of the ordinary rotation function, as all molecules present are accounted for. In fact, in the test case, the correlation coefficient is consistent with the fraction of the structure present in the search model. This symmetry-corrected rotation function may therefore provide a more objective measure of the reliability of possible rotation function solutions.

The ideas presented here also have implications for symmetry effects in self-rotation functions. Our analysis suggests that signal amplification will occur at orientations that leave the point-group symmetry of the crystal invariant. For example, in space group *P*3, we expect anomalously high peaks at orientations corresponding to 180° rotations about axes perpendicular to the threefold crystallographic symmetry axis.

Discussions with D. C. Rees, B. T. Hsu and C. E. Nordman are appreciated. This is publication no. 5597-MB of the Research Institute of Scripps Clinic.

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Cauchy Distribution, Intensity Statistics and Phases of Reflections from Crystal Planes

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Abstract

Recently near-Gaussian distributions have been of much interest in the field of crystallographic statistics. In the present work, expressions for a truncated Cauchy distribution corresponding to acentric and centric cases have been derived. Expressions for P_+, the probability of sign relations for centric crystals, and for P_φ, the probability of the tangent relationship for acentric crystals, have been derived on the basis of the Cauchy distribution of structure factor components. Theoretical $N(Z)$ curves for centric and acentric Cauchy distributions have been compared with those for acentric, centric and bicentric Gaussian distributions. The $N(Z)$ curve for the Cauchy acentric distribution follows closely that for the Gaussian acentric up to $Z=0{\cdot}5$. It then takes an upward turn and surpasses the Gaussian bicentric curve at high Z values. A similar trend is shown by the $N(Z)$ curve for the Cauchy centric distribution after being approximately intermediate between the Gaussian centric and bicentric cases up to $Z=0{\cdot}5$. The results of P_+ and P_φ have been compared with some known crystal data and the agreement is quite satisfactory for the cases studied.

1. Introduction

The intensity statistics introduced by Wilson (1949, 1950) and its further extension to the phase problem by Cochran & Woolfson (1955) and by Cochran (1955) were based on the hypothesis that the structure-factor components obey the Gaussian probability distribution law. Bertaut (1955, 1960), Klug (1958), Mitra & Belgaumkar (1973), Shmueli (1979), Shmueli & Wilson (1981) and others have used near-Gaussian functions like the Gram-Charlier and Edgeworth

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series, as well as Fourier and Fourier–Bessel functions (Wilson, 1986) to represent the distribution law of the structure amplitudes. Mitra & Ghosh (1982) have shown that the $N(Z)$ test indicates which type of distribution is obeyed by the crystal.

One near-Gaussian distribution - the Cauchy or Lorentzian distribution, having no finite moment apart from above and the first - is looked upon with suspicion. But one never works with a distribution function ranging between $\pm\infty$; the function is cut off on the surface of the sphere of reflection. Thus we are actually dealing with a truncated Cauchy distribution function for which second and higher moments exist. The aim of the present work is to explore the possibilities of the truncated Cauchy functions as distribution functions in crystallographic statistics. Expressions for P_+, the probability of the sign relation for centric crystals, and P_φ, the probability of the tangent relationship for acentric crystals, are derived. Theoretical $N(Z)$ curves for acentric and centric Cauchy distributions are compared with acentric, centric and bicentric Gaussian distributions and the results are applied to some known crystal structures.

2. The distribution function and its consequences

Let us consider a crystal with N equal atoms placed randomly in a $P1$ unit cell. The normalized structure factor $E_\mathbf{h}$ for index $\mathbf{h}$ is given by

$$E_\mathbf{h} = F_\mathbf{h} / \left(\sum_{j=1}^{N} f_j^2 \right)^{1/2}$$

where $F_\mathbf{h}$ is the crystal structure factor and f_j the scattering factor of the jth atom.

The cumulative probability distribution $N(Z)$ is defined by

$$N(Z) = \int_0^Z P(Z)\, \mathrm{d}Z$$

where $P(Z)\,\mathrm{d}Z$ is the probability of Z lying between Z and $Z+\mathrm{d}Z$, Z being equal to $|E|^2$.

(i) *Acentric case*

Let the probability distribution function be represented as

$$P(E) = C/(1+E^2), \qquad (1)$$

where C is the normalization constant and comes out to be $1/\pi$ within the limits $\pm\infty$ and $2/\pi$ for the limits between 0 and ∞.

Let the probability distribution function be of the form

$$P(E) = (m/\pi)[1/(1+E^2)] \quad (m>1), \qquad (1a)$$

as for the truncated Cauchy distribution the limits are not specified and m is an adjustable parameter. Let

$$E_\mathbf{h} = X_\mathbf{h} + iY_\mathbf{h}$$

where $X_\mathbf{h}$ and $Y_\mathbf{h}$ are the real and imaginary components of $E_\mathbf{h}$.

The joint probability distribution $P(X_\mathbf{h}, Y_\mathbf{h})$ of $X_\mathbf{h}$ having a value between $X_\mathbf{h}$ and $X_\mathbf{h}+\mathrm{d}X_\mathbf{h}$ and of $Y_\mathbf{h}$ between $Y_\mathbf{h}$ and $Y_\mathbf{h}+\mathrm{d}Y_\mathbf{h}$ is given by

$$P(X_\mathbf{h}, Y_\mathbf{h})\,\mathrm{d}X_\mathbf{h}\,\mathrm{d}Y_\mathbf{h} = (m^2/\pi^2)[1/(1+X_\mathbf{h}^2)][1/(1+Y_\mathbf{h}^2)]\,\mathrm{d}X_\mathbf{h}\,\mathrm{d}Y_\mathbf{h}. \qquad (1b)$$

This gives the probability of a point $(X_\mathbf{h}, Y_\mathbf{h})$ having a structure factor $E_\mathbf{h}$ within the area of $\mathrm{d}X_\mathbf{h}\,\mathrm{d}Y_\mathbf{h}$ in the complex plane containing $(X_\mathbf{h}, Y_\mathbf{h})$. For all points, the probability of the structure factor lying in the range $|E_\mathbf{h}|$ and $|E_\mathbf{h}|+\mathrm{d}|E_\mathbf{h}|$ is given by

$$P(X_\mathbf{h}, Y_\mathbf{h})2\pi|E_\mathbf{h}|\,\mathrm{d}|E_\mathbf{h}| = P(|E_\mathbf{h}|^2)\,\mathrm{d}|E_\mathbf{h}|^2, \quad P(|E_\mathbf{h}|^2) = \pi P(X_\mathbf{h}, Y_\mathbf{h}). \qquad (1c)$$

From (1b) and (1c) we find that the distribution of $Z=|E|^2$ for Z lying between Z and $Z+\mathrm{d}Z$ is given by

$$P(Z) = (m^2/\pi) \times [(1+Z)\cos^2(2\varphi_\mathbf{h}) + (1+Z/2)^2\sin^2(2\varphi_\mathbf{h})]^{-1}, \qquad (2)$$

where $\varphi_\mathbf{h} = \tan^{-1} Y_\mathbf{h}/X_\mathbf{h}$. The cumulative probability distribution $N_0(Z)$ obtained from (2) is

$$N_0(Z) = (m^2/\pi)\int_0^Z\int_0^\pi [(1+Z)\cos^2(2\varphi_\mathbf{h}) + (1+Z/2)^2\sin^2(2\varphi_\mathbf{h})]^{-1}\,\mathrm{d}\varphi_\mathbf{h}\,\mathrm{d}Z = 4m^2\{\tan^{-1}[(1+Z)]^{1/2} - \pi/4\}. \qquad (3)$$

The joint probability of $|E_\mathbf{h}|$ lying between $|E_\mathbf{h}|$ and $|E_\mathbf{h}|+\mathrm{d}|E_\mathbf{h}|$ and that of $\varphi_\mathbf{h}$ lying between $\varphi_\mathbf{h}$ and $\varphi_\mathbf{h}+\mathrm{d}\varphi_\mathbf{h}$ about their mean values as obtained from (1b) is given by

$$P(\varphi_\mathbf{h}, |E_\mathbf{h}|) = (m^2/\pi)\{1 + (|E_\mathbf{h}| - \langle|E_\mathbf{h}|\rangle)^2 + [(|E_\mathbf{h}| - \langle|E_\mathbf{h}|\rangle)^4/8] \times [1-\cos 4(\varphi_\mathbf{h} - \langle\varphi_\mathbf{h}\rangle)]\}^{-1}.$$

$\langle|E_\mathbf{h}|\rangle$ and $\langle\varphi_\mathbf{h}\rangle$ are the mean values of $|E_\mathbf{h}|$ and $\varphi_\mathbf{h}$ respectively. From this, after some simple calculations, we arrive at the expression

$$P(\varphi_\mathbf{h}, |E_\mathbf{h}|, E_\mathbf{k}, E_{\mathbf{h}-\mathbf{k}}) = (m^2/\pi)[1 + (|E_\mathbf{h}| - N^{-1/2}|E_\mathbf{k}E_{\mathbf{h}-\mathbf{k}}|)^2 + \tfrac{1}{8}(|E_\mathbf{h}| - N^{-1/2}|E_\mathbf{k}E_{\mathbf{h}-\mathbf{k}}|)^4]^{-1} \times [1-\cos 4(\varphi_\mathbf{h} - \langle\varphi_\mathbf{h}\rangle)]^{-1} \qquad (4)$$

$$= (m^2/\pi)[1 + r^2 + (r^4/8)(1-\cos 4\varphi_{\mathbf{h}\mathbf{k}})]^{-1}, \qquad (4a)$$

where

$$\begin{aligned} r &= |E_{\mathbf{h}}| - N^{-1/2}|E_{\mathbf{k}}E_{\mathbf{h-k}}| \\ \varphi_{\mathbf{hk}} &= \varphi_{\mathbf{h}} - \langle\varphi_{\mathbf{h}}\rangle \\ \langle\varphi_{\mathbf{h}}\rangle &= \varphi_{\mathbf{k}} + \varphi_{\mathbf{h-k}} \\ \langle|E_{\mathbf{h}}|\rangle &= N^{-1/2}|E_{\mathbf{k}}E_{\mathbf{h-k}}|. \end{aligned} \qquad (4b)$$

The conditional probability $P(\varphi_{\mathbf{h}}||E_{\mathbf{h}}|, E_{\mathbf{k}}, E_{\mathbf{h-k}})$, written as $P(\varphi_{\mathbf{h}})$ (since $|E_{\mathbf{h}}|$, $E_{\mathbf{k}}$, $E_{\mathbf{h-k}}$ are known), is obtained from

$$P(\varphi_{\mathbf{h}}) = \frac{P(\varphi_{\mathbf{h}}, |E_{\mathbf{h}}|, E_{\mathbf{k}}, E_{\mathbf{h-k}})}{\int_0^\pi P(\varphi_{\mathbf{h}}, |E_{\mathbf{h}}|, E_{\mathbf{k}}, E_{\mathbf{h-k}})\, \mathrm{d}\varphi_{\mathbf{h}}}. \qquad (5)$$

Evaluating the integral of the demoninator of (5) and substituting the value of r *etc.* from (4b), we get

$$P(\varphi_{\mathbf{h}}) = \frac{1}{2\pi}\frac{(1+A)A^{1/2}}{A + B(1-\cos 4\varphi_{\mathbf{hk}})} \qquad (6)$$

where

$$A = 1 + r^2 = 1 + |E_{\mathbf{h}}|^2 + \frac{|E_{\mathbf{k}}E_{\mathbf{h-k}}|^2}{N} - \frac{2|E_3|}{N^{1/2}} \qquad (6a)$$

$$B = \frac{r^4}{8} = \frac{1}{8}\left[|E_{\mathbf{h}}|^4 + \frac{2|E_3|}{N^{1/2}}\left(\frac{3|E_3|}{N^{1/2}} - 2|E_{\mathbf{h}}|^2 - 2\frac{|E_{\mathbf{k}}E_{\mathbf{h-k}}|^2}{N}\right) + \frac{|E_{\mathbf{k}}E_{\mathbf{h-k}}|^4}{N^2}\right] \qquad (6b)$$

and

$$|E_3| = |E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|.$$

Again, for $P(\varphi_{\mathbf{h}})$ to be maximum in (6), the denominator would be minimum with

$$\frac{\mathrm{d}}{\mathrm{d}\varphi_{\mathbf{h}}}[A + B(1-\cos 4\varphi_{\mathbf{hk}})] = 0$$

(A and B are fixed and non-zero quantities).

This gives

$$\varphi_{\mathbf{h,k}} = \varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h-k}} = 0, \qquad (7)$$

which is the triplet relationship. Thus

$$\mathrm{d}\varphi_{\mathbf{h,k}} = \mathrm{d}\varphi_{\mathbf{h}} \quad (\text{since } \varphi_{\mathbf{k}} \text{ and } \varphi_{\mathbf{h-k}} \text{ are known})$$

and the distribution of $\varphi_{\mathbf{h}}$ is identical to that of $\varphi_{\mathbf{hk}}$.

(ii) *Centric case*

Let the distribution be given by

$$P_1(E) = C'/(1+E^2/2), \qquad (8)$$

C' being the constant of normalization which is $1/(\pi\sqrt{2})$ within the limits $\pm\infty$ and $\sqrt{2}/\pi$ for limits 0 and ∞. Thus the distribution will be

$$P(E) = (m/\pi\sqrt{2})(1+E^2/2)^{-1}, \qquad (8a)$$

m having the same significance as in the acentric case.

The probability density function as obtained from (8a) is given by

$$P_1(E)\,\mathrm{d}(E) = (m/\pi\sqrt{2})(1+E^2/2)^{-1}\,\mathrm{d}(E). \qquad (9)$$

With this formalism, the expression for $N_1(Z)$ is

$$N_1(Z) = (4m/\pi)\tan^{-1}(Z/2)^{1/2}. \qquad (10)$$

If $\langle E_{\mathbf{h}}\rangle$ is the mean of the structure factors, we have

$$P(E_{\mathbf{h}}) = (m/\pi\sqrt{2})[1 + \tfrac{1}{2}(E_{\mathbf{h}} - \langle E_{\mathbf{h}}\rangle)^2]^{-1}. \qquad (11)$$

Evaluating the mean value of $E_{\mathbf{h}}$ (Woolfson, 1954) and substituting this in (11), we get

$$P(E_{\mathbf{h}}) = (m/\pi\sqrt{2})[1 + \tfrac{1}{2}(E_{\mathbf{h}} - N^{-1/2}E_{\mathbf{k}}E_{\mathbf{h-k}})^2]^{-1}. \qquad (12)$$

When Sayre's probabilistic relation $E_{\mathbf{h}} \simeq E_{\mathbf{k}}E_{\mathbf{h-k}}$ is valid $E_{\mathbf{h}}$ will have the same sign as $E_{\mathbf{k}}E_{\mathbf{h-k}}$. Indicating by P_+ or P_- respectively the probability of $E_{\mathbf{h}}$ having the same sign as $E_{\mathbf{k}}E_{\mathbf{h-k}}$ and the reverse, we have

$$\frac{P_-}{P_+} = \frac{1 + \frac{1}{2}(E_{\mathbf{h}} - N^{-1/2}E_{\mathbf{k}}E_{\mathbf{h-k}})^2}{1 + \frac{1}{2}(E_{\mathbf{h}} + N^{-1/2}E_{\mathbf{k}}E_{\mathbf{h-k}})^2}, \qquad (13)$$

and after some simplifications, we finally obtain

$$P_+ = \frac{1}{2} + \frac{1}{2}\left[\frac{N^{-1/2}|E_{\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{h-k}}|}{1 + \frac{1}{2}(|E_{\mathbf{h}}|^2 + N^{-1}|E_{\mathbf{k}}E_{\mathbf{h-k}}|^2)}\right]. \qquad (14)$$

Equation (14) can be used to estimate the sign of $|E_{\mathbf{h}}|$.

3. Results

The $N(Z)$ functions have been calculated from (3) and (10) by putting $m = 1$ when the function reaches the value of one for $Z = 2$ in centric and $Z = 1{\cdot}83$ in acentric cases, and these are shown in Fig. 1 along with Gaussian acentric, centric and bicentric cases. The Cauchy and Gaussian acentric curves are nearly the same up to $Z = 0{\cdot}5$ and then the difference increases gradually, the Cauchy acentric curve going beyond the Gaussian bicentric and Cauchy centric curves.

The Cauchy centric curve is approximately intermediate between the Gaussian centric and bicentric

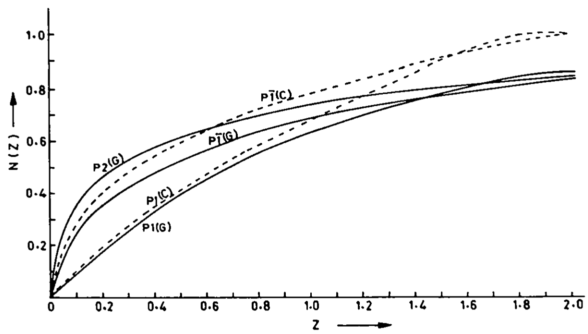

Fig. 1. Comparison of the theoretical distribution $N(Z)$ for Gaussian (solid lines) and Cauchy (broken lines) distributions.

Table 1. *Probability calculations for signs of reflections for α-naphthil*

$|E_h|$ is given by the figures within the brackets; the figures outside the brackets are the Miller indices of the reflection.

Entry number	Magnitude of E_h	Sign of E_h	Magnitude of E_k	Sign of E_k	Magnitude of E_{h-k}	Sign of E_{h-k}	Observed signs of E_kE_{h-k}	Observed signs of E_h	Values of P_+ from Cauchy distribution	Values of P_+ from Gaussian distribution*
1	062 (2·961)	−	$\bar{5}1\bar{2}$ (1·841)	−	554 (2·036)	−	+	−	0·66	0·97
2	115 (3·694)	+	435 (2·584)	+	$\bar{3}\bar{2}0$ (2·129)	−	−	+	0·68	1·00
3	$\bar{6}3\bar{5}$ (2·596)	+	$\bar{3}1\bar{5}$ (2·262)	−	$\bar{3}40$ (1·969)	+	−	+	0·68	0·97
4	$\bar{1}\bar{1}\bar{5}$ (3·694)	+	$\bar{9}4\bar{7}$ (2·279)	+	$8\bar{5}2$ (2·053)	−	−	+	0·66	0·99
5	$\bar{8}\bar{2}6$ (2·681)	+	$\bar{4}\bar{6}2$ (1·867)	−	$\bar{4}44$ (1·345)	+	−	+	0·60	0·88
6	$6\bar{6}2$ (2·908)	+	303 (2·062)	−	$3\bar{2}\bar{1}$ (1·819)	+	−	+	0·65	0·96
7	115 (3·694)	+	$\bar{4}33$ (1·416)	−	$5\bar{2}2$ (1·510)	+	−	+	0·57	0·91
8	$\bar{3}\bar{2}\bar{4}$ (2·716)	−	$\bar{5}2\bar{2}$ (1·724)	+	$2\bar{4}\bar{2}$ (1·694)	+	+	−	0·62	0·91
9	$1\bar{4}1$ (1·947)	+	$\bar{4}75$ (2·170)	+	$4\bar{3}4$ (1·916)	+	+	+	0·69	0·91
10	$\bar{7}42$ (1·971)	−	$\bar{3}0\bar{1}$ (3·317)	+	$\bar{4}43$ (1·946)	−	−	−	0·80	0·90
11	301 (3·317)	+	274 (2·495)	+	$1\bar{7}5$ (2·431)	+	+	+	0·71	1·00
12	$3\bar{1}1$ (2·959)	+	$\bar{4}0\bar{1}$ (2·910)	−	$7\bar{1}2$ (2·052)	−	+	+	0·72	0·99
13	062 (2·961)	−	$86\bar{2}$ (4·721)	+	$\bar{8}04$ (2·762)	−	−	−	0·89	1·00
14	$4\bar{4}\bar{2}$ (2·577)	−	$\bar{6}1\bar{2}$ (2·958)	+	$10\bar{5}0$ (3·031)	−	−	−	0·82	1·00

* P_+ (Gaussian distribution) is calculated from $P_+ = \frac{1}{2} + \frac{1}{2}\tanh(N^{-1/2}|E_hE_kE_{h-k}|)$.

curves up to $Z = 0·5$. It has the same value at $Z = 0·6$ as the Gaussian bicentric curve and after that it ascends, gradually surpassing the Gaussian bicentric case at high Z values.

Fig. 2 shows the experimental $N(Z)$ plots for betulin diacetate (Das, Mukherjee & Ray, 1983) crystallizing in space group $P2_12_12_1$ along with the theoretical Cauchy acentric distribution curve. The $N(Z)$ plots reveal quite well that the distribution is of Cauchy acentric type. The programme *MULTAN*78

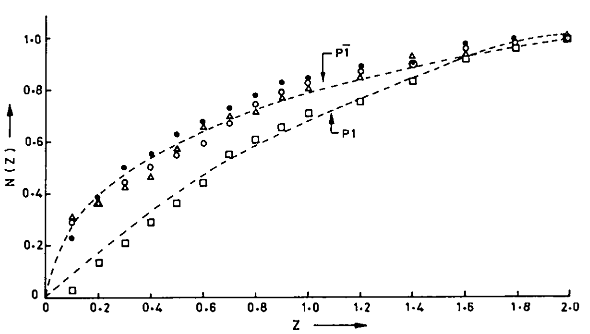

Fig. 2. Comparison of theoretical Cauchy $N(Z)$ values with experimental data for betulin diacetate (squares), α-naphthil (open circles), 2,6-dibutyryl-4-methylphenol (triangles) and 5,9-dimethoxy-3,3,8-trimethyl-7,10-dihydro-3*H*-naphtho[2,1-*b*]-pyran-7,10-dione (solid circles).

(Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) showed acentric distribution of intensity.

In the same figure are shown the experimental $N(Z)$ values of α-naphthil (Mukherjee, Biswas, Ray & Sen, 1987), 2,6-dibutyryl-4-methylphenol (Ray & Sen Gupta, 1986), both crystallizing in space group $P\bar{1}$ and 5,9-dimethoxy-3,3,8-trimethyl-7,10-dihydro-3*H*-naphtho[2,1-*b*]pyran-7,10-dione (Hall, Raston & White, 1978) crystallizing in space group $P2_1/n$. It is observed that the $N(Z)$ values of the three structures agree fairly well with the theoretical centrosymmetric distribution of Cauchy type. The program *NORMAL* (*MULTAN*80; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) gave hypersymmetric $N(Z)$ values for both the $P\bar{1}$ crystals, and the third crystal had a history of *MULTAN* failures. Tables 1 and 2 show the observed magnitudes and signs of the structure amplitudes with the probability values calculated therefrom for α-naphthil and 2,6-dibutyryl-4-methylphenol respectively.

Sayre's (1952) sign relationship for $P\bar{1}$ crystals demands that E_kE_{h-k} has the same sign as that of E_h so that the product will be positive. The probability for this to happen if the structure-factor components have a Gaussian distribution has been calculated by Cochran & Woolfson (1955). In Table 1, entry 4 shows that the probability of the sign of reflection $\bar{1}\bar{1}\bar{5}$ being negative is 99% according to the Gaussian

Table 2. *Probability calculations for signs of reflections for* 2,6-*dibutyryl*-4-*methylphenol*

$|E_h|$ is given by the figure within the brackets; the figures outside the brackets are the Miller indices of the reflection.

Entry number	Magnitude of E_h	Sign of E_h	Magnitude of E_k	Sign of E_k	Magnitude of E_{h-k}	Sign of E_{h-k}	Observed signs of E_kE_{h-k}	Observed signs of E_h	Values of P_+ from Cauchy distribution	Values of P_+ from Gaussian distribution*
1	155 (1·261)	+	236 (1·773)	−	$\bar{1}2\bar{1}$ (1·327)	+	−	+	0·63	0·73
2	122 (2·789)	+	$4\bar{3}\bar{3}$ (1·416)	−	$\bar{3}55$ (1·216)	+	−	+	0·55	0·83
3	$3\bar{5}8$ (2·600)	+	$\bar{1}\bar{2}3$ (1·239)	+	$4\bar{3}5$ (1·230)	−	−	+	0·57	0·79
4	$30\bar{1}$ (1·927)	+	$1\bar{3}\bar{4}$ (1·220)	+	233 (2·008)	−	−	+	0·58	0·83
5	$4\bar{3}3$ (1·498)	−	$30\bar{1}$ (1·927)	+	$1\bar{3}4$ (1·220)	+	+	−	0·63	0·77
6	$\bar{3}23$ (2·104)	−	200 (1·394)	−	$\bar{5}23$ (2·319)	−	+	−	0·68	0·82
7	$\bar{3}\bar{2}\bar{4}$ (2·716)	−	$\bar{5}2\bar{2}$ (1·724)	−	$2\bar{4}\bar{2}$ (1·694)	−	+	−	0·64	0·94
8	$\bar{2}1\bar{4}$ (2·770)	+	$\bar{5}3\bar{2}$ (1·896)	+	$3\bar{2}\bar{2}$ (1·105)	−	−	+	0·60	0·88
9	$\bar{1}1\bar{1}$ (1·246)	+	$\bar{2}\bar{6}2$ (2·788)	−	$17\bar{3}$ (1·574)	−	+	+	0·72	0·86
10	138 (1·488)	−	$2\bar{1}0$ (2·064)	−	$\bar{1}48$ (3·394)	+	−	−	0·81	0·97
11	$22\bar{5}$ (1·957)	+	$\bar{1}7\bar{1}$ (2·905)	+	$3\bar{5}\bar{4}$ (2·175)	+	+	+	0·80	0·98
12	425 (1·954)	−	237 (2·204)	−	$2\bar{1}\bar{2}$ (3·657)	+	−	−	0·84	1·00

* P_+ (Gaussian distribution) is calculated from $P_+ = \frac{1}{2} + \frac{1}{2}\tanh(N^{-1/2}|E_hE_kE_{h-k}|)$.

distribution and that the probability calculated from (14) assuming the distribution to be of the truncated Cauchy form is 66%. The actual sign of the reflection, after solving the structure (α-naphthil), is found to be positive and similar results are shown in entries 1–8 in the same table. In Table 2, it is observed that the probability for the reflection $\bar{3}\bar{2}\bar{4}$ (entry 7) to be positive is 94% according to the Gaussian distribution and that from (14) is 64% while the actual sign of the reflection is found to be negative and other similar results are shown in entries 1–8. Again, the values of the probabilities of 70% and higher, shown in entries 9–14 in Table 1 and in entries 9–12 in Table 2, indicate the correct signs of structure amplitudes for the truncated Cauchy distribution. The Cauchy distribution [(14)] shows that the value of P_+ depends not only on the product $N^{-1/2}|E_hE_kE_{h-k}|$, but also on the sum of the two squares, *i.e.* $|E_h|^2 + N^{-1}|E_hE_kE_{h-k}|^2$. Thus the truncated Cauchy distribution gives a better estimate of the crystal structures studied than the Gaussian distribution hypotheses.

To calculate the values of $P(\varphi_h)$ for the Gaussian and the Cauchy distribution, the experimental data of L-arginine.$2H_2O$ (Karle & Karle, 1964), crystallizing in space group $P2_12_12_1$, were used. For the Gaussian distribution the values are calculated from the well known Cochran distribution (Cochran & Woolfson, 1955), and for the truncated Cauchy distribution these are calculated from (6) at $\varphi_{hk} = 0$.

The triple phase relationship of Sayre for a $P1$ crystal shows that the sum of the phases of two reflections in the triplet will give the most probable value of the phase of the third reflection. According to this the probability of the phase of $E_{0,8,14}$ ($|E|_{0,8,14} = 3{\cdot}07$, $\varphi_{0,8,14} = \pi$) to be $\pi/2$, as obtained from the phases of E_{286} ($|E|_{286} = 1{\cdot}87$, $\varphi_{286} = \pi/2$) and $E_{\bar{2}08}$ ($|E|_{\bar{2}08} = 2{\cdot}59$, $\varphi_{\bar{2}08} = 0$), is 0·79 for the Gaussian and 0·48 for the truncated Cauchy distribution. The actual phase of the reflection obtained is π. Similar situations are observed in some other combinations of triple phases showing that the Gaussian distribution overestimates the incorrect values of the corresponding phases while the Cauchy distribution appears not to depend upon these values. Again, the probable value of the phase of $E_{\bar{3},0,10}$ ($|E|_{\bar{3},0,10} = 3{\cdot}46$, $\varphi_{\bar{3},0,10} = \pi$) obtained as π, from the phases of $E_{0,3,10}$ ($|E|_{0,3,10} = 1{\cdot}85$, $\varphi_{0,3,10} = \pi/2$) and $E_{\bar{3}\bar{3}0}$ ($|E|_{\bar{3}\bar{3}0} = 2{\cdot}17$, $\varphi_{\bar{3}\bar{3}0} = \pi/2$), is 74% for the Gaussian and 54% for the Cauchy distribution. Similar results are obtained for the probable values of $P(\varphi_h)$ calculated from some other triplets. This indicates that a value of 50% for a probable phase obtained from the truncated Cauchy distribution may be acceptable as one is not interested in the actual value of the same. However, for the acentric case, the Gaussian distribution is better (*cf.* Appendix) than the truncated Cauchy distribution, but the certainty of the result is marginal in the cases studied. Further studies are in progress to arrive at a more definite conclusion.

Concluding remarks

The present study shows that the truncated Cauchy distribution may give an alternative method for estimating the signs or phases of triplets and more tests need to be carried out to confirm the effectiveness of this procedure. The authors will report on a formalism for the bicentric case very soon. It would therefore be advantageous to incorporate the Cauchy distribution in a routine which computes normalized structure amplitudes $|E|$ and also evaluates the experimental statistics of this quantity and compares the experimental values with the possible theoretical distributions.

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APPENDIX

We have for the intensity of reflections (I) from a crystal plane $X^2+Y^2=I$. For a given I,

$$X\,dX+Y\,dY=0 \qquad (A1)$$

(since $dI=0$, for a fixed value of I)

$$P(X)P(Y)=P(I) \qquad (A2)$$

$$P'(X)P(Y)\,dX+P'(Y)P(X)\,dY=0 \qquad (A3)$$

[since $dP(X)/dX=P'(X)$, and $P'(I)=0$]. Dividing ($A3$) by ($A2$), we obtain

$$\frac{P'(X)}{P(X)}dX+\frac{P'(Y)}{P(Y)}dY=0. \qquad (A4)$$

Multiplying ($A1$) by α (a constant) and adding ($A4$) we get

$$\left[\frac{P'(X)}{P(X)}+\alpha X\right]dX+\left[\frac{P'(Y)}{P(Y)}+\alpha Y\right]dY=0 \qquad (A5)$$

$$\frac{P'(X)}{P(X)}+\alpha X=0 \qquad (A6)$$

[since the terms within the brackets in ($A5$) are independent of each other].

$$\ln P(X)=-\alpha X^2/2+\ln\beta,$$

where β is a constant [by integrating ($A6$)].

$$P(X)=\beta\exp(-\alpha X^2/2). \qquad (A7a)$$

Similarly

$$P(Y)=\gamma\exp(-\alpha Y^2/2) \qquad (A7b)$$

where γ is a constant. Equations ($A7a$) and ($A7b$) show that $P(I)$ has a great tendency to have a Gaussian distribution in the acentric case.

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