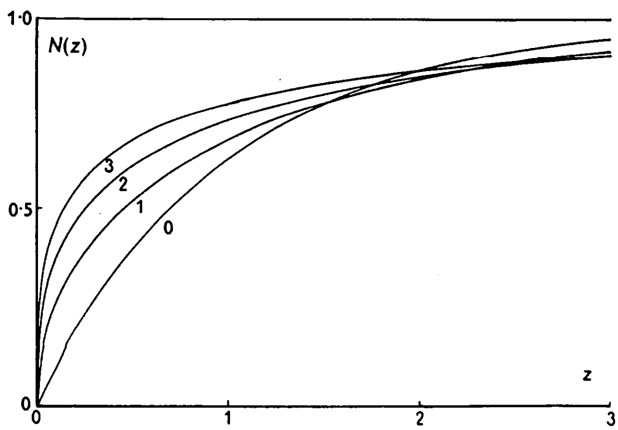

Fig. 3. The cumulative distribution $N(z)$ for the first four hypersymmetric cases, $n = 0, 1, 2, 3$ (Table 1(*a*)).

indicate the comparative forms of these functions for $n = 0, 1, 2, 3$. $N_2(z)$ was evaluated by summation at 5° intervals, while $N_3(z)$ was computed from 15° intervals in both ψ_2 and ψ_3. Higher members of the series were not considered worth computing, as no immediate application is foreseen. The limiting form for $n \to \infty$ is presumably $N(z) = 0$ for $z = 0$, $N(z) = 1$ for $z > 0$.

2·3·2. *The variance and* ϱ *tests.*—The mth absolute moment of P_n is

$$\begin{aligned} \nu_{n,m} &= (2/\pi^n\Sigma) \\ &\times \int_0^\infty \int_0^{\frac{1}{2}\pi} \cdots \int_0^{\frac{1}{2}\pi} F^{m+1}\exp\{-F^2\sec^2\psi_1\ldots\sec^2\psi_n/2^n\Sigma\} \\ &\qquad \times \sec^2\psi_1\ldots\sec^2\psi_n d\psi_1\ldots d\psi_n dF \qquad (31) \\ &= \pi^{-n}2^{n(\frac{1}{2}m+1)}\Gamma(\tfrac{1}{2}m+1)\Sigma^{\frac{1}{2}m} \\ &\qquad \times \int_0^{\frac{1}{2}\pi} \cdots \int_0^{\frac{1}{2}\pi} \cos^m\psi_1\ldots\cos^m\psi_n d\psi_1\ldots d\psi_n \qquad (32) \\ &= \pi^{-\frac{1}{2}n}2^{\frac{1}{2}mn}\Gamma^n(\tfrac{1}{2}m+\tfrac{1}{2})\Gamma^{-n+1}(\tfrac{1}{2}m+1)\,\Sigma^{\frac{1}{2}m}\,. \qquad (33) \end{aligned}$$

Thus $\nu_{n,2} = \Sigma$ for all n, and the test ratio is, from equation (6),

$$\varrho_n = 2^{3n-2}\pi^{-2n+1}\,, \qquad (34)$$

with the successive values shown in Tables 1(*a*) and 1(*b*).

The specific variance is, from equation (7),

$$v_n = 2(\tfrac{3}{2})^n - 1\,, \qquad (35)$$

the successive values of which are given in the same tables. Fig. 4 indicates the relation between the

Table 2(*a*). *Statistical data for a non-centrosymmetric motif repeated n times in a straight line*

n	1	2	3	4
z	$N_1(z)$	$N_2(z)$	$N_3(z)$	$N_4(z)$
0·00	Acentric;	Centric;	0·0000	0·0000
0·05	see	see	0·243$_6$	0·286$_4$
0·1	Table 1,	Table 1,	0·336$_0$	0·394$_8$
0·2	col. 2	col. 3	0·447$_1$	0·517$_9$
0·3			0·520$_0$	0·584$_6$
0·4			0·573$_0$	0·640$_1$
0·5			0·613$_8$	0·676$_3$
0·6			0·646$_6$	0·704$_0$
0·7			0·673$_8$	0·725$_9$
0·8			0·696$_9$	0·744$_0$
0·9			0·716$_9$	0·759$_3$
1·0			0·734$_6$	0·772$_5$
1·5			0·800$_5$	0·820$_8$
2·0			0·845$_0$	0·854$_0$
2·5			0·877$_5$	0·879$_1$
3·0			0·902$_2$	0·899$_0$
ϱ_n	0·785	0·637	0·540	0·473
v_n	1	2	$3\frac{2}{9}$	$4\frac{1}{2}$

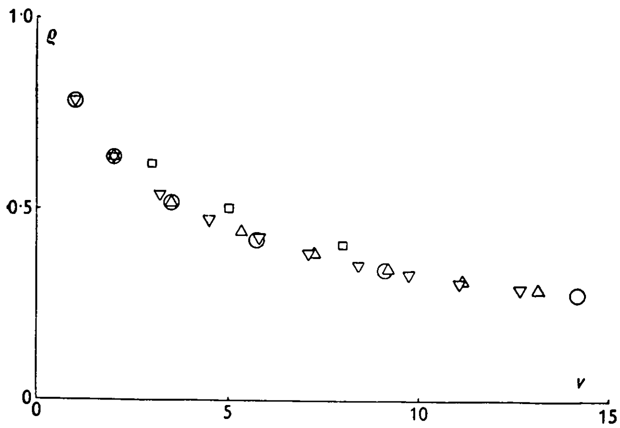

Fig. 4. A comparison of the test ratio, ϱ, and the specific variance, v, for each of the distributions discussed in this paper.

○: hypercentrosymmetry (n = 0, 1, 2, 3, 4).
▽: regular linear repetition of a non-centrosymmetric motif.
△: regular linear repetition of a centrosymmetric motif.
□: multiple random repetition.

specific variance, v_n, and ϱ_n for this and other sequences of hypersymmetric distributions.

3. Regular parallel repetition in line

3·1

For the regular repetition of n motifs at intervals **d** along a straight line, A takes the form

$$\left|\frac{\sin n\psi}{\sin \psi}\right|, \quad \text{where} \quad \psi = \pi \mathbf{s}.\mathbf{d}\,. \tag{36}$$

3·2

3·2·1. *Non-centrosymmetric motif.*—For all points in reciprocal space with the same value of ψ, equation (3*a*) takes the form

$$[(1)P_n(M)dM]_\psi = \frac{2n\sin^2\psi}{\Sigma\sin^2 n\psi}\exp\left\{-\frac{F^2 n\sin^2\psi}{\Sigma\sin^2 n\psi}\right\}FdF\,, \tag{37}$$

where $\Sigma = n\Sigma_M$ and includes all atoms in the cell. For the entire reciprocal lattice

$$(1)P_n(F)dF =$$
$$(4n/\Sigma\pi)\int_0^{\frac{1}{2}\pi}\frac{\sin^2\psi}{\sin^2 n\psi}\exp\left\{-\frac{F^2 n\sin^2\psi}{\Sigma\sin^2 n\psi}\right\}d\psi FdF\,, \tag{38}$$

or, on transforming to z,

$$(1)P_n(z)dz =$$
$$(2n/\pi)\int_0^{\frac{1}{2}\pi}\frac{\sin^2\psi}{\sin^2 n\psi}\exp\left\{-\frac{zn\sin^2\psi}{\sin^2 n\psi}\right\}d\psi dz\,, \tag{39}$$

whence the cumulative probability $N(z)$ becomes

$$(1)N_n(z) = 1-2\pi^{-1}\int_0^{\frac{1}{2}\pi}\exp\left\{-\frac{zn\sin^2\psi}{\sin^2 n\psi}\right\}d\psi\,. \tag{40}$$

For $n = 1$ this is $[1-\exp(-z)]$, the ordinary acentric form. For $n = 2$ (the parallel case of § 2·2) it is possible to show, either by reversing the order of the integrations in the derivation of equation (40), or by expansion and term-by-term integration, that this has the usual centric form, $\operatorname{erf}(\frac{1}{2}z)^{\frac{1}{2}}$. $(1)N_n(z)$ has been evaluated for $n = 3$ and 4 by summation at 5° intervals and the results are given in Table 2(*a*) and Fig. 5.

The first absolute moment is

$$(1)\nu_{n,1} =$$
$$(4n/\Sigma\pi)\int_0^\infty\int_0^{\frac{1}{2}\pi}\frac{\sin^2\psi}{\sin^2 n\psi}\exp\left\{-\frac{F^2 n\sin^2\psi}{\Sigma\sin^2 n\psi}\right\}d\psi F^2 dF \tag{41}$$
$$= \tfrac{1}{2}\left(\frac{\Sigma\pi}{n}\right)^{\frac{1}{2}}\left\{\frac{2}{\pi}\int_0^{\frac{1}{2}\pi}\left|\frac{\sin n\psi}{\sin\psi}\right|d\psi\right\}. \tag{42}$$

For odd values of n $(= 2k+1)$ the term in brackets gives the Lebesgue constants, L_k, which are important

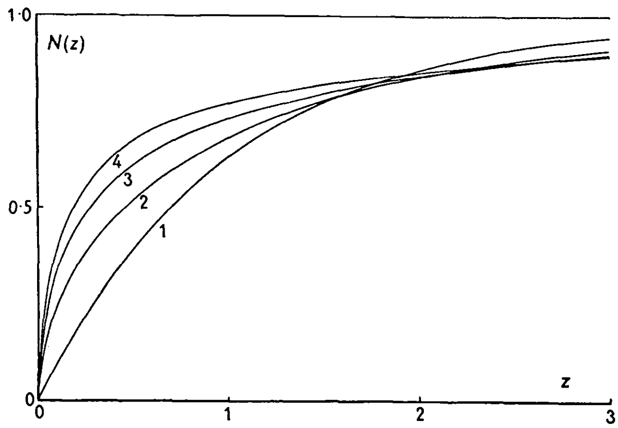

Fig. 5. The cumulative distribution $N(z)$ for n non-centrosymmetric motifs at equal intervals on a straight line ($n = 1, 2, 3, 4$) (Table 2(*a*)).

in the theory of the convergence of Fourier series. Fejér (1910) gives a series which was found convenient for the computation of the earlier constants, and Watson (1930) gives the asymptotic formula

$$L_n = 4\pi^{-2}\,[\ln n + 2{\cdot}441 + \ldots]\,, \qquad (43)$$

which gives values closely in accord with Fejér's down to $k \sim 3$, below which Fejér's exact series was used. Watson's asymptotic formula (but not Fejér's) may be used for the even values of n also, but was supplemented by direct expansion and integration for $n = 2$ and 4.

The second moment is

$$(1)\nu_{n,2} = (2\Sigma/\pi n)\int_0^{\frac{1}{2}\pi} \frac{\sin^2 n\psi}{\sin^2\psi}\,d\psi\,, \qquad (44)$$

which may be integrated with the aid of the Fourier cosine expansion of $\sin^2 n\psi/\sin^2\psi$ (Whittaker & Watson, 1935, equation (84), p. 171) and gives $(1)\nu_2 = \Sigma$ for all n, as expected. The fourth moment is

$$(1)\nu_{n,4} = 4\Sigma^2/\pi n^2\int_0^{\frac{1}{2}\pi} \frac{\sin^4 n\psi}{\sin^4\psi}\,d\psi\,, \qquad (45)$$

which is conveniently evaluated by squaring the series just mentioned and integrating term-by-term. This gives

$$(1)\nu_{n,4} = [4n^{-2}\sum_{j=1}^{n} j^2 - 2]\,\Sigma^2 = [\tfrac{2}{3}n^{-1}(n+1)(2n+1)-2]\,\Sigma^2 \qquad (46)$$

so that the specific variance is

$$(1)v_n = \frac{2}{3}\left(2n+\frac{1}{n}\right)-1\,. \qquad (47)$$

Values of this and the test ratio are given in Tables 2(*a*) and 2(*c*) for $1 \leqslant n \leqslant 10$.

3·2·2. *Centrosymmetric motif.*—The analysis is similar to that of § 3·2·1, and gives

$$(\bar{1})P_n(F)dF = 2\pi^{-1}(2n/\Sigma\pi)^{\frac{1}{2}}\int_0^{\frac{1}{2}\pi}\exp\left\{-\frac{F^2 n\sin^2\psi}{2\Sigma\sin^2 n\psi}\right\}\left|\frac{\sin\psi}{\sin n\psi}\right|d\psi dF\,, \qquad (48)$$

$$(\bar{1})N_n(z) = 2\pi^{-1}\int_0^{\frac{1}{2}\pi}\operatorname{erf}\left[\frac{\sin\psi}{\sin n\psi}\left(\frac{nz}{2}\right)^{\frac{1}{2}}\right]d\psi\,. \qquad (49)$$

This reduces to familiar forms for $n = 1$ and 2, and has been integrated numerically for $n = 3$ and 4 (see Table 2(*b*) and Fig. 6).

The moments are

$$(\bar{1})\nu_{n,1} = 2(2\Sigma/\pi^3 n)^{\frac{1}{2}}\int_0^{\frac{1}{2}\pi}\left|\frac{\sin n\psi}{\sin\psi}\right|d\psi\,, \qquad (50)$$

so that comparison with equation (42) gives

$$(\bar{1})\nu_{n,1} = \frac{2\sqrt{2}}{\pi}\cdot(1)\nu_{n,1}\,. \qquad (51)$$

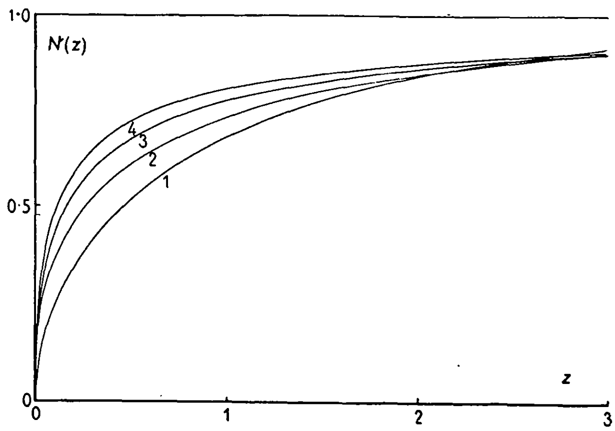

Fig. 6. The cumulative distribution $N(z)$ for n centrosymmetric motifs at equal intervals on a straight line ($n = 1, 2, 3, 4$) (Table 2(*b*)).

Similarly

$$(\bar{1})\nu_{n,2} = (1)\nu_{n,2} = \Sigma\,,$$

$$(\bar{1})\nu_{n,4} = \tfrac{3}{2}(1)\nu_{n,4}\,, \qquad (52)$$

whence

$$(\bar{1})\varrho_n = 8\pi^{-2}(1)\varrho_n \qquad (53)$$

and

$$(\bar{1})v_n = \left(2n+\frac{1}{n}\right)-1\,, \qquad (54)$$

the values of which are listed in Tables 2(*b*) and 2(*c*).

3·3

The corresponding values of v_n and ϱ_n from 3·2·1 and 3·2·2 are plotted in Fig. 4, and it is most remarkable that they should all lie so very near the curve obtained in § 2·3·2, but not quite on it. It is also noteworthy that for a given number of repeated motifs the effects are much more pronounced when they are arranged regularly in a straight line, rather than in some hypersymmetric scheme.

Table 2(*b*). *Statistical data for a centrosymmetric motif repeated n times in a straight line*

n	1	2	3	3
z	$N_1(z)$	$N_2(z)$	$N_3(z)$	$N_4(z)$
0·00	Centric;	Bicentric;	0·0000	0·0000
0·05	see	see	$0{\cdot}349_1$	$0{\cdot}401_0$
0·1	Table 1,	Table 1,	$0{\cdot}439_0$	$0{\cdot}486_4$
0·2	col. 3	col. 4	$0{\cdot}538_2$	$0{\cdot}589_9$
0·3			$0{\cdot}599_3$	$0{\cdot}650_2$
0·4			$0{\cdot}643_4$	$0{\cdot}691_6$
0·5			$0{\cdot}677_2$	$0{\cdot}722_4$
0·6			$0{\cdot}704_1$	$0{\cdot}746_4$
0·7			$0{\cdot}726_7$	$0{\cdot}765_8$
0·8			$0{\cdot}745_8$	$0{\cdot}781_6$
0·9			$0{\cdot}762_2$	$0{\cdot}795_7$
1·0			$0{\cdot}776_6$	$0{\cdot}807_5$
1·5			$0{\cdot}828_8$	$0{\cdot}849_2$
2·0			$0{\cdot}862_6$	$0{\cdot}875_5$
2·5			$0{\cdot}886_8$	$0{\cdot}894_4$
3·0			$0{\cdot}905_2$	$0{\cdot}909_1$
ϱ_n	0·637	0·516	0·438	0·383
v_n	2	$3\frac{1}{2}$	$5\frac{1}{3}$	$7\frac{1}{4}$

Table 2(*c*)

n	5	6	7	8	9	10
$(1)\varrho_n$	0·424	0·385	0·355	0·330	0·309	0·290
$(1)v_n$	$5\frac{4}{5}$	$7\frac{1}{9}$	$8\frac{3}{7}$	$9\frac{3}{4}$	$11\frac{2}{27}$	$12\frac{2}{5}$
$(\bar{1})\varrho_n$	0·343	0·312	0·288	0·268	0·250	0·235
$(\bar{1})v_n$	$9\frac{1}{5}$	$11\frac{1}{6}$	$13\frac{1}{7}$	$15\frac{1}{8}$	$17\frac{1}{9}$	$19\frac{1}{10}$

4. Many parallel repetitions at random

For, say, ten or more motifs repeated randomly but in parallel orientation the modulation pattern is irregular and can be regarded as having a reasonable approximation to one of the usual centric and acentric distributions.

4·1. *Non-centrosymmetric motif in a non-centrosymmetric arrangement*

$$P(M, \mu)\,dMd\mu = (\pi\Sigma_M)^{-1}\exp(-M^2/\Sigma_M)\,MdMd\mu\,, \quad (55)$$

$$P(A, \alpha)\,dAd\alpha = (\pi\Sigma_A)^{-1}\exp(-A^2/\Sigma_A)\,AdAd\alpha\,, \quad (56)$$

where $\Sigma_A = \sum_1^n (1^2) = n$, the 'large' number of repetitions. Hence

$$P(F)dF = (\pi^2 n\Sigma_M)^{-1}\int_0^{2\pi}\int_0^{2\pi}\int_0^\infty \exp\left\{-\frac{F^2}{A^2\Sigma_M}-\frac{A^2}{n}\right\}\frac{dA}{A}\,d\alpha d\mu FdF \quad (57)$$

$$= 4\Sigma^{-1}\int_0^\infty \exp\left\{-\frac{nF^2}{A^2\Sigma}-\frac{A^2}{n}\right\}\frac{dA}{A}\,FdF\,. \quad (58)$$

Putting $x^2 = F^2/\Sigma$ and $y = A^2\Sigma^{\frac{1}{2}}/nF$ gives

$$P(F)dF = 2\Sigma^{-1}FdF\int_0^\infty \exp\left\{-x\left(y+\frac{1}{y}\right)\right\}\frac{dy}{y}\,, \quad (59)$$

so that

$$P(F)dF = 4\Sigma^{-1}K_0(2\Sigma^{-\frac{1}{2}}F)\,FdF \quad (60)$$

(Watson, 1922, p. 183, equation (15)). Transforming to z and integrating with the aid of a standard recurrence relation (Watson, p. 79, equation (5)) gives

$$N(z) = 1-2z^{\frac{1}{2}}K_1(2z^{\frac{1}{2}})\,, \quad (61)$$

which is depicted in Fig. 7 (curve *b*) and tabulated in Table 3, column 1.

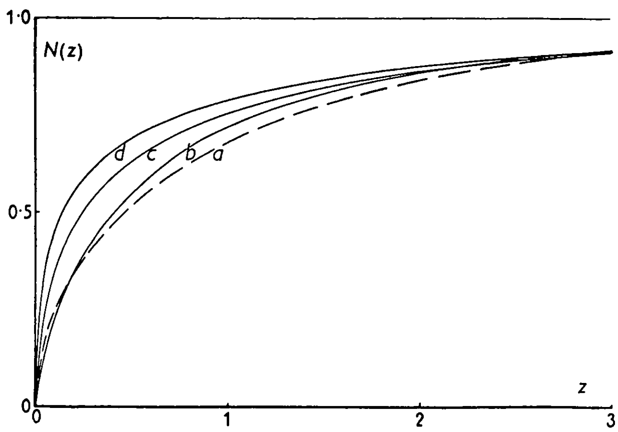

Fig. 7. The cumulative distribution $N(z)$ for a large number of motifs repeated at random, but in parallel orientation (Table 3).
a: Centric (one centrosymmetric motif), or parallel (two non-centrosymmetric parallel motifs).
b: Non-centrosymmetric motif; non-centrosymmetric arrangement.
c: Non-centrosymmetric motif; centrosymmetric arrangement or vice versa.
d: Centrosymmetric motif; centrosymmetric arrangement.

The moments are conveniently evaluated with the aid of the relation (Watson, p. 388)

$$\int_0^\infty K_p(t)t^{q-1}dt = 2^{q-2}\Gamma\left(\frac{q-p}{2}\right)\Gamma\left(\frac{q+p}{2}\right), \qquad (62)$$

and are

$$\nu_1 = \tfrac{1}{4}\pi\Sigma^{\frac{1}{2}}, \qquad (63)$$

$$\nu_2 = \Sigma, \qquad (64)$$

$$\nu_4 = 4\Sigma^2, \qquad (65)$$

whence

$$\varrho = (\pi/4)^2 \fallingdotseq 0\cdot617, \qquad (66)$$

and

$$v = 3. \qquad (67)$$

The $N(z)$ curve closely resembles that for the parallel distribution due to two parallel motifs. The addition to these two of further parallel motifs seems to have only a slight effect on ϱ and $N(z)$; the specific variance, which is so much more sensitive to changes in the distribution of the larger F's, shows a larger change.

4·2. *Centrosymmetric motifs in a non-centrosymmetric arrangement*

In a similar way

$$P(F)dF$$

$$= (2/\pi^3\Sigma n)^{\frac{1}{2}}\int_0^{2\pi}\int_0^\infty \exp\left\{-\frac{F^2n}{2A^2\Sigma}-\frac{A^2}{n}\right\}dAd\alpha dF, \qquad (68)$$

$$= \frac{2F^{\frac{1}{2}}dF}{\pi^{\frac{1}{2}}(2\Sigma)^{\frac{3}{4}}}\int_0^\infty \exp\{-x(y^2+1/y^2)\}dy, \qquad (69)$$

where

$$x^2 = F^2/2\Sigma \quad\text{and}\quad y^2 = (2\Sigma)^{\frac{1}{2}}A^2/nF, \qquad (70)$$

so that

$$P(F)dF = (2/\Sigma)^{\frac{1}{2}}\exp\{-(2/\Sigma)^{\frac{1}{2}}F\}dF, \qquad (71)$$

$$N(z) = 1-\exp\{-(2z)^{\frac{1}{2}}\}, \qquad (72)$$

and the moments are readily determined to be

$$\left.\begin{aligned} \nu_1 &= (\tfrac{1}{2}\Sigma)^{\frac{1}{2}},\\ \nu_2 &= \Sigma,\\ \nu_4 &= 6\Sigma^2, \end{aligned}\right\} \qquad (73)$$

whence and

$$\left.\begin{aligned} \varrho &= \tfrac{1}{2}\\ v &= 5. \end{aligned}\right\} \qquad (74)$$

Values of $N(z)$ are given in Table 3 and are depicted in Fig. 7, curve *c*. It is evident that these results apply equally to the converse case of non-centrosymmetric motifs repeated in a centro-symmetric arrangement. The resulting space group in either scheme is non-centrosymmetric.

4·3. *Centrosymmetric motif in a centrosymmetric arrangement*

For this

$$P(F)dF = (2/\pi\Sigma^{\frac{1}{2}})dF\int_0^\infty \exp\left\{-\frac{F^2n}{2\Sigma A^2}-\frac{A^2}{2n}\right\}\frac{dA}{A} \qquad (75)$$

$$= (dF/\pi\Sigma^{\frac{1}{2}})\int_0^\infty \exp\{-x(y+1/y)\}\frac{dy}{y}, \qquad (76)$$

Table 3. *Statistical data for multiparallel random arrangements*

Non-centrosymmetric motif, non-centrosymmetric random arrangement		Centrosymmetric motif, non-centrosymmetric random arrangement and vice versa	Centrosymmetric motif, centrosymmetric random arrangement	
z	$N(z)$	$N(z)$	z	$N(z)$
0·00	0·0000	0·0000	0·00	0·0000
0·04	0·1263	0·271$_1$	0·05	0·373$_7$
0·09	0·2183	0·360$_6$	0·1	0·460$_8$
0·16	0·3106	0·468$_7$	0·2	0·557$_6$
0·25	0·3981	0·539$_1$	0·3	0·617$_1$
0·36	0·4785	0·591$_2$	0·4	0·659$_9$
0·49	0·5508	0·632$_1$	0·5	0·692$_8$
0·64	0·6150	0·665$_5$	0·6	0·719$_4$
0·81	0·6713	0·693$_6$	0·7	0·741$_6$
1·00	0·7203	0·717$_7$	0·8	0·760$_6$
1·21	0·7626	0·738$_6$	0·9	0·776$_8$
1·44	0·7991	0·756$_9$	1·0	0·791$_0$
1·69	0·8303	0·787$_6$	1·2	0·815$_1$
1·96	0·8569	0·812$_3$	1·4	0·833$_5$
2·25	0·8795	0·832$_9$	1·6	0·850$_3$
2·56	0·8987	0·849$_9$	1·8	0·863$_9$
2·89	0·9150	0·864$_7$	2·0	0·875$_5$
3·24	0·9287	0·893$_1$	2·5	0·899$_4$
3·61	0·9413	0·913$_7$	3·0	0·915$_1$
ϱ	0·617	0·500		0·405
v	3	5		8

where

$$x^2 = F^2/4\Sigma,\ y = A^2\Sigma^{\frac{1}{2}}/Fn\ , \tag{77}$$

so that

$$P(F)dF = (2/\pi\Sigma^{\frac{1}{2}})K_0(F/\Sigma^{\frac{1}{2}})dF \tag{78}$$

(compare equation (60)), and the procedure of § 4·1 gives

$$N(z) = 1-2\pi^{-1}\int_0^{\frac{1}{2}\pi} \exp\{-z^{\frac{1}{2}}\sec\theta\}d\theta\ , \tag{79}$$

$$\left.\begin{aligned} \nu_1 &= 2\pi^{-1}\Sigma^{\frac{1}{2}}\ ,\\ \nu_2 &= \Sigma\ ,\\ \nu_4 &= 9\Sigma^2\ ,\end{aligned}\right\} \tag{80}$$

whence and

$$\left.\begin{aligned} \varrho &= 4/\pi^2 = 0{\cdot}405\ ,\\ v &= 8\ .\end{aligned}\right\} \tag{81}$$

The values of $N(z)$ are given in Table 3 (see also Fig. 7, curve d). The analysis of this paragraph is valid even if none of the centres of symmetry of the motifs coincides with the centres of symmetry of the arrangement, in which unlikely event the unit cell would be non-centrosymmetric.

4·4

Corresponding values of v and ϱ for these cases of random repetition are plotted as squares in Fig. 4, and seem to represent the earlier part of another curve, roughly parallel to those of § 2 and § 3. It is possible to devise systems corresponding to higher points on such a curve, but they are highly improbable and the analysis becomes so complex that their examination is impracticable.

5. Discussion

5·1. *Occurrence*

The various repetition patterns discussed in the preceding sections have resulted from the introduction of symmetry operations (centres of symmetry or translations) unrelated to the space group. It is important to ascertain whether such parallelism of an extended motif could ever occur through space-group symmetry alone. As a result of an extensive, but not exhaustive, search it has been concluded that it can occur only for the ordinary non-primitive cells, in which case the modulation pattern has a simple relation to the reciprocal lattice and results in the familiar and characteristic systematic absences. Parallelism will also occur in projections on to a glide plane, but it is again recognizable directly from the systematic absences produced.

Parallelism of the types envisaged here does not, therefore, appear to occur as a result of space-group symmetry. It can occur, however, as a result of the possession by the molecules of some symmetry elements which are not used in the space group adopted by the crystal. In addition to the examples cited by Lipson & Woolfson (1952) for hypercentrosymmetry we have referred earlier to dibiphenylene ethylene. Further examples are given in Fig. 8(c) and (d). Regular parallel repetition in a straight line or even at random

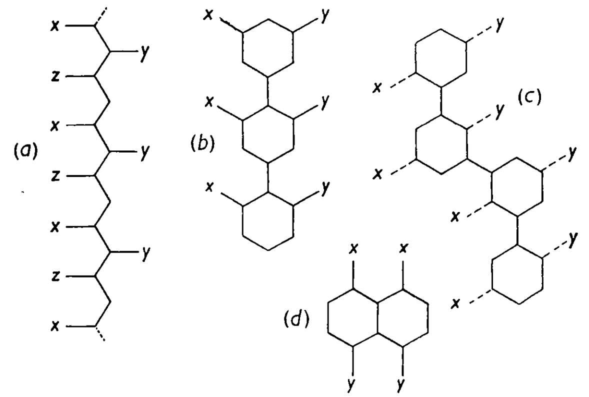

Fig. 8. Examples of molecules exhibiting hypersymmetry.
(a) and (b) Regular repetition in a straight line.
(c) If $X = Y$ this is a perfect example of hypercentrosymmetry ($n = 3$); if $X \neq Y$ it is strictly only hyperparallel ($n = 2$), but would approximate so closely to the former as to be indistinguishable experimentally.
(d) Is strictly an approximation to parallelism, but, unless X, Y are very dissimilar, it approximates very closely to hypercentrosymmetry ($n = 2$).

may occur in some polymers and proteins (Fig. 8(a), (b)), although it is doubtful then whether the repeated motifs would contain more than a fraction of the total scattering power in the unit cell.

5·2. *Recognition of parallelism*

5·2·1. *From inspection or the Patterson map.*—The simpler types of modulation pattern should be evident upon inspection of the weighted reciprocal lattice, but modulation patterns composed of several unrelated fringe systems or the irregular varieties considered in § 4 will not be readily recognizable in this way. Moreover, in many practical problems the structural pseudosymmetry may only approximate to one of those considered here, or may be partial in that the repeated motifs do not account for all the structure. In such cases 'modulation' effects may be observable despite masking, but the foregoing results cannot be expected to hold precisely.

The Patterson synthesis then furnishes more detailed information, for it will contain exceptionally strong peaks due directly to the repetition translations. Thus for the arrangement of § 3 the Patterson map will take the form

$$\mathcal{P}(\mathbf{r}) = \sum_s F^2 \cos(2\pi\mathbf{s}\,.\,\mathbf{r}) \tag{82}$$

$$= \sum_s M^2 \left(\frac{\sin^2 n\psi}{\sin^2 \psi}\right) \cos(2\pi\mathbf{s}\,.\,\mathbf{r})\ , \tag{83}$$

which can be expanded (Whittaker & Watson, 1935, p. 171) as follows:

$$\mathcal{P}(\mathbf{r}) = \sum_s M^2 \cos(2\pi\mathbf{s}.\mathbf{r})\{n+2(n-1)\cos 2\psi + 2(n-2)\cos 4\psi + \ldots + 2\cos 2(n-1)\psi\} \quad (84)$$

$$= \sum_s M^2\{n\cos(2\pi\mathbf{s}.\mathbf{r}) + (n-1)[\cos\{2\pi\mathbf{s}.(\mathbf{r}+\mathbf{d})\} + \cos\{2\pi\mathbf{s}.(\mathbf{r}-\mathbf{d})\}] + \ldots\} \quad (85)$$

This can be interpreted as the superposition of copies of the Patterson map of the motif alone: n copies of the original; $(n-1)$ copies displaced by $+\mathbf{d}$ and an equal number displaced $-\mathbf{d}$; $(n-2)$ copies displaced $+2\mathbf{d}$ and $-2\mathbf{d}$ respectively, and so on.

For the hypersymmetric problem the Patterson function can be written as

$$\mathcal{P}(\mathbf{r}) = \sum_s M^2(2^{n-1}\cos\psi_2\ldots\cos\psi_n)^2\cos(2\pi\mathbf{s}.\mathbf{r})$$

$$= \sum_s M^2 \prod_j^{n-1}(1+\cos 2\psi_j)\cos(2\pi\mathbf{s}.\mathbf{r}) , \quad (86)$$

which can be expanded and interpreted in an analogous fashion as the superposition of displaced copies of the motif Patterson resulting in a number of 'origin' peaks at various points in the cell. Even when there are other atoms in the cell, the repeated motifs will give rise to strong peaks at the same points in Patterson space, but they are then somewhat less conspicuous. Patterson (1949) has already described such peaks occurring in the vector map of a structure containing some parts which conform to what may now be recognized as the Lipson–Woolfson case of hypercentrosymmetry. This approach endorses Patterson's conclusion that to any peak at a point $\mathbf{r}_j$ in the Patterson map of a centrosymmetric structure there is 'some centrosymmetry about the point $\frac{1}{2}\mathbf{r}_j$ in the structure'; the stronger the peak the more extensive is the centrosymmetry about that point.

We see here an analogue of this for non-centrosymmetric structures; namely the well-known fact that to any peak at a point $\mathbf{r}_j$ in Patterson space there correspond some equivalent intervectors in the structure. When the peak is very strong, and cannot be accounted for by heavy-atom vectors, it indicates some measure of non-crystallographic parallelism. The [001] Patterson map of menthol ($C3_1$) shows two exceptionally strong and sharp peaks of this type which indicate extensive parallelism.

Inspection of the weighted reciprocal lattice and the study of the Patterson map are evidently then the most suitable methods in any attempt to detect parallelism, especially since they will reveal partial parallelism. In particular, there should never be any difficulty in practice in deciding whether a distribution of the centric type has arisen from centrosymmetry or the parallelism of two non-centrosymmetric motifs in a non-centrosymmetric cell.

5·2·2. *Recognition by intensity statistics.*—After the foregoing remarks it may be wondered why hypersymmetric distributions have been investigated statistically. Aside from their interest as mathematical curiosities, however, these results may assist in the identification of the kind of repetition, and will make users of statistical methods aware of the existence of additional distribution types. In particular, if the statistical criteria determined in any problem do not indicate unambiguously a centric or an acentric distribution, the Patterson map should be examined for evidence of parallelism; this, when present, always increases the dispersion above that characteristic of the space group. The interpretation of any of the criteria for these more highly dispersive distributions is less easy. The margin of discrimination diminishes for the $N(z)$ plot as the multiplicity of repetition increases, but reference to Fig. 4 shows that a simultaneous determination of v and ϱ may give a more reliable indication of the type of arrangement. The value of v is increased by the presence of experimental errors of intensity estimation, and it may also be necessary to make allowance for the limited number of atoms in the motif (§ 5·3·1). The interpretation of such results may be ambiguous whenever the parallelism is inexact or only partial. Chemical evidence will usually give warning of the possibility of parallelism; the combined evidence from inspection of the reciprocal lattice, the Patterson map and the statistical criteria will then demonstrate its existence and may indicate its extent.

5·3

5·3·1. *Limitation of number of atoms.*—In the original description of the variance test (Wilson, 1951) it was shown that V takes the form $\Sigma^2-\Sigma_4$ for the acentric distribution and $2\Sigma^2-3\Sigma_4$ for the centric distribution, where $\Sigma_4 = \sum_j f_j^4$ for all atoms in the unit cell.

The second term allows for finiteness of the number of atoms in the asymmetric unit. As the repeated motif is never likely to contain many atoms, and as this term appears to have greater significance in the centric case, it was considered desirable to determine its importance in the higher members of the hypersymmetric sequence. For this purpose the central moments are calculated from the moments of the distributions of the individual atomic variables, random as a function of $\mathbf{r}_i$, which make up the structure factor. These are

$$\xi_i = 2^n f_i \cos(2\pi\mathbf{s}.\mathbf{r}_i)\cos\psi_2\ldots\cos\psi_n . \quad (87)$$

Averaging over regions of reciprocal space for which the ψ's are constant gives for the second, fourth and sixth central moments

$$\mu_{n,2}^{(i)} = 2^{2n-1} f_i^2 \cos^2\psi_2\ldots\cos^2\psi_n , \quad (88)$$

$$\mu_{n,4}^{(i)} = 3.2^{4n-3} f_i^4 \cos^4\psi_2\ldots\cos^4\psi_n , \quad (89)$$

$$\mu_{n,6}^{(i)} = 5.2^{6n-4} f_i^6 \cos^6\psi_2\ldots\cos^6\psi_n . \quad (90)$$

Hence, from results given by Cramér (1946, pp. 188–192),

$$\mu_{n,2} = \sum_i \mu_{n,2}^{(i)} = 2^{n-1}\cos^2\psi_2\ldots\cos^2\psi_n\Sigma\,, \tag{91}$$

$$\begin{aligned}\mu_{n,4} &= \sum_i \mu_{n,4}^{(i)} - 3\sum_i[\mu_{n,2}^{(i)}]^2 + 3[\sum_i \mu_{n,2}^{(i)}]^2 \\ &= 3\cos^4\psi_2\ldots\cos^4\psi_n[2^{2n-2}\Sigma^2 - 2^{3n-3}\Sigma_4]\,,\end{aligned} \tag{92}$$

$$\begin{aligned}\mu_{n,6} &= \sum_i \mu_{n,6}^{(i)} - 15\sum_i \mu_{n,2}^{(i)}\mu_{n,4}^{(i)} + 30\sum_i[\mu_{n,2}^{(i)}]^3 \\ &\quad + 15\mu_{n,2}\mu_{n,4} - 30\mu_{n,2}^3 \\ &= 5\cos^6\psi_2\ldots\cos^6\psi_n[3\,.\,2^{3n-3}\Sigma^3 - 9\,.\,2^{4n-4}\Sigma\Sigma_4 + 2^{5n-2}\Sigma_6]\,,\end{aligned} \tag{93}$$

where $\Sigma = 2^n\sum_i f_i^2$, $\Sigma_4 = 2^n\sum_i f_i^4$ and $\Sigma_6 = 2^n\sum_i f_i^6$, the summations including all atoms in the motif.

On averaging over all reciprocal space it follows that

$$\left.\begin{aligned}\langle\mu_{n,2}\rangle &= \Sigma\,, \\ \langle\mu_{n,4}\rangle &= 3^n.2^{-n+1}\Sigma^2 - 3^n\Sigma_4\,, \\ \text{and}\quad \langle\mu_{n,6}\rangle &= 3\,.\,5^n2^{-n+1}\Sigma^3 - 9\,.\,5^n\Sigma\Sigma_4 + 5^n2^{n+2}\Sigma_6\end{aligned}\right\} \tag{94}$$

the leading terms in each expression corresponding with equation (33). The variance is

$$\begin{aligned}V_n &= \langle\mu_{n,4}\rangle - \langle\mu_{n,2}\rangle^2 \\ &= [3^n2^{-n+1}-1]\,\Sigma^2 - 3^n\Sigma_4\,,\end{aligned} \tag{95}$$

which, for $n = 0$ and 1, agrees with the results already quoted. The importance of the correction term increases rapidly with n, becoming of the same order as the term in Σ^2 for $n \sim \log_2 N$, where N is the total number of atoms in the motif. The correction will, therefore, often be significant.

5·3·2. *Series expansions.*—The distribution $P_n(F)$ of equation (12), which appears to have no simple analytic expression, may be expanded as a series involving the Gaussian distribution and its derivatives. The general distribution function $f(x)$ is given by the Gram–Charlier type-A expansion (Cramér, 1946, p. 233)

$$\begin{aligned}f(x) &= \Phi(x) + \frac{1}{4!}[\mu_4/\mu_2^2 - 3]\,\Phi^{\text{IV}}(x) \\ &\quad + \frac{1}{6!}[\mu_6/\mu_3^2 - 15\mu_4/\mu_2^2 + 30]\,\Phi^{\text{VI}}(x) + \ldots\,,\end{aligned} \tag{96}$$

where $\Phi(x)$ is the Gaussian distribution $(2\pi)^{-\frac{1}{2}}\exp(-\frac{1}{2}x^2)$, Φ^{IV} and Φ^{VI} are its fourth and sixth derivatives, and, in the present application, $x = \mu_2{}^{-\frac{1}{2}}F$. Then

$$\begin{aligned}P_n(F) &= \Sigma^{-\frac{1}{2}}\{\Phi(\Sigma^{-\frac{1}{2}}F) \\ &\quad + (3^{n-1}2^{-n-2} - \tfrac{1}{8} - 3^{-n-1}2^{-3}\Sigma_4/\Sigma^2)\Phi^{\text{IV}}(\Sigma^{-\frac{1}{2}}F) \\ &\quad + [3^{-1}2^{-n-3}(5^{n-1}-3^n) + \tfrac{1}{24} - 2^{-4}(5^{n-1}3^{-n-1})\Sigma_4/\Sigma^2 \\ &\quad + 3^{-2}5^{n-1}2^{n-2}\Sigma_6/\Sigma^3]\,\Phi^{\text{VI}}(\Sigma^{-\frac{1}{2}}F) + \ldots\}\,.\end{aligned} \tag{97}$$

So far as the accuracy goes (no account has been taken of atoms in special positions in the above calculation) this reduces to equation (71) of Hauptman & Karle (1952) for $n = 1$.

Unfortunately the terms written are not enough to give reasonable representations of P_0 and P_2, and it would be laborious to find the coefficients of further terms.

5·4. *Reliability index*

It has been shown that for a randomly 'wrong' structure the reliability index, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ cannot exceed 2, and that for the acentric and centric distributions its most likely values are $R_0 = 2-\sqrt{2} = 0·586$ and $R_1 = 2\sqrt{2}-2 = 0·828$ (Wilson, 1950). Efforts to calculate the function $G_n(F)$ required to evaluate R_n have not been successful, even for $n = 2$. However, the proportion of very weak reflexions increases rapidly for $n > 1$, $P_n(0)$ being infinite, and it seems likely that $R_{n>1}$ will considerably exceed $R_1 = 0·828$. The general form of the v versus ϱ graph (Fig. 4) makes it likely that this will also apply to the other types discussed here. Large values of R for trial structures containing parallelism are, therefore, less discouraging than they would be in the absence of parallelism, and they may be expected to drop rapidly on refinement, though probably not reaching quite such low final values. Tetraphenyl-cyclobutane had 0·37, 0·26, 0·19, 0·16 as the values of R in successive stages of refinement (Dunitz, 1949).

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References

Cramér, H. (1946). *Mathematical Methods of Statistics.* Princeton: University Press.
Dunitz, J. D. (1949). *Acta Cryst.* **2**, 1.
Fejér, L. (1911). *Ann. Éc. normale,* [3], **28**, 63.
Fenimore, C. P. (1948). *Acta Cryst.* **1**, 295.
Hauptman, H. & Karle, J. (1952). *Acta Cryst.* **5**, 48.
Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.
Lipson, H. & Woolfson, M. M. (1952). *Acta Cryst.* **5**, 680.
Patterson, A. L. (1949). *Acta Cryst.* **2**, 339.
Watson, G. N. (1922). *A Treatise on the Theory of Bessel Functions.* Cambridge: University Press.
Watson, G. N. (1930). *Quart. J. Math.* **1**, 311.
Whittaker, E. T. & Watson, G. N. (1935). *A Course of Modern Analysis.* Cambridge: University Press.
Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.
Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.
Wilson, A. J. C. (1950). *Acta Cryst.* **3**, 297.
Wilson, A. J. C. (1951). *Research, Lond.* **4**, 141.