# 6. MATHEMATICS OF THERMAL-MOTION PROBABILITY ELLIPSOIDS

It is convenient to develop the physical significance of the anisotropic temperature factor with the notation and terminology of probability theory rather than with the more familiar Fourier transform theory. The results are, of course, identical regardless of the terminology used. The reason for this choice is that the literature of mathematical statistics and probability theory is somewhat neater and easier to follow. The texts by Wilks,[14] Cramer,[15] Miller,[16] Hamilton,[17] and Lukacs and Laha[18] and the handbooks by Burington and May[19] and Owen[20] are found to be particularly useful.

## 6.1 PROBABILITY DENSITY FUNCTION OF A TRIVARIATE NORMAL DISTRIBUTION

Given three chance variables $X_1, X_2, X_3$ and S, which is a region in $X_1, X_2, X_3$ space, the probability $P(S)$ that the point $(X_1, X_2, X_3)$ falls in the region $S$ is given by

$$P(S) = \iiint_S \phi(X_1, X_2, X_3)\; dX_1\, dX_2\, dX_3 \,. \tag{6.1.1}$$

If the integration is carried over all space, then

$$\iiint_{-\infty}^{\infty} \phi(X_1, X_2, X_3)\; dX_1\, dX_2\, dX_3 = 1 \,. \tag{6.1.2}$$

The function $\phi(X_1, X_2, X_3)$ is called the probability density function (pdf) for the joint distribution of $X_1, X_2, X_3$. Using vector notation, we can designate the pdf as $\phi(\mathbf{X})$.

When the distribution is the type said to be normal or Gaussian, the pdf is

$$\phi(\mathbf{X}) = \frac{[\det(\mathbf{M}^{-1})]^{1/2}}{(2\pi)^{3/2}} \exp[-\tfrac{1}{2}(\mathbf{X} - \hat{\mathbf{X}})^{\mathrm{T}} \mathbf{M}^{-1}(\mathbf{X} - \hat{\mathbf{X}})] \,. \tag{6.1.3}$$

The matrix $\mathbf{M}^{-1}$ is the inverse of the symmetrical dispersion (variance-covariance) matrix $\mathbf{M}$, where

$$\mathbf{M} = \begin{pmatrix} \sigma_1^2 & \sigma_1\sigma_2\rho_{12} & \sigma_1\sigma_3\rho_{13} \\ \sigma_1\sigma_2\rho_{12} & \sigma_2^2 & \sigma_2\sigma_3\rho_{23} \\ \sigma_1\sigma_3\rho_{13} & \sigma_2\sigma_3\rho_{23} & \sigma_3^2 \end{pmatrix}.$$

The symbols $\sigma_i^2$ represent the second moments or variance about the mean position $\hat{\mathbf{X}}$. The symbols $\sigma_i\sigma_j\rho_{ij}$ are the corresponding covariances and $\rho_{ij}$ are the correlation coefficients.

## 6.2 EQUIPROBABILITY ELLIPSOIDS

For a proper normal distribution, the quadratic form $(\mathbf{X} - \hat{\mathbf{X}})^T \mathbf{M}^{-1}(\mathbf{X} - \hat{\mathbf{X}})$ is positive definite, and a principal axis transformation (see 6.4) is possible that will make the cross correlation coefficients $\rho_{ij} = 0$ $(i \neq j)$. The result of the transformation is the pdf

$$\phi(y_1, y_2, y_3) = \frac{1}{(2\pi)^{3/2}\sigma_{y_1}\sigma_{y_2}\sigma_{y_3}} e^{-Q/2} , \tag{6.2.1}$$

where

$$Q = \frac{(y_1 - \hat{y}_1)^2}{\sigma^2_{y_1}} + \frac{(y_2 - \hat{y}_2)^2}{\sigma^2_{y_2}} + \frac{(y_3 - \hat{y}_3)^2}{\sigma^2_{y_3}} . \tag{6.2.2}$$

The $y_i$ are coordinates based on the Cartesian principal axis system and $\sigma^2_{y_i}$ are the variances along the principal axes, $i = 1, 2, 3$.

The normal probability density function is constant for points on the ellipsoid $Q = C^2$ where $C$ is a constant. The probability that a random point $(y_1, y_2, y_3)$ in the distribution will fall inside the ellipsoid is

$$P(C) = (2/\pi)^{1/2} \int_0^C r^2 e^{-r^2/2}\, dr . \tag{6.2.3}$$

This result is derived from Eqs. 6.1.1, 6.2.1, and 6.2.2 by transforming to spherical coordinates.

When $C = 1.5382$, $P = 0.5$ and the corresponding ellipsoid is called the 50% probability ellipsoid. Table 6.1 is a table of $P$ versus $C$ values that were calculated by integrating Eq. 6.2.3 using Gaussian quadrature. Quadruple precision calculations were required to match the values found on page 203 of Owen's handbook.[20]

## 6.3 CHARACTERISTIC FUNCTION OF A TRIVARIATE NORMAL DISTRIBUTION

The characteristic function $\Phi(\mathbf{T})$ corresponding to a trivariate distribution $\phi(\mathbf{X})$ is the expected value of $e^{i\mathbf{T}^T\mathbf{X}}$, namely,

$$\Phi(\mathbf{T}) = \int_{-\infty}^{\infty} \phi(\mathbf{X}) e^{i\mathbf{T}^T\mathbf{X}}\, d\mathbf{X} . \tag{6.3.1}$$

For the trivariate normal pdf, Eq. 6.1.3, the corresponding characteristic function is

$$\Phi(\mathbf{T}) = \exp\left[\, i\mathbf{T}^T\hat{\mathbf{X}} - \tfrac{1}{2}\mathbf{T}^T\mathbf{M}\mathbf{T} \,\right] , \tag{6.3.2}$$

where $\mathbf{M}$ is the variance-covariance dispersion matrix described in Section 6.1 and $\hat{\mathbf{X}}$ is the center of mass of the distribution.

**Table 6.1. Critical values for probability ellipsoids of a trivariate normal distribution.**

| P | C | P | C | P | C |
|---|---|---|---|---|---|
| 0.01 | 0.3389 | 0.41 | 1.3842 | 0.81 | 2.1824 |
| 0.02 | 0.4299 | 0.42 | 1.4013 | 0.82 | 2.2114 |
| 0.03 | 0.4951 | 0.43 | 1.4183 | 0.83 | 2.2416 |
| 0.04 | 0.5479 | 0.44 | 1.4354 | 0.84 | 2.2730 |
| 0.05 | 0.5932 | 0.45 | 1.4524 | 0.85 | 2.3059 |
| 0.06 | 0.6334 | 0.46 | 1.4695 | 0.86 | 2.3404 |
| 0.07 | 0.6699 | 0.47 | 1.4866 | 0.87 | 2.3767 |
| 0.08 | 0.7035 | 0.48 | 1.5037 | 0.88 | 2.4153 |
| 0.09 | 0.7349 | 0.49 | 1.5209 | 0.89 | 2.4563 |
| 0.10 | 0.7644 | 0.50 | 1.5382 | 0.90 | 2.5003 |
| 0.11 | 0.7924 | 0.51 | 1.5555 | 0.91 | 2.5478 |
| 0.12 | 0.8192 | 0.52 | 1.5729 | 0.92 | 2.5997 |
| 0.13 | 0.8447 | 0.53 | 1.5904 | 0.93 | 2.6571 |
| 0.14 | 0.8694 | 0.54 | 1.6080 | 0.94 | 2.7216 |
| 0.15 | 0.8932 | 0.55 | 1.6257 | 0.95 | 2.7955 |
| 0.16 | 0.9162 | 0.56 | 1.6436 | 0.96 | 2.8829 |
| 0.17 | 0.9386 | 0.57 | 1.6616 | 0.97 | 2.9912 |
| 0.18 | 0.9605 | 0.58 | 1.6797 | 0.98 | 3.1365 |
| 0.19 | 0.9818 | 0.59 | 1.6980 | 0.99 | 3.3682 |
| 0.20 | 1.0026 | 0.60 | 1.7164 | 0.991 | 3.4019 |
| 0.21 | 1.0230 | 0.61 | 1.7351 | 0.992 | 3.4390 |
| 0.22 | 1.0430 | 0.62 | 1.7540 | 0.993 | 3.4806 |
| 0.23 | 1.0627 | 0.63 | 1.7730 | 0.994 | 3.5280 |
| 0.24 | 1.0821 | 0.64 | 1.7924 | 0.995 | 3.5830 |
| 0.25 | 1.1012 | 0.65 | 1.8119 | 0.996 | 3.6492 |
| 0.26 | 1.1200 | 0.66 | 1.8318 | 0.997 | 3.7325 |
| 0.27 | 1.1386 | 0.67 | 1.8519 | 0.998 | 3.8465 |
| 0.28 | 1.1570 | 0.68 | 1.8724 | 0.999 | 4.0331 |
| 0.29 | 1.1751 | 0.69 | 1.8932 | 0.9991 | 4.0607 |
| 0.30 | 1.1932 | 0.70 | 1.9144 | 0.9992 | 4.0912 |
| 0.31 | 1.2110 | 0.71 | 1.9360 | 0.9993 | 4.1256 |
| 0.32 | 1.2288 | 0.72 | 1.9580 | 0.9994 | 4.1648 |
| 0.33 | 1.2464 | 0.73 | 1.9804 | 0.9995 | 4.2107 |
| 0.34 | 1.2638 | 0.74 | 2.0034 | 0.9996 | 4.2661 |
| 0.35 | 1.2812 | 0.75 | 2.0269 | 0.9997 | 4.3365 |
| 0.36 | 1.2985 | 0.76 | 2.0510 | 0.9998 | 4.4335 |
| 0.37 | 1.3158 | 0.77 | 2.0757 | 0.9999 | 4.5943 |
| 0.38 | 1.3330 | 0.78 | 2.1012 | 0.99999 | 5.0894 |
| 0.39 | 1.3501 | 0.79 | 2.1274 | 0.999999 | 5.5376 |
| 0.40 | 1.3672 | 0.80 | 2.1544 | 0.9999999 | 5.9503 |

The crystallographic structure factor equation that incorporates general anisotropic temperature factor coefficients is

$$F(\mathbf{h}) = \sum_n f_n(\mathbf{h}) \exp(2\pi i \mathbf{h}^{\mathrm{T}}\hat{\mathbf{X}}_n) \exp(-\mathbf{h}^{\mathrm{T}}\mathbf{B}_n\mathbf{h}) , \tag{6.3.3}$$

where

| | |
|---|---|
| $\mathbf{h}$ | is a vector giving the Miller indices, |
| $\mathbf{X}_n$ | is a vector giving the fractional unit cell coordinates of the $n$th atom, |
| $\mathbf{B}_n$ | is the anisotropic temperature factor coefficient matrix, and |
| $f_n(\mathbf{h})$ | is the atom form factor value for atom $n$. |

If a change of variables $\mathbf{T} = 2\pi\mathbf{h}$ is made, then Eq. 6.3.3 can be rewritten as

$$F(\mathbf{T}) = \sum_n f_n(\mathbf{T}) \exp\left( i\mathbf{T}^{\mathrm{T}}\hat{\mathbf{X}}_n - \tfrac{1}{2}\mathbf{T}^{\mathrm{T}}\frac{\mathbf{B}_n}{2\pi^2}\mathbf{T} \right). \tag{6.3.4}$$

The scaled anisotropic temperature factor matrix $(1/2\pi^2)\mathbf{B}$ is seen to be identical with the variance-covariance dispersion matrix $\mathbf{M}$ in Eq. 6.3.2.

The corresponding crystal space trivariate normal pdf for any particular atom $n$ is

$$\phi(\mathbf{X}) = \frac{[2\pi^2 \det(\mathbf{B}^{-1})]^{1/2}}{(2\pi)^{3/2}} \exp[-\pi^2(\mathbf{X}-\hat{\mathbf{X}})^{\mathrm{T}}\,\mathbf{B}^{-1}(\mathbf{X}-\hat{\mathbf{X}})] ; \tag{6.3.5}$$

or if $\mathbf{M}^{-1} = 2\pi^2\mathbf{B}^{-1}$, then

$$\phi(\mathbf{X}) = \frac{\det(\mathbf{M}^{-1})}{(2\pi)^{3/2}} \exp[-\tfrac{1}{2}(\mathbf{X}-\hat{\mathbf{X}})^{\mathrm{T}}\,\mathbf{M}^{-1}(\mathbf{X}-\hat{\mathbf{X}})] , \tag{6.3.6}$$

which is identical to Eq. 6.1.3.

## 6.4 PRINCIPAL AXIS TRANSFORMATION

The transformation of anisotropic temperature factor coefficients (for the general triclinic case) to principal axes of thermal motion is discussed by Waser,[21] Busing and Levy,[22] and Cruickshank *et al.*[23]

The principal axis transformation is necessary to find the thermal-motion probability ellipsoids discussed in Section 6.2. The principal axes of the matrix $\mathbf{M}^{-1}$ in Eq. 6.3.6 are the vectors $\mathbf{y}_1$, $\mathbf{y}_2$, $\mathbf{y}_3$ for which the inner vector product $(\mathbf{y}_i, \mathbf{y}_i)$ has a stationary value subject to the constraint

$$(\mathbf{y}_i, \mathbf{M}^{-1}\mathbf{y}_i) = 1, \quad i = 1, 2, 3 . \tag{6.4.1}$$

For the general triclinic crystal system, this means that the quadratic form $\mathbf{y}^{\mathrm{T}}\mathbf{G}^{-1}\mathbf{y}$ has a stationary value subjected to the constraint

$$\mathbf{y}^{T}\mathbf{G}^{-1}\mathbf{M}^{-1}\mathbf{y} = 1 \tag{6.4.2}$$

where $\mathbf{G}^{-1}$ is the metric tensor with components $\mathbf{a}_i \cdot \mathbf{a}_j$ , where $\mathbf{a}_i \cdot \mathbf{a}_j$ is the scalar vector product of two of the three unit cell vectors. Introducing the Lagrange multiplier $1/\lambda$ leads to

$$\left[\mathbf{G}^{-1} - \frac{1}{\lambda_i}\mathbf{M}^{-1}\right]\mathbf{y}_i = 0 \quad (i = 1, 2, 3)\ ; \tag{6.4.3}$$

premultiplying by $\mathbf{M}$ yields

$$\left[\mathbf{M}\mathbf{G}^{-1} - \frac{1}{\lambda_i}\mathbf{I}\right]\mathbf{y}_i = 0 \quad (i = 1, 2, 3)\ . \tag{6.4.4}$$

Or we can do some additional rearranging and obtain

$$[\ \mathbf{G}\mathbf{M}^{-1} - \lambda_i\mathbf{I}\ ]\mathbf{y}_i = 0 \quad (i = 1, 2, 3)\ . \tag{6.4.5}$$

Eq. 6.4.4 is equivalent to one of the results derived by Busing and Levy,[22] except the $\lambda_i$ obtained here are the reciprocals of their $\lambda_i$ because we are doing the principal axis transformation on $\mathbf{M}^{-1}$ while their formulation performs the transformation on $\mathbf{M}$. The numerical procedure used in ORTEP finds the eigenvalues and eigenvectors of the unsymmetrical matrix $\mathbf{M}\mathbf{G}^{-1}$ in Eq. 6.4.4.