<div align="center">4.5. POLYMER CRYSTALLOGRAPHY</div>

4.5.2.3.1. Helix symmetry

The presence of a unique axis about which there is rotational disorder means that it is convenient to use cylindrical polar coordinate systems in fibre diffraction. We denote by (r, φ, z) a cylindrical polar coordinate system in real space, in which the z axis is parallel to the molecular axes. The molecule is said to have u_v helix symmetry, where u and v are integers, if the electron density $f(r, \varphi, z)$ satisfies

$$f\left(r, \varphi + (2\pi m v / u), z + (mc/u)\right) = f(r, \varphi, z), \qquad (4.5.2.2)$$

where m is any integer. The constant c is the period along the z direction, which is referred to variously as the *molecular repeat distance*, the *crystallographic repeat*, or the *c repeat*. The helix *pitch P* is equal to c/v. Helix symmetry is easily interpreted as follows. There are u subunits, or *helix repeat units*, in one c repeat of the molecule. The helix repeat units are repeated by integral rotations of $2\pi v/u$ about, and translations of c/u along, the molecular (or helix) axis. The helix repeat units may therefore be referenced to a helical lattice that consists of points at a fixed radius, with relative rotations and translations as described above. These points lie on a helix of pitch P, there are v turns (or pitch-lengths) of the helix in one c repeat, and there are u helical lattice points in one c repeat. A u_v helix is said to have 'u residues in v turns'.

Since the electron density is periodic in φ and z, it can be decomposed into a Fourier series as

$$f(r, \varphi, z) = \sum_{l=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} g_{nl}(r) \exp\left(i[n\varphi - (2\pi l z/c)]\right), \quad (4.5.2.3)$$

where the coefficients $g_{nl}(r)$ are given by

$$g_{nl}(r) = (c/2\pi) \int_0^c \int_0^{2\pi} f(r, \varphi, z) \exp\left(i[-n\varphi + (2\pi l z/c)]\right) d\varphi \, dz. \qquad (4.5.2.4)$$

Assume now that the electron density has helical symmetry. Denote by $g(r, \varphi, z)$ the electron density in the region $0 < z < c/u$; the electron density being zero outside this region, *i.e.* $g(r, \varphi, z)$ is the electron density of a single helix repeat unit. It follows that

$$f(r, \varphi, z) = \sum_{m=-\infty}^{\infty} g[r, \varphi + (2\pi m v/u), z + (mc/u)]. \qquad (4.5.2.5)$$

Substituting equation (4.5.2.5) into equation (4.5.2.4) shows that $g_{nl}(r)$ vanishes unless $(l - nv)$ is a multiple of u, *i.e.* unless

$$l = um + vn \qquad (4.5.2.6)$$

for any integer m. Equation (4.5.2.6) is called the *helix selection rule*. The electron density in the helix repeat unit is therefore given by

$$g(r, \varphi, z) = \sum_l \sum_n g_{nl}(r) \exp\left(i[n\varphi - (2\pi l z/c)]\right), \qquad (4.5.2.7)$$

where

$$g_{nl}(r) = (c/2\pi) \int \int g(r, \varphi, z) \exp\left(i[-n\varphi + (2\pi l/c)]\right) d\varphi \, dz, \qquad (4.5.2.8)$$

and where in equation (4.5.2.7) (and in the remainder of this section) the sum over l is over all integers, the sum over n is over all integers satisfying the helix selection rule and the integral in equation (4.5.2.8) is over one helix repeat unit. The effect of helix symmetry, therefore, is to restrict the number of Fourier coefficients $g_{nl}(r)$ required to represent the electron density to those whose index n satisfies the selection rule. Note that the selection rule is usually derived using a rather more complicated argument by considering the convolution of the Fourier transform of a continuous filamentary helix with a set of planes in reciprocal space (Cochran *et al.*, 1952). The approach described above, which follows that of Millane (1991), is much more straightforward.

4.5.2.3.2. Diffraction by helical structures

Denote by (R, ψ, Z) a cylindrical polar coordinate system in reciprocal space (with the Z and z axes parallel), and by $F(R, \psi, Z)$ the Fourier transform of $f(r, \varphi, z)$. Since $f(r, \varphi, z)$ is periodic in z with period c, its Fourier transform is nonzero only on the *layer planes* $Z = l/c$ where l is an integer. Denote $F(R, \psi, l/c)$ by $F_l(R, \psi)$; using the cylindrical form of the Fourier transform shows that

$$F_l(R, \psi) = \int_0^c \int_0^{2\pi} \int_0^{\infty} f(r, \varphi, z) \exp\left(i \, 2\pi \left[Rr\cos(\psi - \varphi)\right.\right.$$
$$\left.\left. + (lz/c)\right]\right) r \, dr \, d\varphi \, dz. \qquad (4.5.2.9)$$

It is convenient to rewrite equation (4.5.2.9) making use of the Fourier decomposition described in Section 4.5.2.3.1, since this allows utilization of the helix selection rule. The *Fourier–Bessel structure factors* (Klug *et al.*, 1958), $G_{nl}(R)$, are defined as the Hankel transform of the Fourier coefficients $g_{nl}(r)$, *i.e.*

$$G_{nl}(R) = \int_0^{\infty} g_{nl}(r) J_n(2\pi Rr) 2\pi r \, dr, \qquad (4.5.2.10)$$

and the inverse transform is

$$g_{nl}(r) = \int_0^{\infty} G_{nl}(R) J_n(2\pi Rr) 2\pi R \, dR. \qquad (4.5.2.11)$$

Using equations (4.5.2.7) and (4.5.2.11) shows that equation (4.5.2.9) can be written as

$$F_l(R, \psi) = \sum_n G_{nl}(R) \exp\left(in[\psi + (\pi/2)]\right), \qquad (4.5.2.12)$$

where, as usual, the sum is over only those values of n that satisfy the helix selection rule. Using equations (4.5.2.8) and (4.5.2.10) shows that the Fourier–Bessel structure factors may be written in terms of the atomic coordinates as

$$G_{nl}(R) = \sum_j f_j(\rho) J_n(2\pi Rr_j) \exp\left(i[-n\varphi_j + (2\pi l z_j/c)]\right), \qquad (4.5.2.13)$$

where $f_j(\rho)$ is the (spherically symmetric) atomic scattering factor (usually including an isotropic temperature factor) of the jth