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Probability distribution of normalized structure factor magnitudes for a centrosymmetric crystal with planar molecules in the unit cell

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Abstract. The reasons and conditions for applicability of the Cauchy distribution law for crystal structure factor components are discussed. It is shown that the standardized structure factors of centrosymmetric crystals are quite prone to be Cauchy distributed for crystals having planar molecules in their unit cells.

Keywords. Cauchy distribution; planar molecules.

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1. Introduction

Recently Mitra and Das [1] considered the use of Cauchy distribution law for the structure factor components and derived an expression for the probability of the Sayre relation being valid.

It is to be pointed out that Mitra and Das (*loc. cit.*) have established that for noncentrosymmetric crystals, there is a high probability of the distribution function being Gaussian. Hence in this paper only centrosymmetric crystals have been discussed.

2. Theoretical considerations for the Cauchy distribution

Since we are discussing the case of centrosymmetric crystals only because of the reasons mentioned above, we may write down the expression for the structure factor $F(hkl)$ for a general reflection (hkl) as

$$F(hkl) = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j), \tag{1}$$

where f_j is the atomic scattering factor for the jth atom in the asymmetric unit of the unit cell in the (hkl) direction while $(x_j\, y_j\, z_j)$ are its fractional components in the a, b and c directions which are the repetition vectors along the principal crystallographic axes. The multiplicity factor 2 for space group $p\bar{1}$ has been omitted from equation (1) since it acts only as a constant scale factor. For space group $p\bar{1}$, only the equivalent pair of positions $(x_j\, y_j\, z_j)$ and $(\bar{x}_j\, \bar{y}_j\, \bar{z}_j)$ is relevant. For other space groups containing centres of

symmetry, other equivalent positions all connected by the relation as above are present. Thus, for a centrosymmetric crystal, equation (1) serves as a general form for discussing its distribution.

In statistical literature [2], the ratio t is given by

$$t = \frac{\zeta}{\sqrt{[l/n \Sigma_j^n (\zeta_n - a)^2]}}, \tag{2}$$

(where ξ is a Gaussian statistical variate, a and n are the average and number of variates in the population considered) is known to be distributed according to the student's distribution law

$$P(t) = \frac{\Gamma((m+1)/2)}{\sqrt{m\pi}\Gamma(m/2)} \left(1 + \frac{t^2}{m}\right)^{-((m+1)/2)} \tag{3}$$

In equation (3), $\Gamma(n)$ is a gamma function and $(m+1)$ is the appropriate degree of freedom.

Now let $F_{\underset{\sim}{h}}$ - the structure factor of the reflection $\underset{\sim}{h} = (h, k, l)$ take the place of ξ in (2). Evidently $a = \langle F_{\underset{\sim}{h}} \rangle = 0$ and

$$t = \frac{F_{\underset{\sim}{h}}}{\sqrt{(1/n)\Sigma F_{\underset{\sim}{h}n}^2}}$$

$$= \frac{F_{\underset{\sim}{h}}}{\sqrt{\langle F^2 \rangle}}$$

$$= \frac{F_{\underset{\sim}{h}}}{\sqrt{\Sigma_j f_j^2}}$$

$$= E_{\underset{\sim}{h}} \quad \text{(by definition)}.$$

3. Discussion

Let us consider the case of centrosymmetric crystals consisting of planar molecules. Let us examine the simplest case of the molecule lying along the face $x \circ z$ with $(x \circ z)$ and $(\bar{x} \circ \bar{z})$ being the corresponding positions of atom in the characteristic space group $P\bar{1}$. In other space groups of the centrosymmetric system, there will be additional equivalent positions $(x_1 \circ z_1)$ and $(\bar{x}_1 \circ \bar{z}_1)$, $(x_2 \circ z_2)$ and $(\bar{x}_2 \circ \bar{z}_2)$ etc., Each such pair gives rise to the standardized structure factor

$$E_{hkl} = \sum_j e_j \cos 2\pi (hx_j + lz_j) \tag{4}$$

$$= \sum_j e_j \cos 2\pi\, hx_j \cos 2\pi\, lz_j - \sum_j e_j \sin 2\pi\, hx_j \sin 2\pi\, lz_j. \tag{5}$$

Here,

$$e_j = \frac{f_j}{\sqrt{\Sigma_j f_j^2}}$$

and

$$e_j^2 = \frac{f_j^2}{\Sigma_j f_j^2}.$$

Therefore,

$$\sqrt{\langle e_j^2 \rangle} = \sqrt{\left\langle \left[\frac{\Sigma_j f_j^2}{\Sigma_j f_j^2} \right] \right\rangle} = 1$$

When the molecule lies partially along the plane $x \circ z$, but at a fixed height Y above it along the Y-direction, we have

$$\begin{aligned} E_{hkl} &= \sum_j e_j \cos 2\pi (hx_j + K\,Y + lz_j) \\ &= \sum_j \{ e_j \cos 2\pi\, K\, Y (\cos 2\pi\, hx_j \cos 2\pi lz_j - \sin 2\pi hx_j \sin 2\pi lz_j) \\ &\quad - e_j \sin 2\pi\, K Y (\cos 2\pi\, hx_j \sin 2\pi lz_j + \sin 2\pi hx_j \cos 2\pi lz_j) \}. \end{aligned} \tag{6}$$

Characteristic terms in equations (5) and (6) are

$$\begin{pmatrix} \cos 2\pi hx \\ \sin 2\pi hx \end{pmatrix} \quad (\cos 2\pi lz \quad -\sin 2\pi lz)$$

and

$$\begin{pmatrix} \cos 2\pi hx \\ \sin 2\pi hx \end{pmatrix} \quad (\cos 2\pi lz \quad -\sin 2\pi lz)$$

$$-\begin{pmatrix} \cos 2\pi hx \\ \sin 2\pi hx \end{pmatrix} \quad (\sin 2\pi lz \quad \cos 2\pi lz)$$

respectively. In either case, the smallest number of independent variables on which the form may be brought by a nonsingular linear transformation (Cramer, *ibid.*) is two. Thus the t for E_{hkl} is E_{hkl} and $m+1$ of equation (3) is 2. Hence $m = 1$. Substituting these in (3) we have

$$P(E) = \frac{1}{\pi}(1 + E^2)^{-1} \tag{7}$$

which is the standard Cauchy's distribution.

If due to other space group symmetries, there are pairs of equivalent points $(x_1 \circ z_1)$ $(\bar{x}_1 \circ \bar{z}_1)$; $(x_2 \circ z_2)$ $(\bar{x}_2 \circ \bar{z}_2)$ etc., and the net standardized structure factor E will be sum of them i.e.

$$E = E_1 + E_2 + \cdots + E_n + \cdots,$$

where E_n is the standardized structure factor due to the atom pair at $(x_n \circ z_n)$ and $(\bar{x}_n \circ \bar{z}_n)$, then as per discussions above, each of E_1, E_2 etc., will have distributions of Cauchy type. The distribution of E will then be a convolution of distributions of E_1, E_2

etc. Since the convolution of a number of Cauchy distributions will be a Cauchy distribution itself, E will again have a distribution of the Cauchy type. Thus we have established that centrosymmetric crystals containing planar molecules lying on a face of the unit cell or parallel to it will have structure factor components distributed according to Cauchy's law.

When the molecules lie parallel to a general plane $(x\,y\,z)$, it can be considered to have been originally lying parallel to the $(x\circ z)$ plane and then through one or more rotations (not necessarily crystallographic) attained its final orientation. Gnedenko [3] has shown that such rotation leaves the law of distribution unaltered. So the Cauchy distribution derived for the $(x\circ z)$ plane remains Cauchy distributed even when the planar molecule lies parallel to a general (xyz) plane. Thus, it is evident that centrosymmetric crystals having planar molecules in their unit cells will have great likelihood of having its standardized structure factors being Cauchy distributed. This rationalizes the conclusions of Mitra and Das [*loc. cit.*] arrived at empirically through experimental observations only.

It has already been mentioned in Mitra and Das [1] that the distribution discussed by them is a truncated Cauchy distribution. While for the pure Cauchy distribution the moments do not exist, for the truncated Cauchy distribution all the moments exist. A real intensity distribution has necessarily a minimum readable value for intensity which constitutes the limit of truncation.

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References

[1] G B Mitra and S Das, *Acta Cryst.* **A45**, 314 (1989)
[2] H Cramer, *Mathematical methods of Statistics* (Princeton University Press, 1957) p. 237
[3] B V Gnedenco, *The theory of probability* (Mir Publishers, 1978) p. 155