

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

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

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