

## 6. INTERPRETATION OF DIFFRACTED INTENSITIES

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

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  $\mu^{jkl}$  contributes to all higher-order quasi-moment terms and *vice versa*. Hence, a given cumulant expansion is to an extent arbitrarily truncated (Kuks, 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  $\lambda^2$  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  $r, z, \varphi$  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  $u, \theta, \varphi$  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  $\tau$  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  $\sigma^2$  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  $\sigma^2$  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  $\sigma^2$  (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 ( $S, \theta$ ) 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  $\theta_0$ , 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  $\theta$  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),