

6.1. INTENSITY OF DIFFRACTED INTENSITIES

Table 6.1.1.8. Cubic harmonics $K_{ij}(\theta, \varphi)$ for cubic site symmetries

$K_{ij}(\theta, \varphi)$	N_{ij}	Site symmetry				
		23	$m\bar{3}$	432	$\bar{4}3m$	$m\bar{3}m$
$K_0 = Y_{00+} = 1$	4π	×	×	×	×	×
$K_3 = Y_{32-}$	$\frac{240\pi}{7}$	×			×	
$K_4 = Y_{40+} + \frac{1}{168} Y_{44+}$	$\frac{16\pi}{21}$	×	×	×	×	×
$K_{6,1} = Y_{60+} - \frac{1}{360} Y_{64+}$	$\frac{32\pi}{13}$	×	×	×	×	×
$K_{6,2} = Y_{62+} - \frac{1}{792} Y_{66+}$	$\frac{512\pi}{13} \cdot \frac{105}{11}$	×	×			
$K_7 = Y_{72-} + \frac{1}{1560} Y_{76-}$	$\frac{256\pi}{15} \cdot \frac{567}{13}$	×			×	
$K_8 = Y_{80+} + \frac{1}{5940} (Y_{84+} + \frac{1}{672} Y_{88+})$	$\frac{256\pi}{17 \cdot 33}$	×	×	×	×	×
$K_{9,1} = Y_{92-} - \frac{1}{2520} Y_{96-}$	$\frac{512\pi}{19} \cdot 165$	×			×	
$K_{9,2} = Y_{94-} - \frac{1}{4080} Y_{98-}$	$\frac{2048\pi}{19} \cdot \frac{243 \cdot 5005}{17}$	×		×		
$K_{10,1} = Y_{10,0+} - \frac{1}{5460} (Y_{10,4} + \frac{1}{4320} Y_{10,8+})$	$\frac{512\pi}{21} \cdot \frac{3}{65}$	×	×	×	×	×
$K_{10,2} = Y_{10,2+} + \frac{1}{43680} (Y_{10,6+} + \frac{1}{456} Y_{10,10+})$	$\frac{2048\pi}{21} \cdot \frac{4455}{247}$	×	×			

The mean-square displacement of the atom from its mean position in the direction of the vector \mathbf{v} is given by

$$\langle \mathbf{u}^2 \rangle_{\mathbf{v}} = \mathbf{v}^T \mathbf{g}^T \boldsymbol{\sigma}_{\mathbf{u}} \mathbf{g} \mathbf{v} / (\mathbf{v}^T \mathbf{g} \mathbf{v}), \quad (6.1.1.32)$$

where g_{ij} is the covariant metric tensor with the scalar products of the unit-cell vectors $\mathbf{a}_i \cdot \mathbf{a}_j$ as components.

The thermal motion for atoms in crystals is often displayed as surfaces of constant probability density. The surface for the thermal displacement \mathbf{u} is defined by

$$\mathbf{u}^T \boldsymbol{\sigma}_{\mathbf{u}}^{-1} \mathbf{u} = C^2. \quad (6.1.1.33)$$

The square of the distance from the origin to the equiprobability surface in the direction \mathbf{v} is

$$C^2 \mathbf{v}^T \mathbf{g} \mathbf{v} / (\mathbf{v}^T \boldsymbol{\sigma}_{\mathbf{u}}^{-1} \mathbf{v}). \quad (6.1.1.34)$$

This is equal to (6.1.1.32) for C unity only if \mathbf{v} coincides with a principal axis of the vibration ellipsoid.

The probability that a displacement falls within the ellipsoid defined by C is

$$(2/\pi)^{1/2} \int_0^C q^2 \exp(-q^2/2) dq. \quad (6.1.1.35)$$

6.1.1.6. The generalized temperature factor

The Gaussian model of the probability density function (p.d.f.) $\rho_o(\mathbf{u})$ for atomic thermal motion defined in (6.1.1.30) is adequate in many cases. Where anharmonicity or curvilinear motion is important, however, more elaborate models are needed.

In the classical (high-temperature) regime, the generalized temperature factor is given by the Fourier transform of the one-particle p.d.f.:

$$\rho(\mathbf{u}) = N^{-1} \exp[-V(\mathbf{u})/kT], \quad (6.1.1.36)$$

where

$$N = \int \exp[-V(\mathbf{u})/kT] d\mathbf{u}. \quad (6.1.1.37)$$

In the cases where the potential function $V(\mathbf{u})$ is a close approximation to the Gaussian (harmonic) potential, series expansions based on a perturbation treatment of the anharmonic terms provide a satisfactory representation of the temperature factors. That is, if the deviations from the Gaussian shape are small, approximations obtained by adding higher-order corrections to the Gaussian model are satisfactory.

In an arbitrary coordinate system, the number of significant high-order tensor coefficients for the correction is large. It may be helpful to choose coordinates parallel to the principal axes for the harmonic approximation so that

$$V(\mathbf{u})/kT = 1/2 \sum_{i=1}^3 (B_i u_i)^2, \quad (6.1.1.38)$$

in which case (6.1.1.36) may be written as

$$\rho_o(\mathbf{u}) = \frac{1}{N_0} \exp \left[-1/2 \sum_i (B_i u_i)^2 \right], \quad (6.1.1.39)$$

where

$$N_0 = \frac{B_1 B_2 B_3}{8\pi^3}. \quad (6.1.1.40)$$

The harmonic temperature factor is

$$T_o(\mathbf{S}) = \exp \left[-1/2 \sum_i (b_i S_i)^2 \right], \quad (6.1.1.41)$$

where b_i and B_i are related by the reciprocity condition

$$b_i B_i = 1. \quad (6.1.1.42)$$

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Table 6.1.1.9. $f_{nl}(\alpha, S) = \int_0^\infty r^n \exp(-\alpha r) j_l(Sr) dr$

n	l	1	2	3	4
0		$\frac{1}{(S^2 + \alpha^2)}$	$\frac{2\alpha}{(S^2 + \alpha^2)^2}$	$\frac{2(3\alpha^2 - S^2)}{(S^2 + \alpha^2)^3}$	$\frac{24\alpha(\alpha^2 - S^2)}{(S^2 + \alpha^2)^4}$
1			$\frac{2S}{(S^2 + \alpha^2)^2}$	$\frac{8S\alpha}{(S^2 + \alpha^2)^3}$	$\frac{8S(5\alpha^2 - S^2)}{(S^2 + \alpha^2)^4}$
2				$\frac{8S^2}{(S^2 + \alpha^2)^3}$	$\frac{48S^2\alpha}{(S^2 + \alpha^2)^4}$
3					$\frac{48S^3}{(S^2 + \alpha^2)^4}$

6.1.1.6.1. Gram-Charlier series

In the Gram-Charlier series expansion (Kuznetsov, Stratonovich & Tikhonov, 1960), the general p.d.f. $\rho(\mathbf{u})$ is approximated by

$$\left[1 - c^j D_j + \frac{c^{jk}}{2!} D_j D_k - \dots + (-)^p \frac{c^{jk\dots\zeta}}{p!} D_\alpha D_\beta \dots D_\zeta \right] \rho_o(\mathbf{u}). \quad (6.1.1.43)$$

The operator $D_\alpha D_\beta \dots D_\zeta$ is the p th partial (covariant) derivative $\partial^p / \partial u_\alpha \partial u_\beta \dots \partial u_\zeta$, and $c^{jk\dots\zeta}$ is a contravariant component of the coefficient tensor. The quasi-moment coefficient tensors are symmetric for all permutations of indices. The first four have three, six, ten, and fifteen unique components for site symmetry 1. The third- and fourth-order terms describe the skewness and the kurtosis of the p.d.f., respectively.

The Gram-Charlier series may be rewritten using general multidimensional Hermite polynomial tensors, defined by

$$H_{\alpha\beta\dots\zeta}(\mathbf{u}) = (-)^p \exp\left(\frac{1}{2}\sigma_{jk}^{-1}u^j u^k\right) \times D_\alpha D_\beta \dots D_\zeta \exp\left(-\frac{1}{2}\sigma_{jk}^{-1}u^j u^k\right). \quad (6.1.1.44)$$

For $w_j = \sigma_{jk}^{-1}u^k$, and with $\sigma_{jk}^{-1} = \sigma_{kj}^{-1}$ and $w_j w_k = w_k w_j$, the first few general Hermite polynomials may be expressed as

$$\begin{aligned} {}^0H(\mathbf{u}) &= 1 \\ {}^1H_j(\mathbf{u}) &= w_j \\ {}^2H_{jk}(\mathbf{u}) &= w_j w_k - \sigma_{jk}^{-1} \\ {}^3H_{jkl}(\mathbf{u}) &= w_j w_k w_l - w_j \sigma_{kl}^{-1} - w_k \sigma_{lj}^{-1} - w_l \sigma_{jk}^{-1} \\ &= w_j w_k w_l - 3w_{(j} \sigma_{kl)}^{-1} \\ {}^4H_{jklm}(\mathbf{u}) &= w_j w_k w_l w_m - 6w_{(j} w_k \sigma_{lm)}^{-1} + 3\sigma_{j(k}^{-1} \sigma_{lm)}^{-1}. \end{aligned} \quad (6.1.1.45)$$

Indices in parentheses indicate terms to be averaged over all unique permutations of those indices.

The Gram-Charlier series is then

$$\rho_o(\mathbf{u}) \left[1 + \frac{1}{3!} c^{jkl} H_{jkl}(\mathbf{u}) + \frac{1}{4!} c^{jklm} H_{jklm}(\mathbf{u}) + \dots \right], \quad (6.1.1.46)$$

in which the mean and the dispersion of $\rho_o(\mathbf{u})$ have been chosen to make c^j and c^{jk} vanish.

The Fourier transform, after truncating at the quartic term, gives an approximation to the generalized temperature factor:

$$T(\mathbf{S}) = T_o(\mathbf{S}) \left[1 + \frac{i^3}{3!} c^{jkl} S_j S_k S_l + \frac{i^4}{4!} c^{jklm} S_j S_k S_l S_m \right], \quad (6.1.1.47)$$

i.e. the Fourier transform of the Hermite polynomial expansion about the Gaussian p.d.f. is a power-series expansion about the

Table 6.1.1.10. Indices nmp allowed by the site symmetry for the functions $H_n(z)\Phi_{mp}(\varphi)$; μ, ν and j are integers such that $m, n \geq 0$; $(-)^n$ implies $p = -$ for n odd and $p = +$ for n even

Site symmetry	Coordinate axes	Indices
$\frac{1}{1}$	Any Any	All (n, m, p) $(n, n + 2j, p)$
2	$2 \parallel x$ $2 \parallel y$ $2 \parallel z$	$(n, m, (-)^n)$ $(n, m, (-)^{n-m})$ $(n, 2\nu, p)$
m	$m \perp x$ $m \perp y$ $m \perp z$	$(n, m, (-)^m)$ $(n, m, +)$ $(2\mu, m, p)$
$2/m$	$2 \parallel x, m \perp x$ $2 \parallel y, m \perp y$ $2 \parallel z, m \perp z$	$(m + 2j, m, (-)^m)$ $(m + 2j, m, +)$ $(2\mu, 2\nu, p)$
222 $mm2$	$2 \parallel z, 2 \parallel y$ $2 \parallel x, m \perp z$ $2 \parallel y, m \perp z$ $2 \parallel z, m \perp y$	$(n, 2\nu, (-)^n)$ $(2\mu, m+)$ $(2\mu, m, (-)^m)$ $(n, 2\nu, +)$
mmm	$m \perp z, m \perp y, m \perp x$	$(2\mu, 2\nu, +)$
$\frac{4}{4}$	$4 \parallel z$	$(n, 4\nu, p)$
$\frac{4}{4}$	$4 \parallel z$	$(n, 2n + 4j, p)$
$4/m$	$4 \parallel z, m \perp z$	$(2\mu, 4\nu, p)$
422	$4 \parallel z, 2 \parallel y$	$(n, 4\nu, (-)^n)$
$4mm$	$4 \parallel z, m \perp y$	$(n, 4\nu, +)$
$\bar{4}2m$	$4 \parallel z, 2 \parallel x$	$(n, 2n + 4j, (-)^n)$
	$4 \parallel z, m \perp y$	$(n, 2n + 4j, +)$
$4/mmm$	$4 \parallel z, m \perp z, m \perp x$	$(2\mu, 4\nu, +)$
$\frac{3}{3}$	$3 \parallel z$	$(n, 3\nu, p)$
$\frac{3}{3}$	$3 \parallel z$	$(m + 2j, 3\nu, p)$
32	$3 \parallel z, 2 \parallel y$ $3 \parallel z, 2 \parallel x$	$(n, 3\nu, (-)^{n-m})$ $(n, 3\nu, (-)^n)$
$3m$	$3 \parallel z, m \perp y$ $3 \parallel z, m \perp x$	$(n, 3\nu, +)$ $(n, 3\nu, (-)^m)$
$\bar{3}m$	$\bar{3} \parallel z, m \perp y$ $\bar{3} \parallel z, m \perp x$	$(m + 2j, 3\nu, +)$ $(m + 2j, 3\nu, (-)^m)$
$\frac{6}{6}$	$6 \parallel z$	$(n, 6\nu, p)$
$\frac{6}{6}$	$6 \parallel z$	$(2\mu, 3\nu, p)$
$6/m$	$6 \parallel z, m \perp z$	$(2\mu, 6\nu, p)$
622	$6 \parallel z, 2 \parallel y$	$(n, 6\nu, (-)^n)$
$6mm$	$6 \parallel z, m \perp y$	$(n, 6\nu, +)$
$\bar{6}m2$	$6 \parallel z, m \perp y$ $6 \parallel z, m \perp x$	$(2\mu, 3\nu, +)$ $(2\mu, 3\nu, (-)^m)$
$6/mmm$	$6 \parallel z, m \perp z, m \perp y$	$(2\mu, 6\nu, +)$

Gaussian temperature factor with even-order terms real and odd-order terms imaginary.

Because of the symmetry of the relationship between the Fourier transform of a real function and its inverse, the functional form of the p.d.f. and that of the temperature factor can be interchanged. Exchanging the role of the Hermite polynomials and the power series from the Gram-Charlier expansion has been studied by Scheringer (1985), with the objective of obtaining the one-particle potentials more directly.

6.1.1.6.2. Fourier-invariant expansions

When truncated, an expression for a multipole expansion, p.d.f. or temperature factor must retain those terms essential to the accuracy required of the expansion. Some authors (*e.g.*

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Table 6.1.1.11. Indices n_x, n_y, n_z allowed for the basis functions $H_{n_x}(Ax)H_{n_y}(By)H_{n_z}(Cz)$; $\lambda, \mu,$ and ν are non-negative; conditions for other choices of axes are derived by cyclic permutation

Symmetry	Coordinate axes	Allowed indices
$\frac{1}{1}$	Any Any	All (n_x, n_y, n_z) $n_x + n_y + n_z = 2\lambda$
2 m $2/m$ 222	$2 \parallel z$ $m \perp z$ $2 \parallel z, m \perp z$ $2 \parallel z, 2 \parallel y$	$n_x + n_y = 2\lambda$ $n_z = 2\nu$ $n_x + n_y = 2\lambda, n_z = 2\nu$ n_x, n_y, n_z all even or all odd
$mm2$ mmm	$2 \parallel z, m \perp y$ $m \perp z, m \perp y, m \perp z$	$n_x = 2\lambda, n_y = 2\mu$ $n_x = 2\lambda, n_y = 2\mu, n_z = 2\nu$

Stewart, 1980*b*) strongly favour classes of truncated expansion that retain symmetry properties appropriate to particular classes of transformation, such as rotation or Fourier inversion. Others, emphasizing simplicity, retain the minimum set of terms required to preserve the accuracy needed in the expansion. In either case, it is desirable for the expansion to converge rapidly, and to have a form related to physical theory.

In principle, the one-particle potential may be expanded in any complete set of functions. Harmonic oscillator functions simplify simultaneous interpretation of the probability distribution in real and reciprocal space because their form does not change under Fourier inversion (Kurki-Suonio, Merisalo & Peltonen, 1979).

If both anharmonicity and anisotropy are small, the p.d.f. may be expressed as a rapidly converging expansion in spherical polar coordinates u, θ, φ :

$$\rho(\mathbf{u}) = \rho_o(\mathbf{u}) \frac{N_0}{N} \left[1 - \sum_{n,l,m,p} a_{nlmp} R_{nl}(Bu) Y_{lmp}(\theta, \varphi) \right] \quad (6.1.1.48)$$

for non-cubic and

$$\rho(\mathbf{u}) = \rho_o(\mathbf{u}) \frac{N_0}{N} \left[1 - \sum_{n,l,j} a_{nlj} R_{nl}(Bu) K_{lj}(\theta, \varphi) \right] \quad (6.1.1.49)$$

for cubic site symmetry. The radial term may be written as

$$R_{nl}(x) = x^l L_{(n-l)/2}^{l+1/2}(x^2), \quad (6.1.1.50)$$

where the associated Laguerre polynomial is

$$L_k^\alpha(t) = \sum_{\nu=0}^k \binom{k+\alpha}{k-\nu} \frac{(-t)^\nu}{\nu!} \quad (6.1.1.51)$$

with

$$\binom{p}{q} = \frac{\Gamma(p+1)}{[\Gamma(q+1)\Gamma(p-q+1)]} \quad (6.1.1.52)$$

and the normalizing factor

$$N = \frac{8\pi^3}{B^3} \left[1 - \sum_{\nu} (-)^\nu \frac{(2\nu+1)!}{2^{2\nu}(\nu!)^2} a_{2\nu 00+} \right]. \quad (6.1.1.53)$$

The real spherical harmonics $Y_{lmp}(\theta, \varphi)$ and the cubic harmonics $K_{lj}(\theta, \varphi)$ are as defined in Subsection 6.1.1.4. As in the case of multipole expansions, the non-zero coefficients in these expressions are limited by the site symmetry. The restrictions on the temperature factor are identical to those for the generalized scattering factor listed in Tables 6.1.1.7 and 6.1.1.8.

From the Fourier invariance of harmonic oscillator functions,

$$T(\mathbf{S}) = \frac{N_0}{N} \exp(-b^2 S^2/2) \times \left[1 - \sum_{n,l,m,p} a_{nlmp} i^n R_{nl}(bS) Y_{lmp}(\theta_S, \varphi_S) \right] \quad (6.1.1.54)$$

and

$$T(\mathbf{S}) = \frac{N_0}{N} \exp(-b^2 S^2/2) \times \left[1 - \sum_{n,l,j} a_{nlj} i^n R_{nl}(bS) K_{lj}(\theta_S, \varphi_S) \right] \quad (6.1.1.55)$$

for non-cubic and cubic site symmetries, respectively. θ_S and φ_S are polar coordinates in reciprocal space.

With an appropriate choice of origin, the first-order (110+) and (111±) terms vanish. The isotropic harmonic (200+) and constant (000+) terms have been removed from the summation. If coordinate axes are chosen coincident with the principal axes for the harmonic approximation, (221±) and (222-) vanish. (220+) indicates the prolateness and (222+) the non-axiality in the harmonic approximation (Kurki-Suonio, 1977). Terms with $n \geq 2$ describe the anharmonicity.

The approximations in (6.1.1.48) to (6.1.1.55) fail if the anisotropy, indicated by the size of the (220+) and (222+) terms, or the anharmonicity is large. If the anharmonicity and non-axiality are small, one can invoke Fourier-invariant expansions in cylindrical polar coordinates u_r, u_z, φ :

$$\rho(\mathbf{u}) = \rho_o(\mathbf{u}) \frac{N_0}{N} \times \left[1 - \sum_{n_z, n_r, m, p} b_{n_z n_r m p} H_{n_z}(B_z u_z) \mathbf{P}_{nm}(B_r u_r) \Phi_{mp}(\varphi) \right] \quad (6.1.1.56)$$

and

$$T(S) = \frac{N_0}{N} \exp[-\frac{1}{2}(b_r^2 S_r^2 + b_z^2 S_z^2)] \times \left[1 - \sum_{n_z, n_r, m, p} b_{n_z n_r m p} H_{n_z}(b_z S_z) \mathbf{P}_{nm}(b_r S_r) \Phi_{mp}(\varphi_S) \right], \quad (6.1.1.57)$$

where S_r, S_z, φ_S are cylindrical coordinates for S .

$$\mathbf{P}_{nm}(x) = x^n L_{(n-m)/2}^m(x^2), \quad \Phi_{m\pm}(\varphi) = \frac{\cos m\varphi}{\sin m\varphi} \quad (6.1.1.58)$$

and

$$N = \frac{8\pi^3}{B_r^2 B_z} \left[1 - \sum_{\mu\nu} (-)^\nu \frac{(2\mu)!}{\mu!} b_{2\mu 2\nu 0+} \right]. \quad (6.1.1.59)$$

The indices allowed for the site symmetrical basis are as indicated in Table 6.1.1.10.

Again, the first-order (100+) and (011±) terms vanish with the appropriate choice of origin. For coordinate axes coinciding with the principal axes of the harmonic approximation, (111±) and (022-) vanish. (020+), (200+), and (000+) have been removed from the summation.

Equations (6.1.1.56) and (6.1.1.57) apply accurately to non-cubic symmetries with rotation axes higher than twofold where non-axiality vanishes. Where non-axiality is large, it is preferable to use the Cartesian Fourier invariant expansion

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$$\rho(\mathbf{u}) = \frac{N_0}{N} \exp \left[-1/2 \sum_i B_i^2 u_i^2 \right] \times \left[1 - \sum_{n_x, n_y, n_z} c_{n_x n_y n_z} H_{n_x}(B_x u_x) H_{n_y}(B_y u_y) H_{n_z}(B_z u_z) \right] \quad (6.1.1.60)$$

and

$$T(\mathbf{S}) = \frac{N_0}{N} \exp \left[-1/2 \sum_i b_i^2 u_i^2 \right] \times \left[1 - \sum_{n_x, n_y, n_z} c_{n_x n_y n_z} H_{n_x}(b_x u_x) H_{n_y}(b_y u_y) H_{n_z}(b_z u_z) \right], \quad (6.1.1.61)$$

where

$$N = \frac{8\pi^3}{B_x B_y B_z} \left[1 - \sum_{\lambda, \mu, \nu} \frac{(2\lambda)!(2\mu)!(2\nu)!}{\lambda! \mu! \nu!} c_{2\lambda 2\mu 2\nu} \right]. \quad (6.1.1.62)$$

The indices allowed under the site symmetry are listed in Table 6.1.1.11.

The first-order terms vanish with suitable choice of origin. (110), (101), and (011) vanish if the coordinates coincide with the principal axes for the harmonic approximation, and (200), (020), (002), and (000) are removed from the summation. Only anharmonic terms remain.

6.1.1.6.3. Cumulant expansion

In a cumulant expansion (Johnson & Levy, 1974), the entire series is expressed in exponential form. The cumulant expansion about $\mathbf{S} = 0$ for the generalized temperature factor is

$$T(\mathbf{S}) = \exp \left[1 + i\kappa^j S_j + \frac{i^2}{2!} \kappa^{jk} S_j S_k + \frac{i^3}{3!} \kappa^{jkl} S_j S_k S_l + \frac{i^4}{4!} \kappa^{jklm} S_j S_k S_l S_m + \dots \right], \quad (6.1.1.63)$$

where the coefficient tensor $\kappa^{\alpha\beta\dots\zeta}$, a symmetric tensor of order p , is the p th-order cumulant. The inverse Fourier transform is the Edgeworth expansion around the Gaussian p.d.f. Cumulants can be expressed in terms of moments and *vice versa*. The p th moment $\mu^{\alpha\beta\dots\zeta}$ (if it exists) of a general p.d.f., $\rho(\mathbf{x})$, is a symmetric tensor defined as

$$\mu^{\alpha\beta\dots\zeta}(\mathbf{x}) = \int_{-\infty}^{\infty} x^\alpha x^\beta \dots x^\zeta \rho(\mathbf{x}) \, d\mathbf{x}. \quad (6.1.1.64)$$

The relations between the lower-order moments and cumulants are

$$\begin{aligned} \mu^j &= \kappa^j \\ \mu^{jk} &= \kappa^{jk} + \kappa^j \kappa^k \\ \mu^{jkl} &= \kappa^{jkl} + \kappa^j \kappa^{kl} + \kappa^k \kappa^{lj} + \kappa^l \kappa^{jk} + \kappa^j \kappa^k \kappa^l \\ &= \kappa^{jkl} + 3\kappa^{(j} \kappa^{kl)} + \kappa^j \kappa^k \kappa^l \\ \mu^{jklm} &= \kappa^{jklm} + 3\kappa^{j(k} \kappa^{lm)} + 4\kappa^{(j} \kappa^{klm)} \\ &\quad + 6\kappa^{(j} \kappa^k \kappa^{lm)} + \kappa^j \kappa^k \kappa^l \kappa^m \end{aligned} \quad (6.1.1.65)$$

and, conversely,

$$\begin{aligned} \kappa^j &= \mu^j \\ \kappa^{jk} &= \mu^{jk} - \mu^j \mu^k \\ \kappa^{jkl} &= \mu^{jkl} - 3\mu^{(j} \mu^{kl)} + 2\mu^j \mu^k \mu^l \\ \kappa^{jklm} &= \mu^{jklm} - 3\mu^{j(k} \mu^{lm)} - 4\mu^{(j} \mu^{klm)} \\ &\quad + 12\mu^{(j} \mu^k \mu^{lm)} - 6\mu^j \mu^k \mu^l \mu^m. \end{aligned} \quad (6.1.1.66)$$

In the Gram–Charlier and Fourier-invariant expansions, the Fourier-transform relationship between the p.d.f. and the temperature factor to given order can be made exact. Each cumulant μ^{jkl} contributes to all higher-order quasi-moment terms and *vice versa*. Hence, a given cumulant expansion is to an extent arbitrarily truncated (Kuhs, 1983). Care is required when interpreting the coefficients (Zucker & Schulz, 1982).

On the other hand, the cumulant expansion has the advantage of yielding tractable expressions for the one-particle potential in the quantum regime (Mair, 1980a). In that regime, equation (6.1.1.36) for the one-particle potential is invalid, and the expressions relating $V(\mathbf{u})$ to $\rho(\mathbf{u})$ in the Gram–Charlier and Fourier-invariant expansions are cumbersome (Mair & Wilkins, 1976).

Coefficients obtained by applying least-squares methods to structure-factor equations related to the truncated cumulant expansions do not necessarily yield non-negative p.d.f.'s nor are the linear-term coefficients necessarily faithful representations of the mean. Caution must be exercised in interpreting the results.

All the methods are satisfactory in the case of rapidly converging potential series. The methods are equivalent up to λ^2 in the van Hove order parameter (Mair, 1980b). Difficulties are encountered with convergence of the series in the case of strong anharmonicity, in which case numerical or alternative analytical models may be necessary. If the anharmonicity is such that the difference between the expansions is significant, it may be preferable to evaluate the Fourier transforms directly, as recommended by Mackenzie & Mair (1985).

6.1.1.6.4. Curvilinear density functions

For groups of atoms moving on the surface of a circle or sphere, perturbation expansions in Cartesian coordinates may converge slowly. Methods of representing curvilinear density functions that are multimodal or have large amplitude are described by Press & Hüller (1973).

For atoms constrained to rotate about a single axis,

$$a(\mathbf{u}) = \frac{1}{2\pi\tau} \delta(r - \tau) \delta(z) f(\varphi), \quad (6.1.1.67)$$

where r, z, φ are cylindrical coordinates for the displacement \mathbf{u} . Setting

$$f(\varphi) = \sum_{m=0} c_m \exp(im\varphi) + c_m^* (-im\varphi) \quad (6.1.1.68)$$

and

$$\exp(i\mathbf{S} \cdot \mathbf{r}) = \exp(iS_z z) \exp[iS_r r \cos(\varphi_S - \varphi)] \quad (6.1.1.69)$$

and using

$$\exp[iS_r r \cos(\varphi_S - \varphi)] = \sum_{l=0} (2 - \delta_{l0}) i^l J_l(S_r r) \cos[l(\varphi_S - \varphi)] \quad (6.1.1.70)$$

yields

$$T(\mathbf{S}) = \sum_{l=0} i^l J_l(S_r \tau) [c_l \exp(il\varphi_S) + c_l^* \exp(-il\varphi_S)]. \quad (6.1.1.71)$$

6.1. INTENSITY OF DIFFRACTED INTENSITIES

For atoms moving on the surface and a sphere, the density function may be written

$$\rho(\mathbf{u}) = \sum_{l=0}^{\infty} \sum_{j=1}^{2l+1} a_{lj}(u) K_{lj}(\theta, \varphi), \quad (6.1.1.72)$$

where u, θ, φ are spherical polar displacement coordinates and the K_{lj} are cubic harmonics. Thus, for a rigid molecule, the density function for nuclei confined to move on a spherical shell of radius τ is

$$a_{lj}(\mathbf{u}) = c_{lj} \delta(u - \tau) / u^2. \quad (6.1.1.73)$$

Expansion of $\exp(i\mathbf{S} \cdot \mathbf{r})$ in cubic harmonics

$$\exp(i\mathbf{S} \cdot \mathbf{r}) = 4\pi \sum_{l,j} i^l j_l(Sr) K_{lj}(\theta_S, \varphi_S) K_{lj}(\theta, \varphi) \quad (6.1.1.74)$$

leads to

$$T(\mathbf{S}) = 4\pi \sum_{l,j} i^l c_{lj} j_l(S\tau) K_{lj}(\theta_S, \varphi_S). \quad (6.1.1.75)$$

Equations (6.1.1.71) and (6.1.1.75) are useful when the p.d.f.'s (6.1.1.67) and (6.1.1.72) can be approximated by a limited number of significant terms. They are readily adapted to the case of oscillations about axes of symmetry (Press & Hüller, 1973).

6.1.1.6.5. Model-based curvilinear density functions

For rotational oscillations, which are the curvilinear coordinate analogues of the p.d.f.'s approximating harmonic rectilinear motion, techniques for evaluating the temperature factor are described by Johnson & Levy (1974).

The p.d.f. for an atom in a group of atoms undergoing large-amplitude rotational oscillation (libration) can sometimes be approximated satisfactorily by a standard p.d.f. on the circle or on the sphere. The closest analogues of the rectilinear Gaussian p.d.f. are the Brownian-diffusion p.d.f.'s defined on the closed spaces of the circle and the sphere. For statistical analysis, two other p.d.f.'s, the von Mises 'circular normal' and the Fisher 'spherical normal', are often substituted for the Brownian-diffusion density functions because of their simpler forms.

The p.d.f. for Brownian diffusion on a circle, also called the 'wrapped normal' p.d.f. (Feller, 1966; Lévy, 1938), is given by

$$\rho(\theta) = \frac{1}{(2\pi)^{1/2} \sigma} \sum_{n=-\infty}^{\infty} \exp[-(\theta - 2n\pi)^2 / 2\sigma^2], \quad (6.1.1.76)$$

which may be transformed (Bellman, 1961) into

$$\rho(\theta) = \frac{1}{2\pi} \sum_{m=0}^{\infty} (2 - \delta_{m0}) \exp(-m^2 \sigma^2 / 2) \cos(m\theta). \quad (6.1.1.77)$$

The von Mises p.d.f. (Gumbel, Greenwood & Durand, 1953; Mardin, 1972; von Mises, 1918) is

$$\rho(\theta) = \frac{\exp(k_c \cos \theta)}{2\pi I_0(k_c)} = \frac{1}{2\pi} \sum_{m=0}^{\infty} (2 - \delta_{m0}) \frac{I_m(k_c)}{I_0(k_c)} \cos(m\theta). \quad (6.1.1.78)$$

$I_m(x)$ is the m th-order Bessel function of the first kind with imaginary argument. The parameter σ^2 is the variance; k_c is a measure of concentration such that when k_c is zero the probability density is uniformly distributed over the circle, and when k_c is large the density is concentrated around the modal vector at $\theta = 0$. An approximate relation between σ^2 and k_c can be obtained by equating expressions for the centres of mass of the circular Brownian diffusion and von Mises p.d.f.'s (Stephens, 1963),

$$\exp(-\sigma^2/2) = \frac{I_1(k_c)}{I_0(k_c)}. \quad (6.1.1.79)$$

For small σ^2 (large k_c), we find that

$$\sigma^2 \simeq 1/k_c. \quad (6.1.1.80)$$

Equations (6.1.1.76) to (6.1.1.78) can be generalized to describe multimodal density functions with modes (maxima) arranged symmetrically about the circle. The p.d.f. for the s -modal Brownian-diffusion p.d.f. with one of the s modes at $\theta = \theta_0$ is

$$\begin{aligned} \rho(\theta) &= \frac{1}{\sqrt{2\pi s \sigma}} \sum_{m=-\infty}^{\infty} \exp[-(\theta - \theta_0 - 2\pi m/s)^2 / 2\sigma^2] \\ &= \frac{1}{2\pi} \sum_{m=0}^{\infty} (2 - \delta_{m0}) \exp[-(ms\sigma)^2 / 2] \cos[ms(\theta - \theta_0)]. \end{aligned} \quad (6.1.1.81)$$

The two-dimensional Fourier transform (Chidambaram & Brown, 1973) of the last equation in terms of the polar coordinates (S, θ) of the reciprocal-space vector \mathbf{S} relative to an origin at the centre of the circle is

$$T(\mathbf{S}) = \sum_{j=0}^{\infty} (2 - \delta_{j0}) i^{js} J_{js}(Sr) \exp[-(js\sigma)^2 / 2] \cos js\theta_0, \quad (6.1.1.82)$$

where $J_n(x)$ is the Bessel function of the first kind of order n with real argument. Corresponding equations for the von Mises s -modal density function (Atoji, Watanabe & Lipscomb, 1953; King & Lipscomb, 1950; Mardin, 1972) are

$$\begin{aligned} \rho(\theta) &= \frac{1}{2\pi I_0(K_c)} \exp[K_c \cos s(\theta - \theta_0)] \\ &= \frac{1}{2\pi} \sum_{m=0}^{\infty} (2 - \delta_{m0}) \frac{I_m(K_c)}{I_0(K_c)} \cos ms(\theta - \theta_0) \end{aligned} \quad (6.1.1.83)$$

and

$$T(\mathbf{S}) = \sum_{j=0}^{\infty} (2 - \delta_{j0}) i^{js} J_{js}(Sr) \frac{I_j(K_c)}{I_0(K_c)} \cos js\theta_0, \quad (6.1.1.84)$$

where K_c , a measure of concentration over $1/s$ th of the circle about θ_0 , is substituted for the k_c parameter of the unimodal von Mises density function and K_c is related to k_c approximately by

$$I_1(k_c) / I_0(k_c) = I_s(K_c) / I_0(K_c). \quad (6.1.1.85)$$

For symmetrical Brownian diffusion on a sphere (Furry, 1957; Lévy, 1938; Mardin, 1972; Perrin, 1928), the p.d.f. in terms of the angular displacement θ from the pole is

$$\rho(\theta) = \sum_{n=0}^{\infty} \frac{2n+1}{4\pi} \exp[-n(n+1)V] P_n(\cos \theta) \sin \theta, \quad (6.1.1.86)$$

where $P_n(x)$ is the n th-order Legendre polynomial. The Fisher (1953) 'spherical normal' p.d.f. (Mardin, 1972) is a similar density function given by

$$\begin{aligned} \rho(\theta) &= \frac{k_s}{4\pi \sinh k_s} \exp(k_s \cos \theta) \sin \theta \\ &= \sum_{n=0}^{\infty} \frac{(2n+1)}{4\pi} \frac{I_{n+1/2}(k_s)}{I_{1/2}(k_s)} P_n(\cos \theta) \sin \theta. \end{aligned} \quad (6.1.1.87)$$

The parameters V (variance) and k_s are measures of concentration analogous to those for the circle and may be related (Roberts & Ursell, 1960) by an equation analogous to (6.1.1.79),

6. INTERPRETATION OF DIFFRACTED INTENSITIES

$$\exp(-V/2) = \coth k_s - \frac{1}{k_s} = \frac{I_{3/2}(k_s)}{I_{1/2}(k_s)}, \quad (6.1.1.88)$$

the small V approximation being

$$V \simeq 2/k_s. \quad (6.1.1.89)$$

Equations (6.1.1.86) and (6.1.1.87) are generalized to place the mode of the density at (r, θ', φ') by replacing $\cos \theta$ by $\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\varphi - \varphi')$ and by replacing $P_n(\cos \theta)$ by

$$P(\cos \theta)P_n(\cos \theta') + 2 \sum_{m=1}^n \frac{(n-m)!}{(n-m)!} \times P_n^m(\cos \theta)P_n^m(\cos \theta') \cos m(\varphi - \varphi').$$

The three-dimensional Fourier transform of the generalized form of (6.1.1.86) in terms of \mathbf{S} in spherical coordinates (S, θ_S, φ_S) is

$$T(\mathbf{S}) = \sum_{q=0}^{\infty} i^q \frac{(2q+1)}{r^2} \exp[-q(q+1)V] \times \sum_{s=0}^{\infty} \frac{4}{2p+1} Y_{qs+}(\theta', \varphi') Y_{qs+}(\theta_S, \varphi_S) j_q(Sr), \quad (6.1.1.90)$$

where r is the radius of the sphere, and j_n is the n th-order spherical Bessel function of the first kind. The real spherical harmonics Y_{lmp} are normalized as in (6.1.1.22).

The Fourier transform of the generalized form of (6.1.1.87) is identical to (6.1.1.90) except that the term $\exp[-q(q+1)V]$ in (6.1.1.90) is replaced by $I_{q+1/2}(k_s)/I_{1/2}(k_s)$.

The foregoing equations describe isotropic distributions on a sphere. The p.d.f. for general anisotropic Brownian diffusion (or rotation) on a sphere is not available in a convenient form. However, some of the results of Perrin (1934) and Favro (1960) on rotational Brownian motion are applicable to thermal motion. For example, the centre of mass of a p.d.f. resulting from anisotropic diffusion on a sphere is given by equation (6.8) of Favro (1960). The following equation valid in Cartesian coordinates is obtained if the diffusion tensor \mathbf{D} of Favro's equation is replaced by the substitution $\mathbf{L} = 2\mathbf{D}$

$$\langle \mathbf{x} \rangle = \exp[-\frac{1}{2}(\text{tr}(\mathbf{L})\mathbf{I} - \mathbf{L})\mathbf{r}] = \mathbf{r} - \frac{1}{2}[\text{tr}(\mathbf{L})\mathbf{I} - \mathbf{L}]\mathbf{r} + \frac{1}{8}[\text{tr}(\mathbf{L})\mathbf{I} - \mathbf{L}]^2\mathbf{r} - \dots, \quad (6.1.1.91)$$

where \mathbf{r} is the vector from the centre of the sphere to the mode of the p.d.f. on the sphere and $\langle \mathbf{x} \rangle$ is the vector to the centre of mass. This equation, which is valid for all amplitudes of libration \mathbf{L} , can be used to describe the apparent shrinkage effect in molecules undergoing librational motion.

6.1.1.6.6. The quasi-Gaussian approximation for curvilinear motion

The p.d.f.'s defined by (6.1.1.77), (6.1.1.78), (6.1.1.86) and (6.1.1.87), and their Fourier transforms given in §6.1.1.6.5 may be considered 'inverted series' since zero-order terms describe uniform distributions. The inverted series converge slowly if the density is concentrated near the mode. If σ^2 in (6.1.1.76) is sufficiently small, the cyclic overlap on the circle becomes unimportant and the summation for $n \neq 0$ can be neglected. In this limiting case, the p.d.f. assumes the same form as a one-dimensional rectilinear Gaussian density function except that the variable is the angle φ . A similar relation must exist between the p.d.f. on the sphere and the two-dimensional Gaussian function. This 'quasi-Gaussian' approximation is the basis for a number of structure-factor equations for atoms with relatively small

amplitude components of curvilinear motion (Dawson, 1970; Kay & Behrendt, 1963; Kendall & Stuart, 1963; Maslen, 1968; Pawley & Willis, 1970).

6.1.1.7. Structure factor

The amplitude of coherent scattering from the contents of one unit cell in a crystalline material is the structure factor

$$F(\mathbf{S}) = \int \rho(\mathbf{r}) \exp(i\mathbf{S} \cdot \mathbf{r}) d\mathbf{r}, \quad (6.1.1.92)$$

where the integration extends over the unit cell. If there are N atoms in the cell, this may be expressed as

$$F(\mathbf{S}) = \sum_{j=1}^N f_j T_j \exp(i\mathbf{S} \cdot \mathbf{r}_j), \quad (6.1.1.93)$$

where \mathbf{r}_j is the mean position and T_j is the temperature factor of the j th atom. In an ideal model of the scattering process in which (6.1.1.93) is exact, f_j is the atomic scattering factor derived from (6.1.1.7). In practice, there are wavelength-dependent changes to the amplitude and phase of the atom's scattering due to dispersion or resonance. To correct for this, each scattering factor may be written

$$f = f^0 + f' + if'', \quad (6.1.1.94)$$

where f^0 is the kinematic scattering factor and f' and f'' are real and imaginary corrections for dispersion.

6.1.1.8. Reflecting power of a crystal

The reflecting power of a small crystal of volume ΔV , rotated at angular velocity ω through a Bragg reflection, defined as the ratio of ω times the reflected energy to the incident-beam intensity, is

$$r_e^2 \left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \right) \lambda^3 \frac{F(\mathbf{S})^2}{V_c^2} \Delta V, \quad (6.1.1.95)$$

where V_c is the unit-cell volume. This expression, which assumes negligible absorption, shows that the integrated intensity is proportional to the crystal volume. The maximum intensity is proportional to $(\Delta V)^2$, but the angular width of the reflecting region varies inversely as ΔV .

In the kinematic theory of diffraction, it is assumed that the crystal is comprised of small domains of perfect crystals for which the intensities are additive. In that case, (6.1.1.95) applies also to finite crystals.

6.1.2. Magnetic scattering of neutrons (By P. J. Brown)

6.1.2.1. Glossary of symbols

m_n	Neutron mass
m_e	Electron mass
γ	Neutron magnetic moment in nuclear magnetons (-1.91)
μ_B	Bohr magneton
μ_N	Nuclear magneton
r_e	Classical electron radius $\mu_B e^2 / 4\pi m_e$
\mathbf{P}_i	Electron momentum operator
\mathbf{S}_e	Electron spin operator
\mathbf{S}_n	Neutron spin operator
$\mathbf{M}(r)$	Magnetization density operator
\mathbf{k}	Scattering vector ($H/2\pi$)
$\hat{\mathbf{k}}$	A unit vector parallel to \mathbf{k}
\mathbf{r}_n	A lattice vector
\mathbf{g}	A reciprocal-lattice vector ($h/2\pi$)
τ	Propagation vector for a magnetic structure