THE FOURIER TRANSFORM

In one-dimension the Fourier transform is mathematically expressed in the following way:

$$F(X) = \int_{-\infty}^{\infty} \rho(x) e^{(2\pi i x X)} dx \tag{III.C.6.1}$$

$F(X)$ is called the scattering function and $\rho(x)$ is called the electron density function. The integration is over **all** values x in the structure. For the case in which there is a discrete summation over **sampled** points in the structure the above expression becomes:

$$F(X) = \sum_{x} \rho(x) e^{(2\pi i x X)} \tag{III.C.6.2}$$

F is a shorthand notation for the Fourier transform of ρ, i.e. $F = T(\rho)$, where **"T"** represents the **forward** Fourier transformation operation.

A property of Fourier transforms is that the **inverse relationship** holds, namely:

$$\rho(x) = \int_{-\infty}^{\infty} F(X) e^{(-2\pi i x X)} dX \tag{III.C.6.3}$$

Thus, ρ is the **inverse transform** of F, i.e. $\rho = T^{-1}(F)$, where "T^{-1}" signifies an **inverse** Fourier transformation operation.

Thus, $\rho = T^{-1}(T(\rho))$ (III.C.6.4)

FOURIER SYNTHESIS

Any periodic function may be represented by a summation of a series of sinusoidal waves. In one-dimension, the Fourier synthesis can be mathematically expressed in the following way:

$$\rho(x) = \sum_{n=-\infty}^{\infty} A_n \cos(2\pi n x / a) \tag{III.C.6.5}$$

where

$\rho(x)$	= one-dimensional density function
x	= coordinate of a point in the object
a	= repeat distance
A_n	= Fourier coefficient (amplitude term) for wave number n
n	= wave number (frequency) or cycles per repeat distance a
$(2\pi n x / a)$	= phase term (position of wave with respect to a fixed origin point in the repeating structure)

BRAGG DIFFRACTION

Diffraction in the three-dimensional crystal from the hkl **set of planes, separated a distance** d_{hkl}, **only occurs for certain orientations of the incident radiation,** according to the Bragg relation:

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \tag{III.C.6.6}$$

where

n	= integer
λ	= wavelength of incident radiation
d_{hkl}	= crystal lattice spacing between the [hkl] set of crystal planes
θ_{hkl}	= angle of incidence and also of reflection
hkl	= Miller indices of a plane

STRUCTURE FACTOR

The **structure factor describes the scattering of all atoms of the unit cell for a given reflection.** Each diffracted ray, or reflection, is described by a structure factor, F_{hkl}. It is a **complex number** whose **magnitude** can be **determined from the intensity of the** *hkl* **reflection.** Each structure factor may be regarded as a sum of the contributions of the x-rays scattered from all atoms within the unit cell. The mathematical formulation of the structure factor depends on whether the object is considered to be continuous or made of a discrete number of atoms.

Objects consisting of discrete atoms

For **an object with** n **atoms,** the structure factor equation is:

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp\left[2\boldsymbol{pi}\left(hx_j + ky_j + lz_j\right)\right]$$

(III.C.6.7)

f_j is the **atomic scattering factor for atom j.** This is the ratio of the amplitude scattered by the atom to the amplitude scattered by a single electron. At zero scattering angle, f_j = atomic number, but, as the scattering angle increases, the value of f_j decreases because of the finite volume over which the electrons in the atom extend. *hkl* refers to the particular set of diffracting planes and x_j, y_j, z_j are the fractional unit cell coordinates for each of the atoms in the unit cell.

Since $e^{i\theta} = \cos\theta + i\sin\theta$, equation III.C.6.7 can be rewritten:

$$F_{hkl} = \sum_{j=1}^{n} f_j \left\{\cos\left[2\boldsymbol{p}\left(hx_j + ky_j + lz_j\right)\right] + i\sin\left[2\boldsymbol{p}\left(hx_j + ky_j + lz_j\right)\right]\right\}$$

(III.C.6.8)

$$= \sum_{j=1}^{n} f_j \cos\left[2\boldsymbol{p}\left(hx_j + ky_j + lz_j\right)\right] + i\sum_{j=1}^{n} f_j \sin\left[2\boldsymbol{p}\left(hx_j + ky_j + lz_j\right)\right]$$

(III.C.6.9)

$$= A_{hkl} + iB_{hkl}$$

(III.C.6.10)

F_{hkl} is a complex quantity, with a **real** and an **imaginary** part represented by A_{hkl} and B_{hkl}.

Argand representation

F_{hkl} is conveniently depicted as a vector in an **Argand diagram** in which the horizontal axis represents the **real axis** and the vertical axis represents the **imaginary axis.** In this representation, the vector quantity F_{hkl} can be thought of as composed of the vector sum of A_{hkl}, the **real component,** and B_{hkl}, the **imaginary component.** The vector F_{hkl} makes an angle α_{hkl} with respect to the real axis. The magnitudes of the vectors A_{hkl} and B_{hkl} are, respectively, $|F_{hkl}|\cos(\alpha_{hkl})$ and $|F_{hkl}|\sin(\alpha_{hkl})$.

The **structure factor amplitude** is defined as the modulus or magnitude of F_{hkl}. That is:

$$|F_{hkl}| = [(A_{hkl})^2 + (B_{hkl})^2]^{1/2}$$

(III.C.6.11)

The **structure factor phase** of F_{hkl} is equal to the angle α_{hkl}.

Since $F_{hkl} = A_{hkl} + iB_{hkl}$

(III.C.6.12)

$$= |F_{hkl}|\cos(\alpha_{hkl}) + |F_{hkl}|i\sin(\alpha_{hkl})$$

(III.C.6.13)

$$= |F_{hkl}|\exp(i\alpha_{hkl})$$

(III.C.6.14)

If θ_j is substituted for $2\pi(hx_j + ky_j + lz_j)$, the structure factor equation can be expressed in a simpler form:

$$F_{hkl} = \sum_{j=1}^{n} f_j e^{i\mathbf{f}_j} \qquad \text{(III.C.6.15)}$$

$$= \sum_{j=1}^{n} f_j \left(\cos \mathbf{f}_j \right) + i \sin \mathbf{f} \qquad \text{(III.C.6.16)}$$

Structure with continuous density

For a three-dimensional structure with **continuous density,** $\rho(xyz)$, the structure factor equation becomes:

$$F_{hkl} = V\iiint \rho(xyz) e^{2\pi i(hx+ky+lz)} dx\,dy\,dz \qquad \text{(III.C.6.17)}$$

In this expression, the integration is over the entire unit cell volume, *V*.

CONVOLUTION AND MULTIPLICATION (SAMPLING)

These concepts provide a fundamental basis for understanding diffraction from crystalline objects. Holmes and Blow (1965) give a general statement of the operation of convolution of two functions:

> *"Set down the origin of the first function in every possible position of the second, multiply the value of the first function in each position by the value of the second at that point and take the sum of all such possible operations."*

This is expressed in mathematical terms as:

$$c(u) = \int_{-\infty}^{\infty} f(x) g(u-x) dx \qquad \text{(III.C.6.18)}$$

This is known as the **convolution** of $f(x)$ and $g(x)$, and may be written as:

$$c(u) = f(x) * g(x) \qquad \text{(III.C.6.19)}$$

The **convolution theorem** provides a precise way to describe the relationship between objects in real space and transforms in reciprocal space. It states:

1) The Fourier transform of the convolution of two functions is the product of their Fourier transforms.

$$T(f * g) = \mathbf{F} \times \mathbf{G} \quad \text{(III.C.6.20)}$$

The converse of the above also holds:

2) The Fourier transform of the product of two functions is equal to the convolution of the transforms of the individual functions.

$$T(f \times g) = \mathbf{F} * \mathbf{G} \quad \text{(III.C.6.21)}$$

The symbols, $*$ and x, correspond to the convolution and multiplication operations. *f* and *g* represent two functions and **F** and **G** are the respective Fourier transforms.

THE RECIPROCAL LATTICE

Parameters of the crystal lattice (real-space) and reciprocal lattice are related by:

$$d^* = K/d\sin\gamma^* \qquad \text{(III.C.6.24)}$$

$$\text{and} \quad \gamma^* = 180 - \gamma \qquad \text{(III.C.6.25)}$$