Thus the Fourier transform of $X^2I(X)$ would lead directly to the size distribution function. This equivalence sheds new light on the experimental difficulty to be solved. The asymptotic behaviour of the intensity is of primordial importance: even if for X large, $I(X)$ takes small values, its product by X^2 may be non-negligible. Thus one replaces one difficulty by another one.'

This problem of the effect of finite summation on $g(m)$ has been considered from a theoretical point of view (Bertaut, 1952, 1963). In a paper with the title *Correction of oscillations in the distribution functions of particle size obtained from diffraction profiles*, my co-workers (de Bergevin & Germi, 1972) consider the problem from an experimental point of view and get satisfactory plots of $g(m)$ taking advantage of the measurement of the second moment

$$\int X^2 I(X)\, dX / \int I(X)\, dX$$

(Wilson, 1962; Langford, 1968) and adjusting $g(m)$ so that $g(0) = 0$.

One should notice that de Bergevin & Germi (1972) consider from the start the Fourier transform of $X^2 I(X)$.

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On evaluating the standard deviation of U_{eq}.*

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Abstract

For roughly isotropic and orthic cases the variance of U_{eq} is about one-sixth of the average of the variances of U_{11}, U_{22}, and U_{33}, *i.e.* only about one-half of what would be estimated on ignoring the covariances of the diagonal elements of $\mathbf{U}$.

For some time, *Acta Crystallographica* has required that, except in special cases, the anisotropic Gaussian quadratic amplitudes be deposited as supplementary material and replaced in the published paper by 'equivalent' isotropic measures, U_{eq} (or B_{eq}). Another requirement, now removed at least for U_{eq} and B_{eq} (*Notes for Authors*, 1983, p. 181), has been that all derived measures of any kind should be accompanied by their e.s.d.'s, although the computer programs used in many crystallographic laboratories do not permit ready access to the covariances cov(U_{ij}, U_{kl}) that are necessary for a proper evaluation of $\sigma_{U_{eq}}$. Moreover, in none we know of are the covariances regularly so used, despite the well-known need for them and Waser's thorough reminder (Waser, 1973); instead, the usual practice, it seems, is to estimate $\sigma_{U_{eq}}$ from the readily available e.s.d.'s, $\sigma_{U_{ij}}$, ignoring the covariances.

We derive simple expressions for variances and co-variances of the *principal* values of $\mathbf{U}$ and proceed to expressions for $\sigma_{U_{eq}}$. Our expressions for the variances and covariances extend somewhat those derived rather less directly and under more restrictive assumptions by Scheringer (1966) and Hirshfeld & Shmueli (1972, H & S), and our expressions for $\sigma_{U_{eq}}$ may prove useful in practice even when the underlying assumptions are hardly valid, but the main point to be made is that $\sigma_{U_{eq}}$ is substantially smaller than the usual estimates, the covariances being substantially negative.

We assume that the atoms are of Gaussian shape, so that each $\mathbf{U}$ is the sum of parts due to the (known) atom shape and to the crystal disorder (if the Gaussian atom approximation is good, the e.s.d.'s and covariances of a total $\mathbf{U}$ will be just those of its disorder, *i.e.* 'thermal' part); use Cartesian coordinates aligned with the principal axes of $\mathbf{U}$ for the atom of interest at the moment; and move the origin of coordinates to the position of that atom. Its contribution to an F is then

$$F_s = \exp\left[-\sum_{k=1}^{3} u_k s_k^2 / 2\right]$$
$$= \exp\left[-(at^2 + bv^2 + cw^2)/2\right],$$

where, taking advantage of $U_{ij} = 0$ for $i \neq j$, we omit one or both indices, writing $u_k = U_{11}$, U_{22}, $U_{33} = a, b, c$; $s_k = t, v, w$; and $|s| = 4\pi(\sin\theta)/\lambda$. For unit weights it is then easy to form the least-squares matrix $\mathbf{B}$, its inverse $\mathbf{B}^{-1}$, and the correlation matrix, appropriately replacing the usual summation over all reflections by integration over all $\mathbf{s}$:

$$\frac{\partial F_s}{\partial u_i} = -(1/2)\, s_i^2 \exp\left(-\sum u_k s_k^2/2\right),$$

$$B_{ij} = (1/4) \int\int\int s_i^2 s_j^2 \exp\left(-\sum u_k s_k^2\right) dt\, dv\, dw$$

$$= K(1 + 2\delta_{ij})/u_i u_j,$$

$$B_{ij}^{-1} = u_i u_j (5\delta_{ij} - 1)/(10K),$$

$$K = \pi^{3/2}/16\sqrt{abc},$$

$$\rho_{ij} = (5\delta_{ij} - 1)/4.$$

Aside from the constant factor $(\sigma^2 F)_{\mathrm{av}}$, our $\mathbf{B}^{-1}$ is an estimate of the part of the variance–covariance matrix that is needed for calculating $\sigma_{U_{eq}}$. The correlation coefficients ρ_{ij}, at $-1/4$, are relatively large.

We then find

$$\sigma^2_{U_{eq}} = \sigma^2_{(a+b+c)/3}$$

$$= [(\sigma_F^2)_{\mathrm{av}}/(45K)]\,[2(a^2 + b^2 + c^2)$$

$$- (ab + ac + bc)] \qquad (1)$$

and

$$\frac{\sigma^2_{U_{eq}}}{\sigma^2_{U_{11}} + \sigma^2_{U_{22}} + \sigma^2_{U_{33}}} = (1/9)\left[1 - \frac{ab + ac + bc}{2(a^2 + b^2 + c^2)}\right], \qquad (2)$$

which for $a = b = c$ (an isotropic Gaussian) becomes

$$\frac{\sigma^2_{U_{eq}}}{\sigma^2_{U_{11}} + \sigma^2_{U_{22}} + \sigma^2_{U_{33}}} = 1/18 \qquad (3)$$

or

$$\sigma_{U_{eq}}/\sigma_a = 1/\sqrt{6}. \qquad (4)$$

To a first approximation, then, the relative error in U_{eq} (or B_{eq}) is smaller by the factor $1/\sqrt{6}$ than the relative error of a principal component U_{ii}, and smaller by the factor $1/\sqrt{2}$ than would result if the errors in U_{11}, U_{22}, and U_{33} were uncorrelated. For anisotropic U's the expected effect of covariance is less, finally vanishing, for example, as b and c approach zero. We emphasize that this estimate is based on the variances and covariances of the *principal* values of U.

It remains to be seen how well (2) fits actual covariances, whether when applied correctly to the principal components of U or to the (merely) diagonal elements as referred to orthic or even appreciably anorthic crystal axes. It may be hoped that neither the deviations of the atomic scattering factors from the Gaussian form nor the complex variation of error weights with (h,k,l) will have much effect. H & S give examples in which rotating to non-principal orthogonal axes indeed had little effect on the calculated covariances, whereas the use of anorthic axes caused 'serious errors'. We have found that (1) is fairly good in several actual cases. For example, three coordination compounds – two ortho-

rhombic and one monoclinic $(\beta \simeq 92°)$ – for which the correlation matrices were available had respective average off-diagonal ρ's and scatter e.s.d.'s -0.239 (67), -0.225 (76), and -0.217 (56) Å^2 from 21, 25, and 23 atoms, with over-all range -0.385 to 0.042 Å^2, all averaged without rejections directly from the XRAY CRYLSQ output (Stewart, Machin, Ammon, Dickinson, Heck & Flack, 1976), and thus referred to the crystal axes without regard to degree of anisotropy, inclination of the principal axes, or anorthicity of the axes. For the first of these structures the $\sigma^2_{U_{eq}}$ values evaluated properly (with the covariance terms) and in the usual way (without the covariance terms) were compared: the average ratio, for 21 atoms, is 0.530 with scatter e.s.d. 0.084 and range 0.444–0.808 (second-highest value 0.625); the value predicted from (2) is 0.50. There is no obvious correlation between this ratio and the apparent anisotropy of a U (*i.e.* the deviations of U_{ii}/U_{jj} from unity). Accordingly, we suggest that a reasonable rough procedure for estimating the variance of U_{eq} in any roughly isotropic and orthic case is to average the variances of U_{11}, U_{22}, and U_{33}, and divide by six; and for a badly anisotropic case to use (2) directly, hoping that the effects of inclination of the principal axes away from the crystal axes will not be too great. (Better by far would be to let the computer find the correct estimate of $\sigma_{U_{eq}}$ directly from the covariance matrix – but, then, who really cares about U_{eq} and $\sigma_{U_{eq}}$, which are next to meaningless, if he has full information about the U_{ij}'s at his fingertips?*)

APPENDIX

It is easy by the above method to find the remaining terms of **B** and $\mathbf{B}^{-1}$. The non-zero terms of **B** are $B_{44} = 4K/ab$, $B_{55} = 4K/ac$, and $B_{66} = 4K/bc$, and of $\mathbf{B}^{-1}$ the corresponding reciprocals. For $a = b = c$, **B** and $\mathbf{B}^{-1}$ reduce to essentially the matrices given by H & S.

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* *Editorial note:* The decision that anisotropic thermal parameters in structural papers should generally be deposited rather than published [*Acta Cryst.* (1977), A33, 347] was taken as a major means of reducing journal production costs. In consequence, most structural papers were published thereafter without thermal parameters except for isotropic values. Since the additional cost of including U_{eq} or B_{eq} is small and the information contained of considerable value to many readers, these equivalents have been required [*Acta Cryst.* (1979), A35, 500] since 1980. However, the full set of anisotropic thermal parameters must still be supplied and is available, *gratis*, on request to The Executive Secretary of the IUCr.