Table 2. *Comparison of results for B values of* Nb

B (Å^2)	Θ (K)	$\overline{(u^2)}^{1/2}$ (Å)	Method	Reference
0·53	270	0·142	Inelastic neutron scattering data	Grimvall & Grimvall (1968)
0·45	285	0·131	Inelastic neutron scattering data	Sharp (1969)
0·50	279	0·138	Inelastic neutron scattering data	Powell, Martel & Woods (1977)
0·45 (2)	285 (5)	0·131 (1)	X-ray powder diffraction	Linkoaho & Rantavuori (1970)
0·45 (1)	284 (6)	0·134 (1)	X-ray powder diffraction	Linkoaho (1971)
0·52 (8)	260 (20)	0·140 (40)	X-ray powder diffraction (not corrected for TDS)	Korsunskii, Genkin & Vigdorchik (1977)
0·56	260	0·146	Elastic constant data	Padyukha & Chernyi (1966)
0·51	275	0·139	Elastic constant data	Jones, Moss & Rose (1969)
0·56	256	0·146	Elastic constant data	Gololobov, Mager, Mezhevich & Pan (1983)
0·49	281	0·136	Theoretical (model calculations)	Gupta (1985)
0·55 (5)	262 (12)	0·145 (6)	Elastic neutron powder diffraction	Present work

References

BEG. M. M., ASLAM, J., BUTT, N. M., KHAN, Q. H. & ROLANDSON, S. (1974). *Acta Cryst.* A30, 662–667.
GOLOLOBOV, E. M., MAGER, E. L., MEZHEVICH, Z. V. & PAN, L. K. (1983). *Phys. Status Solidi B*, 119, K139–K142.
GRIMVALL, S. & GRIMVALL, G. (1968). *Acta Cryst.* A24, 612–613.
GUPTA, O. P. (1985). *Solid State Commun.* 54, 163–166.
INTERNATIONAL UNION OF CRYSTALLOGRAPHY (1985). *Acta Cryst.* B41, 374.
JONES, K. A., MOSS, S. C. & ROSE, R. M. (1969). *Acta Metall.* 17, 365–372.

KORSUNSKII, M. I., GENKIN, YA, E. & VIGDORCHIK, L. I. (1977). *Sov. Phys. Solid State*, 19, 503–504.
LINKOAHO, M. (1971). *Philos. Mag.* 23, 191–198.
LINKOAHO, M. & RANTAVUORI, E. (1970). *Phys. Status Solidi*, 37, K89–K91.
NAKAGAWA, Y. & WOODS, A. D. B. (1963). *Phys. Rev. Lett.* 11, 271–274.
PADYUKHA, M. & CHERNYI, V. G. (1966). *Fiz. Met. Metalloved.* 22, 114–120.
POWELL, B. M., MARTEL, P. & WOODS, A. D. B. (1977). *Can. J. Phys.* 55, 1601–1620.
SHARP, R. I. (1969). *J. Phys. C*, 2, 421–443.

A Multisolution Procedure *via* Tendentially Maximally Entropical Starting Sets

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Abstract

Large starting sets of random phases are in general inconsistent with positivity and atomicity of the electron density. A correct solution can be achieved from them because the tangent formula is a process which maximizes entropy under physical constraints involving the positivity and atomicity of electron density. Starting sets which are themselves tendentially maximally entropical can be created by associating phase shifts Δ, generated according to the von Mises distribution of each triplet phase, to some (from 50 to 300) triplet invariants. Then the phases generated *via* these perturbed triplets are samples of the phase population expected to be maximally entropical on the basis of the prior information. Experimental tests show that the method may be a useful alternative to other conventional multisolution methods.

1. Introduction

Multisolution direct-methods computer programs are today a powerful tool for solving structures containing up to 70 or 80 atoms in the asymmetric unit. Various sets of phases, among which the correct solution is usually found, are produced by application of the tangent formula or similar techniques. The unknown phase values among the reflexions chosen to start the phase determination are usually represented by a magic-integer sequence (White & Woolfson,

1975; Main, 1978). Alternatively, randomly chosen phase values sometime constitute a useful starting point (Baggio, Woolfson, Declercq & Germain, 1978; Declercq, Germain & Woolfson, 1979).

Both magic integers and random approaches are economical and efficient ways of generating starting sets of phases. Until some years ago the unknown phases in the starting set were given all combinations of the values $\pm\pi/4$, $\pm 3\pi/4$; so, for m unknown phases, 4^m sets of phases can be produced by quadrant permutation. If the m phases are represented by magic integers $\varphi_i = m_i x$, then the errors can be evenly distributed among the φ_i and the root-mean-square error is controlled by appropriate choice of the integers m_i. All the possible combinations of the φ_i's can then be explored simply by sampling the variable x. In a wide sense the magic-integers approach may be considered as a generator of m pseudo-random phase values (under the condition that the phase space is systematically explored): m (the dimensionality of the phase space to be explored) is required to be large enough to warrant the use of a large number of phase relationships in the early stages of the phasing procedure, and sufficiently small to reduce computer cost and errors in the phase representation. From the above point of view the logical jump from the magic-integers representation to a completely random starting set is rather small.

Convergence from a random starting set to a correct set of phases may be secured by the use of phase relationships. The competitiveness of the method relies on the fact that a correct starting set is not a necessary or a sufficient condition for a correct phase expansion: sometimes wrong starting phases are expanded into correct sets of phases, and, *vice versa*, correct starting phases are developed into wrong solutions (Declercq, Germain & Woolfson, 1979).

The availability of a large starting set is certainly an important advantage of the random approaches; this potential is emphasized in *RANTAN* (Yao Jiaxing 1981), in which several hundreds of phases are often generated as a starting set. A further advantage, so far not quoted in the literature, may be expressed thus: in the absence of any information on the nature of the diffracting matter, a (large) random set of phases is maximally entropical. Indeed, phases are evenly distributed between 0 and 2π: their Fourier transform hardly produces an electron distribution concentrated into few peaks. Conversely, starting sets which are probably useless (too small content of entropy) are not produced in practice by a random process. Thus, a saving in computer time is obtained.

However, large sets of random phases are in general inconsistent with positivity and atomicity of the electron density. The application to random phases of the tangent formula or similar methods can be considered as a procedure for maximizing entropy under physical constraints on the positivity and atomicity

of the electron density [see Bricogne (1984) and literature therein quoted]. Such a process is not always easy: indeed, constraints are represented in reciprocal space by probabilistic phase relationships whose strength is not always sufficient to lead random phases to correct values, especially for large structures.

It seems therefore of some interest to have a procedure which generates starting sets of phases which are themselves tendentially compatible with positivity and atomicity of the electron density, and are tendentially maximally entropical under these constraints. It may be hoped that such sets, assumed as starting sets, can be expanded and refined into correct phases more easily than sets of random phases uncorrelated with physical constraints.

The description of the above procedure is the first aim of this paper. The procedure has been implemented in the *SIR* program (Cascarano *et al.*, 1985) as an option which may be chosen by the user, for example, when other options fail. Some experimental tests are also described.

2. Maximally entropical starting sets

Let us suppose that the origin has been fixed by assigning a suitable set of phases and that other phases have been reliably estimated by means of probabilistic methods. Then an unknown phase φ_h is distributed (Karle & Hauptman, 1956; Karle & Karle, 1966) according to

$$P(\varphi_h|\{\varphi_{k_j}, \varphi_{h-k_j}, G_j\}) = M(\varphi_h; \theta_h, \alpha_h),$$

where $G_j = 2|E_h E_{k_j} E_{h-k_j}|/N^{1/2}$, M is the von Mises distribution,

$$M(\varphi_h; \theta_h, \alpha_h) = [2\pi I_0(\alpha_h)]^{-1} \exp[\alpha_h \cos(\varphi_h - \theta_h)], \tag{1}$$

θ_h, the most probable value for φ_h, is given by

$$\tan\theta_h = \frac{\sum_j G_j \sin(\varphi_{k_j} + \varphi_{h-k_j})}{\sum_j G_j \cos(\varphi_{k_j} + \varphi_{h-k_j})} = \frac{T_h}{B_h}, \tag{2}$$

and

$$\alpha_h = (T_h^2 + B_h^2)^{1/2}. \tag{3}$$

From (1),

$$\int_0^{2\pi} \cos\varphi_h M(\varphi_h; \theta_h, \alpha_h) \, d\varphi_h = D_1(\alpha_h) \cos\theta_h, \tag{4}$$

$$\int_0^{2\pi} \sin\varphi_h M(\varphi_h; \theta_h, \alpha_h) \, d\varphi_h = D_1(\alpha_h) \sin\theta_h, \tag{5}$$

from which the so-called *circular variance*, $V_h = [1 - D_1(\alpha_h)]$, may be derived.

Since the entropy of a distribution $q(\varphi)$ is defined to be

$$-\int_0^{2\pi} q(\varphi) \log q(\varphi) \, d\varphi,$$

the entropy associated with the von Mises distribution $M(\varphi_h; \theta_h, \alpha_h)$ is

$$-\alpha D_1(\alpha) + \log [2\pi I_0(\alpha)].$$

It may be shown that, among all distributions, the von Mises distribution has maximum entropy (see the Appendix) under the condition that the mean direction θ_h and the circular variance V_h are fixed (it should be remembered that this characterization on the line produces the normal distribution). Positivity and atomicity of the diffracting matter, together with known phases $(\varphi_{k_j} + \varphi_{h-k_j})$, constitute all the prior information available at a certain moment. It is just this information which fixes the distribution with parameters θ_h and α_h. Thus the application of the tangent formula may be considered as a simple mathematical tool for assigning phases according to the maximum-entropy principle (see also Bricogne, 1984).

Even if prior information fixes the distribution of φ_h, its phase value is actually unknown. Indeed, φ_h may be considered as an element of a population of phases distributed according to the von Mises distribution with parameters θ_h and α_h: the actual value of each element is unpredictable because it is fixed by the unknown crystal structure. This observation suggests how, from a small starting set of phases, a multisolution procedure may be generated, each solution starting from a kernel of phases which is already tendentially maximally entropical. The logical basis of the process may be described in the following way.

Let $\theta_h = (\varphi_k + \varphi_{h-k})$ be a known quantity: then φ_h is distributed according to $M(\varphi_h; \theta_h, G)$. If a phase shift Δ (from now on referred to as a von Mises shift) is randomly generated according to the von Mises distribution $M(\Delta; 0, G)$ then the variable $(\theta_h + \Delta)$ has the same distribution as φ_h and may be used as a starting estimate of φ_h. In particular, each trial of a multisolution process may be started by randomly generating n_p von Mises phase shifts $\{\Delta_1, \Delta_2, \ldots, \Delta_{n_p}\}$, each shift associated with a properly chosen triplet invariant. Subsequent extension of phases by tangent formula or similar methods will lead to various sets of phases, each of them having exploited a particular set $\{\Delta_j\}$.

The difference between the present method and the magic-integer or random-phase approaches is now clear. Magic-integer or random procedures define starting sets of n phases which are evenly or randomly distributed in the n-dimensional phase space. By contrast, in the present method phases are generated *via* perturbed triplets so as to produce phase values which

are samples of the population expected on the basis of the prior information.

As a simple bidimensional example let us suppose that in a multisolution process the origin has been defined by φ_{n_1}, φ_{n_2}, φ_{n_3}, and that φ_{n_4} and φ_{n_5} are distributed according to $M(\varphi_{n_4}; \theta_4, G_4)$ and $M(\varphi_{n_5}; \theta_5, G_5)$ respectively, where

$$\theta_4 = (\varphi_{n_1} + \varphi_{n_2}) = 30°, \quad G_4 = 3,$$

$$\theta_5 = (\varphi_{n_1} + \varphi_{n_3}) = 65°, \quad G_4 = 2.$$

If von Mises phase shifts Δ_1 and Δ_2 are randomly generated according to $M(\Delta_1; 0°, 3)$ and $M(\Delta_2; 0°, 2)$ respectively, then the variables $(\theta_4 + \Delta_1)$ and $(\theta_5 + \Delta_2)$ (which are the starting values associated with φ_{n_4} and φ_{n_5} in the various trials of the multisolution processes) will be distributed according to the prior information. In Fig. 1 the first 1000 generated pairs of values $(\theta_4 + \Delta_1, \theta_5 + \Delta_2)$ are shown in the bidimensional space $(\varphi_{n_4}, \varphi_{n_5})$. As may be seen, the space is not evenly frequented: even if all phase values are accessible for $(\theta_4 + \Delta_1)$ and $(\theta_5 + \Delta_2)$, regions for which

$$\theta_4 + \Delta_1 \simeq 30° \quad \text{and} \quad \theta_5 + \Delta_2 \simeq 65°$$

are more densely frequented.

A further relevant aspect of the method is that large starting sets are no longer necessary. Indeed, the role of the variable starting phases is here replaced by the von Mises perturbation of triplets.

Too small a number n_p of perturbed triplets can give rise to solutions of which only a few are different from one another; a very large number of perturbed triplets does not add significant advantages to the method. In our experience n_p values between 100 and 250 are sensible choices.
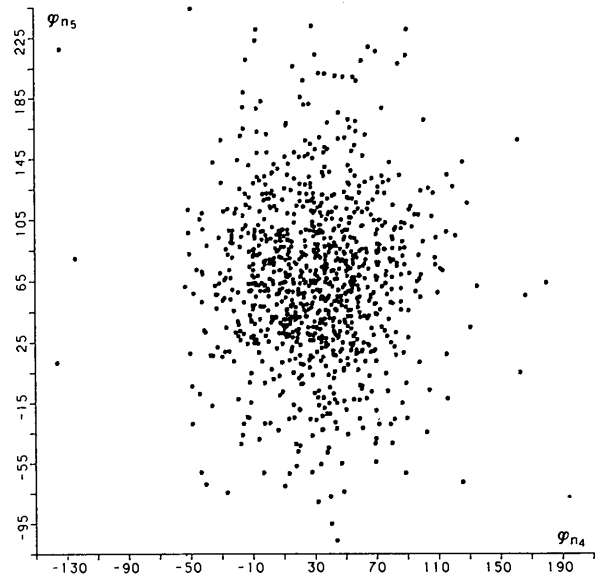

Fig. 1. Distribution in the bidimensional space $(\varphi_{n_4}, \varphi_{n_5})$ of the first 1000 generated pairs of values $(\theta_4 + \Delta_1, \theta_5 + \Delta_2)$.

3. The practical procedure

The practical procedure may be described according to the following scheme:

(1) The origin is defined by a convergence procedure (Germain, Main & Woolfson, 1970). Some (up to eight) weak links are picked up for (possible) subsequent use in the phasing process [see step (3)].

(2) In order to define the enantiomorph tentatively, for each trial n_e von Mises phase shifts Δ_j may be associated (in modulus and sign) with n_e triplets lying at the bottom of the convergence map. The enantiomorph is considered to be fixed if $|\Delta_j| \geq 30°$; $n_e = 2$ is a sensitive choice (in any tentative definition of the enantimorph, large n_e values cannot be used because the signs of Δ_j are usually inconsistent with the same enantiomorph; on the other hand $n_e = 1$ may occasionally be associated with an enantiomorph-insensitive triplet).

(3) The modified tangent formula

$$\tan \theta_h = \frac{\sum G_j \sin (\varphi_{k_j} + \varphi_{h-k_j} + \Delta_j)}{\sum G_j \cos (\varphi_{k_j} + \varphi_{h-k_j} + \Delta_j)} = \frac{T_h}{B_h} \qquad (6)$$

with concentration parameter

$$\alpha_h = (T_h^2 + B_h^2)^{1/2}$$

is applied. In the first stages of the phasing process, equation (6) works only on the hundred reflexions at the bottom of the convergence map. As in *MULTAN*, phase indications are accepted if α_h is larger than a given cutoff CUT, which is lowered cycle by cycle by the factor 0·65.

Equation (6) involves on the right-hand side known phase pairs $(\varphi_{k_j}, \varphi_{h-k_j})$, both with and without phase shifts Δ_j (phases correspond to origin-fixing reflexions, or weak links or phases previously fixed by the tangent formula).

(4) If θ_h, as given by equation (6), is accepted as a reliable estimate of φ_h, then the triplet values

$$T_j = (\theta_h - \varphi_{k_j} - \varphi_{h-k_j}) \quad (-\pi \leq T_j < \pi)$$

are calculated. If $|T_j| \leq 20°$ no action is undertaken. If $|T_j| > 20°$ then a random von Mises phase shift Δ_j is generated and associated with it with the same sign as T_j. If $|\Delta_j| > 2|T_j|$ then $|\Delta_j|$ is set to $2|T_j|$.

The simple and fast algorithm by Best & Fisher (1979) is used to simulate samples from a von Mises distribution for any value of the concentration parameter.

(5) If fewer than five phases are accessible (*via* triplet and two-phase relationships) for the current CUT value, then a weak-link phase (selected by the convergence procedure) is generated with flat distribution and introduced to make phase extension easier. At least two weak-link phases for non-centrosymmetric and three for centrosymmetric structures are generated to emphasize the randomicity of the procedure.

(6) Steps (3), (4), (5) are repeated until n_p values of Δ_j are assigned.

(7) When tangent cycles over the 100 reflexions at the bottom of the convergence map are terminated, the n_p phase shifts Δ_j are reset to zero, and the determined phases are used as a starting set to expand and refine all the reflexions together until self-consistency is achieved.

(8) In centrosymmetric space groups, triplet perturbation can only change the phase values by π. Among the n_p triplets, a subset of negative ones will be created in each trial according to the following scheme: for each triplet a random number p [in the interval $(0, 1)$] is generated. If $p > [0·5 + 0·5 \tanh (|E_h E_k E_{h+k}| N^{1/2})]$ then the triplet phase is changed by π. The multisolution nature of the procedure is secured by the fact that the triplets which are positive in one trial may be negative in another one and *vice versa*. Furthermore, the percentage of negative triplets is automatically correlated with the structural complexity, according to common sense. On the average, for large structures a relatively larger percentage of negative triplets will be produced than for small structures because of the smaller frequencies of large G values.

4. Experimental results and conclusions

The procedure described in § 3 has been applied to the 24 crystal structures quoted in Table 1. The reliability of the various triplets was first estimated according to the second representation formula P_{10} (Cascarano, Giacovazzo, Camalli, Spagna, Burla, Nunzi & Polidori, 1984). Triplets estimated as positive were actively used in the phasing process while triplets estimated as negative were used as a figure of merit (Cascarano, Giacovazzo & Viterbo, 1987). For each structure only 100 routinary trials were made: in column 7 the number of respective solutions is shown. It may be noted that:

(a) for some structures the ratio (number of correct solutions/number of trials) is high. Some of them (APAPA, RIFOLO) can be considered 'difficult'.

(b) No solution was routinely found in six cases (GRA4, SCHWZ2, TPH, MUNICH1, TUR10, TPALA). However, it need not be concluded that the present method is unable to solve those structures. Indeed, for three of them (TPH, TUR10, TPALA), solutions were easily found by introducing one-and two-phase structure seminvariants in the phasing process. Furthermore, it cannot be ruled out that solutions for the last three cases (GRA4, SCHWZ2, MUNICH1) may be found among 200–300 trials or after some variations of the parameters used in the routine procedure.

Even if the above results can be considered quite satisfactory, the present procedure has to be considered as a first achievement. In our opinion the

Table 1. *Abbreviations, references, space groups and chemical data for 24 test structures*

In the last column the number of correct solutions among the first 100 trials is given for each structure.

Code	Reference*	Space group	Formula	Z	Number of non-H atoms in the cell	Number of solutions
INOS	G	$P2_1/n$	$C_6H_{12}O_6.H_2O$	8	104	27
ERGO	G	$P2_12_12_1$	$C_{28}H_{44}O$	8	232	1
RIFOLO	†	$P2_1$	$C_{39}H_{49}NO_{13}$	2	106	35
GRA4	Y	$P\bar{1}$	$C_{30}H_{22}N_2O_4$	2	72	—
QUINO	G	$R\bar{3}$	C_6O_2	54	432	14
DIOLE	G	$I\bar{4}2d$	$C_{10}H_{18}O_2$	16	192	5
APAPA	G	$P4_12_12$	$C_{30}H_{35}N_{15}O_{16}P_2$	8	504	23
PROLINA	‡	$P2_1$	$C_{26}H_{40}N_4O_7$	2	74	3
CEPHAL	G	$C2$	$C_{18}H_{21}NO_3$	8	176	2
NEWQB	G	$P\bar{1}$	$C_{24}H_{20}N_2O_5$	4	124	2
NO55	G	$Fdd2$	$C_{20}H_{24}N_4$	16	384	8
SCHWZ2	G	$P1$	$C_{46}H_{70}O_{27}$	1	73	—
LOGANIN	G	$P2_12_12_1$	$C_{17}H_{26}O_{10}$	4	68	15
SELENID	G	$P2_1$	$C_{22}H_{28}O_2Se$	2	50	46
TPH	G	$C222_1$	$C_{24}N_2H_{20}$	12	312	1§
BED	G	$I4$	$C_{26}H_{26}N_4O_4$	8	272	8
MGHEX	G	$P3_1$	$C_{48}H_{68}N_{12}O_{12}Mg-$ $(ClO_4)_2(CH_3CN)_4$	3	285	3
LITHO	Y	$P2_12_12_1$	$C_{24}H_{40}O_3$	4	108	13
GOLDMAN	G	Cc	$C_{28}H_{16}$	8	224	14
MUNICH1	G	$C2$	$C_{20}H_{16}$	8	160	—
AZET	G	$Pca2_1$	$C_{21}H_{16}ClNO$	8	192	6
DIAM	G	$P4_2/n$	$C_{14}H_{20}O$	8	120	13
TUR10	G	$P6_322$	$C_{15}H_{24}O_2$	12	204	33§
TPALA	G	$P2_1$	$C_{28}H_{42}O_7N_4$	2	78	1§

* Complete references for test structures are not given for the sake of brevity. For most of them the reader is referred to magnetic tapes distributed by the crystallographic groups in York (Y) and Göttingen (G).
† Cerrini, Lamba, Nunzi, Burla & Polidori (1987).
‡ Colapietro, De Santis, Nocilli, Palleschi & Spagna (1985).
§ No routine solution found. See text for further discussion.

method has a large reserve of power still not exploited. Further efforts will be devoted in the near future to optimize the process.

Thanks are due to referees for useful suggestions.

APPENDIX

The entropy of a distribution $q(\varphi)$ is defined to be

$$-\int_0^{2\pi} q(\varphi) \log q(\varphi) d\varphi. \qquad (A1)$$

According to Mardia (1972) the von Mises distribution has maximum entropy under the condition that the mean direction and the circular variance are fixed. The mean direction θ and the circular variance V are defined according to

$$\int_0^{2\pi} (\cos \varphi) q(\varphi) d\varphi = \rho \cos \theta, \qquad (A2)$$

$$\int_0^{2\pi} (\sin \varphi) q(\varphi) d\varphi = \rho \sin \theta, \qquad (A3)$$

$$V = [1 - \rho]. \qquad (A4)$$

The theorem may be proved in the following way. Let $m(\varphi)$ be a further distribution. It is known from information theory (Rao, 1965) that

$$-\int_0^{2\pi} q(\varphi) \log [q(\varphi)/m(\varphi)] d\varphi \le 0; \qquad (A5)$$

equality holds if $q(\varphi)$ and $m(\varphi)$ are almost everywhere equal.

If $m(\varphi)$ is chosen to be a von Mises-type distribution satisfying $(A2)-(A4)$ then

$$\log m(\varphi) = \alpha \cos (\varphi - \theta) - \log [2\pi I_0(\alpha)], \qquad (A6)$$

where α is the solution of the equation $D_1(\alpha) = \rho$.
On using $(A6)$ in $(A5)$ we obtain

$$-\int_0^{2\pi} q(\varphi) \log [q(\varphi)] d\varphi$$

$$\le -\int_0^{2\pi} \{\alpha \cos (\varphi - \theta) - \log [2\pi I_0(\alpha)]\} q(\varphi) d\varphi$$

which, because of $(A2)$ and $(A3)$, reduces to

$$-\int_0^{2\pi} q(\varphi) \log q(\varphi) d\varphi \le D,$$

where $D = -\alpha\rho + \log [2\pi I_0(\alpha)]$.

D is therefore the upper bound to the entropy under the conditions fixed by $(A2)-(A4)$. It is easily seen that, if q is chosen to be equal to m, $(A1)$ reduces to D. Hence, we obtain the required result.

The above theorem may also be stated according to Bricogne's (1984) formalism: when the mean direction θ and the circular variance $V = (1-p)$ of a distribution $q(\varphi)$ are given and $m(\varphi) = 1/(2\pi)$ is a uniform prior distribution, then the entropy of q with respect to m {say $S_m(q) = -\int q(\varphi) \log[q(\varphi)/m(\varphi)] \, d\varphi$} is maximal when $q(\varphi)$ equals the von Mises distribution $M(\varphi; \theta, \alpha)$ with $D_1(\alpha) = p$.

In general, if

$$c_j = \langle C_j(\varphi) \rangle = \int_0^{2\pi} q(\varphi) C_j(\varphi) \, d\varphi \qquad \text{(ME0)}$$

are the M constraint equations, then the final expression for $q^{\mathrm{ME}}(\varphi)$ is given by the maximum-entropy equations

$$q^{\mathrm{ME}}(\varphi) = [m(\varphi)/Z(\lambda_1, \ldots, \lambda_M)] \exp\left[\sum_{j=1}^{M} \lambda_j C_j(\varphi) \right], \qquad \text{(ME1)}$$

where

$$Z(\lambda_1, \ldots, \lambda_M) = \int_0^{2\pi} m(\varphi) \exp\left[\sum_{j=1}^{M} \lambda_j C_j(\varphi) \right] d\varphi, \qquad \text{(ME2)}$$

$$\delta/\delta\lambda_j (\log Z) = c_j \quad (j = 1, 2, \ldots, M). \qquad \text{(ME3)}$$

λ_j are Lagrange multipliers.

In our case

$$c_1 = \int_0^{2\pi} q(\varphi) \cos(\varphi - \theta) \, d\varphi = p$$

with $C_1(\varphi) = \cos(\varphi - \theta)$, and

$$c_2 = \int_0^{2\pi} q(\varphi) \sin(\varphi - \theta) \, d\varphi = 0$$

with $C_2(\varphi) = \sin(\varphi - \theta)$. Consequently

$$Z(\lambda_1, \lambda_2) = \int_0^{2\pi} m(\varphi) \exp[\lambda_1 C_1(\varphi) + \lambda_2 C_2(\varphi)] \, d\varphi$$

$$= (1/2\pi) \int_0^{2\pi} \exp\{\alpha \cos[\varphi - (\theta + \xi)]\} \, d\varphi$$

$$= I_0(\alpha)$$

where $\alpha = (\lambda_1^2 + \lambda_2^2)^{1/2}$.

From (ME3),

$$\delta(\log Z)/\delta\lambda_1 = (\lambda_1/\alpha) D_1(\alpha) = p, \qquad (A7)$$

$$\delta(\log Z)/\delta\lambda_2 = (\lambda_2/\alpha) D_1(\alpha) = 0. \qquad (A8)$$

Therefore $\lambda_2 = 0$ and $\alpha = \lambda_1$, so that, according to $(A7)$, $D_1(\alpha) = p$. Then, according to (ME1),

$$q^{\mathrm{ME}}(\varphi) = [2\pi I_0(\alpha)]^{-1} \exp\{[p\alpha/D_1(\alpha)]\cos(\varphi - \theta)\},$$

which coincides with $M(\varphi; \theta, \alpha)$.

References

BAGGIO, R., WOOLFSON, M. M., DECLERCQ, J.-P. & GERMAIN, G. (1978). *Acta Cryst.* A34, 883–892.

BEST, D. J. & FISHER, N. T. (1979). *Appl. Stat.* 28, 2, 152–157.

BRICOGNE, G. (1984). *Acta Cryst.* A40, 410–445.

CASCARANO, G., GIACOVAZZO, C., BURLA, M. C., NUNZI, A., POLIDORI, G., CAMALLI, M., SPAGNA, R. & VITERBO, D. (1985). 9th Eur. Crystallogr. Meet., Torino, Italy. Abstract 1-046.

CASCARANO, G., GIACOVAZZO, C., CAMALLI, M., SPAGNA, R., BURLA, M. C., NUNZI, A. & POLIDORI, G. (1984). *Acta Cryst.* A40, 278–283.

CASCARANO, G., GIACOVAZZO, C. & VITERBO, D. (1987). *Acta Cryst.* A43 22–29.

CERRINI, S., LAMBA, D., NUNZI, A., BURLA, M. C. & POLIDORI, G. (1987). In preparation.

COLAPIETRO, M., DE SANTIS, P., NOCILLI, F., PALLESCHI, A. & SPAGNA, R. (1985). *Acta Cryst.* C41, 126–130.

DECLERCQ, J.-P., GERMAIN, G. & WOOLFSON, M. M. (1979). *Acta Cryst.* A35, 622–626.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.

KARLE, I. & KARLE, J. (1966). *Acta Cryst.* 21, 849–859.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* 9, 635–651.

MAIN, P. (1978). *Acta Cryst.* A34, 31–38.

MARDIA, K. V. (1972). *Statistics of Directional Data.* London: Academic Press.

RAO, C. R. (1965). *Linear Statistical Inference and its Applications.* New York: Wiley.

WHITE, P. S. & WOOLFSON, M. M. (1975). *Acta Cryst.* A31, 53–56.

YAO JIA-XING (1981). *Acta Cryst.* A37, 642–644.