The Fourier Transform, the Wave Equation and Crystals

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https://www.acameeting.com/
35000 ft view of X-ray Structure Analysis

X-rays

Crystal

Intensity $I_{(hkl)}$

Electron density $\rho(r)$

Molecular Model

Phases

Fourier Transform
Fourier Theory

• Originally proposed by Jean-Bapiste Joseph Fourier in 1822 in *The Analytical Theory of Heat*

• Described discrete functions as the infinite sum of sines
What is a circle?

\[ e^{i\varphi} = \cos \varphi + i \sin \varphi \]

\[ e^{n\pi} = e^{-n\pi} = -1 \text{ for } n \text{ odd} \]
\[ e^{n\pi} = e^{-n\pi} = 1 \text{ for } n \text{ even} \]
\[ e^{0.5i\pi} = i \]
\[ e^{1.5i\pi} = -i \]

http://en.wikipedia.org/wiki/Euler's_formula
The Fourier Transform

\[ F(k) = \int_{-\infty}^{\infty} f(x) e^{i k x} \, dx \]

\[ F(k) = Tf(x) \]

In the three dimensions this is generalized to:

\[ F(k) = \int_{\mathbb{R}^3} f(\mathbf{r}) e^{i k \mathbf{r}} \, d\mathbf{r} = Tf(\mathbf{r}) \]
The Dirac $\delta$ function

$$\delta(x-x_0)\begin{cases} +\infty, & (x-x_0) = 0 \\ 0, & (x-x_0) \neq 0 \end{cases}$$

$$\int_{-\infty}^{\infty} \delta(x-x_0) \, dx = 1$$

A 3D lattice may be described as a three-dimensional array of delta functions.

$$r = pa + qb + rc$$

$$l(r) = \sum_{\text{all } p, q, r} \delta(r-[pa+qb+rc])$$

An important property of the $\delta$ function is that acts as a sift:

$$\int_{-\infty}^{\infty} f(x)\delta(x-x_0) \, dx = f(x_0) \int_{-\infty}^{\infty} \delta(x-x_0) \, dx = f(x_0)$$

In three dimensions:

$$\int_{-\infty}^{\infty} f(r)\delta(r-r_0) \, dr = f(r_0)$$
Fourier transforms and $\delta$ functions

One $\delta$ function:

$$F(k) = \int_{-\infty}^{\infty} f(x)e^{ikx} \, dx$$

$$= \int_{-\infty}^{\infty} \delta(x)e^{ikx} \, dx = \left[ e^{ikx} \right]_{x=0} = e^0 = 1$$

Two $\delta$ functions:

$$f(x) = \delta(x + x_0) + \delta(x - x_0)$$

$$F(k) = \int_{-\infty}^{\infty} f(x)e^{ikx} \, dx$$

$$= \int_{-\infty}^{\infty} \delta(x + x_0)e^{ikx} \, dx + \int_{-\infty}^{\infty} \delta(x - x_0)e^{ikx} \, dx$$

$$= e^{-ikx_0} + e^{ikx_0}$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}, \quad \theta = kx_0$$

$$F(k) = 2 \cos kx_0$$
Waves and Electromagnetic Radiation

• What is a wave?
  – Direction of propagation
  – Amplitude
    • Wave crest
    • Wave trough
  – Wavelength
    • Period
    • Frequency

Waves and Electromagnetic Radiation

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\[ \psi(x, 0) = \psi_0 \cos \left( \frac{2\pi x}{\lambda} \right) \]

\[ \psi(0, t) = \psi_0 \cos \left( \frac{2\pi t}{\tau} \right) \]

\[ \psi(x, t) = \psi_0 \cos \left( 2\pi \frac{x}{\lambda} - 2\pi \frac{t}{\tau} \right) \]

\[ k = \frac{2\pi}{\lambda} \]

\[ \omega = \frac{2\pi}{\tau} \]

\[ \psi(x, t) = \psi_0 \cos \left( kx - \omega t \right) \]

\[ \Delta x = \frac{k}{\omega} = v \]
\[ \frac{\partial^2 \psi(x, y, z, t)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z, t)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z, t)}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x, y, z, t)}{\partial t^2} \]

\[ \psi(x, y, z, t) = \psi_0 \cos(k_x x + k_y y + k_z z - \omega t) \]

\[ k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{v^2} \]

\[ \mathbf{r} = (x, y, z) \]

\[ \mathbf{k} = (k_x, k_y, k_z) \]

\[ \mathbf{k} \cdot \mathbf{r} = (k_x x + k_y y + k_z z) \]

\[ \psi(\mathbf{r}, t) = \psi_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \]

\[ \psi(\mathbf{r}, t) = \psi_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi) \]

\[ \psi(\mathbf{r}, t) = \psi_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi)} \]

\[ I = |\psi(\mathbf{r}, t)|^2 \]
Diffraction

- Diffraction by one dimensional objects
- Diffraction by two dimensional objects
- Diffraction by three dimensional objects
Diffraction by a one dimensional object

\[ \mathbf{k} = (k_x, 0, k_z) \]
\[ \mathbf{k} \cdot \mathbf{r} = (k_x, 0, k_z) \cdot (x, 0, 0) \]
\[ \mathbf{k} \cdot \mathbf{r} = k_x x \]
\[ k_x = k \sin \theta_s \]
\[ \mathbf{k} \cdot \mathbf{r} = k x \sin \theta_s \]

\[ F(\mathbf{k}) = \int_{-\infty}^{\infty} f(x) e^{ikx \sin \theta_s} \, dx \]

\[ F(\sin \theta_s) = \int_{-\infty}^{\infty} f(x) e^{ikx \sin \theta_s} \, dx \]
Diffraction by one narrow slit

A narrow slit is defined by:

\[ f(x) = \delta(x) \text{ and } \delta(0) = +\infty \]

\[
F(\sin \theta_s) = \int_{-\infty}^{\infty} \delta(x)e^{ikx\sin\theta_s} \, dx = \int_{-\infty}^{\infty} \delta(x) \, dx = 1
\]

\[
F(\sin \theta_s) = 1
\]

\[
|F(\sin \theta_s)|^2 = 1
\]
Diffraction by one wide slit

\[ f(x) = 0 \text{ if } -\infty < x < -X_0 \]
\[ f(x) = 1 \text{ if } -X_0 < x < X_0 \]
\[ f(x) = 0 \text{ if } X_0 < x < \infty \]

\[ F(\sin \theta_s) = \int_{-\infty}^{\infty} f(x) e^{ikx \sin \theta_s} \, dx = \int_{-X_0}^{X_0} e^{ikx \sin \theta_s} \, dx = \left[ \frac{e^{ikx \sin \theta_s}}{ikx \sin \theta_s} \right]_{-X_0}^{X_0} = \frac{e^{ikX_0 \sin \theta_s} - e^{-ikX_0 \sin \theta_s}}{ikX_0 \sin \theta_s} = 2X_0 \frac{\sin(kX_0 \sin \theta_s)}{kX_0 \sin \theta_s} \]

\[ |F(\sin \theta_s)|^2 = 4X_0^2 \frac{\sin^2(kX_0 \sin \theta_s)}{(kX_0 \sin \theta_s)^2} \]
Diffraction by two narrow slits

Two narrow slits are defined by:

\[ f(x) = \delta(x + x_0) + \delta(x - x_0) \] and \( \delta(x_0) = +\infty \) and \( \delta(-x_0) = +\infty \)

\[ F(\sin \theta_s) = \int_{-\infty}^{\infty} f(x)e^{ikx\sin \theta_s} \, dx = 2\cos(kx_0 \sin \theta_s) \]

\[ F(\sin \theta_s) = 2\cos(kx_0 \sin \theta_s) \]

\[ |F(\sin \theta_s)|^2 = 4\cos^2(kx_0 \sin \theta_s) \]
Diffraction by Two Wide Slits

\[ f(x) = 0 \text{ if } -\infty < x < -(x_0 + X_0) \]
\[ f(x) = 1 \text{ if } -(x_0 + X_0) \leq x \leq -(x_0 - X_0) \]
\[ f(x) = 0 \text{ if } -(x_0 - X_0) < x < (x_0 - X_0) \]
\[ f(x) = 1 \text{ if } (x_0 - X_0) \leq x \leq (x_0 + X_0) \]
\[ f(x) = 0 \text{ if } (x_0 + X_0) < x < \infty \]

\[ f(\text{two wide slits}) = f(\text{one wide slit}) \times f(\text{two narrow slits}) \]
Diffraction by Two Wide Slits
• The position of the main peaks in a diffraction pattern is determined solely by the lattice spacing of the object.
• The shape of each main peak is determined by the overall shape of the object.
• The effect of the object (motif) is to alter the intensity of each main peak, but the positions of the main peaks remain unchanged.
• The positions of the main peaks give information about the lattice
• The shape of each main peak gives information on the overall object shape.
• The set of intensities of the main peaks gives information on the structure of the motif.
Diffraction by a 3D Lattice

\[ r = pa + qb + rc \]

\[ f(r) = \sum_{all\ p,q,r} \delta(r - [pa + qb + rc]) \]

\[ F(\Delta k) = \int_{all \ r} f(r)e^{i\Delta k \cdot r} \, dr \]

\[ F(\Delta k) = \sum_{all \ r} \delta(r - [pa + qb + rc])e^{i\Delta k \cdot r} \]

\[ F(\Delta k) = \sum_{all \ p,q,r} e^{ip\Delta k \cdot a} \cdot e^{iq\Delta k \cdot b} \cdot e^{ir\Delta k \cdot c} \]

\[ |F(\Delta k)|^2 = \frac{\sin^2 \frac{P\Delta k \cdot a}{2}}{\sin^2 \frac{\Delta k \cdot a}{2}} \cdot \frac{\sin^2 \frac{Q\Delta k \cdot b}{2}}{\sin^2 \frac{\Delta k \cdot b}{2}} \cdot \frac{\sin^2 \frac{R\Delta k \cdot c}{2}}{\sin^2 \frac{\Delta k \cdot c}{2}} \]

Maxima are seen at \( \Delta k \cdot a = 2h\pi \) where \( h \) is a positive or negative integer
Diffraction by a 3D Object

\[ e^{i(k \cdot r_1 - \omega t)} \] and \( f(r_1) \, dr_1 \)

diffracted wave from element \( dr_1 = f(r_1) e^{i(k \cdot r_1 - \omega t)} \, dr_1 \)

diffracted wave from element \( dr_2 = f(r_2) e^{i(k \cdot r_2 - \omega t)} \, dr_2 \)

diffracted wave from all elements \( dr_n = \sum f(r_n) e^{i(k \cdot r_n - \omega t)} \, dr_n \)

diffraction pattern \( = \int_V f(r) e^{i(k \cdot r - \omega t)} \, dr \)

diffraction pattern \( = e^{-\omega t} \int_V f(r) e^{i k \cdot r} \, dr \)

diffraction pattern \( = \int_V f(r) e^{i k \cdot r} \, dr \)

If \( r \) is outside the object, \( f(r) = 0 \)

diffraction pattern \( = \int_{all \, r} f(r) e^{i k \cdot r} \, dr \Rightarrow T[f(r)] \)
Thomson Scattering by a Single Electron

\[ a = \frac{e}{m} E_{in} \]

\[ \frac{E_{scat}}{E_{in}} = \frac{e^2}{4\pi\varepsilon_0 rmc^2} \sqrt{\frac{1 + \cos^2 2\theta}{2}} \]

\[ \varepsilon_0 = 8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1} \]

\[ c = \text{speed of light} \]

\[ r = \text{radius of interaction} \]

\[ \theta = \text{Bragg angle} \]
Thomson Scattering by a Group of Electrons (I)

\[
\frac{E_{\text{scat}}}{E_{\text{in}}} = \frac{e^2}{4\pi \varepsilon_0 rmc^2} \sqrt{\frac{1 + \cos^2 2\theta}{2}}
\]

\[
f_e = \frac{e^2}{4\pi \varepsilon_0 rmc^2}
\]

\[
\frac{E_{\text{scat}}}{E_{\text{in}}} = f_e \sqrt{\frac{1 + \cos^2 2\theta}{2}}
\]

but if the beam is polarized we can write:

\[
\frac{E_{\text{scat}}}{E_{\text{in}}} = f_e p(2\theta)
\]

where \(p(2\theta)\) is the polarization factor.

For now let's ignore \(p(2\theta)\).
Thomson Scattering by a Group of Electrons (II)

\[
E_{scat}\left(A\right) = f_e E_{in} \\
E_{scat}\left(B\right) = f_e E_{in} e^{i\phi} \\
E_{scat}\left(tot\right) = E_{scat}\left(A\right) + E_{scat}\left(B\right) \\
\frac{E_{scat}\left(tot\right)}{E_{in}} = f_e + f_e e^{i\phi} \\
\frac{E_{scat}\left(tot\right)}{E_{in}} = \sum_{n} f_n e^{i\phi_n} \\
\]

Remember

\[
F(\Delta k) = \int_{all\ r} f(r)e^{i\Delta k \cdot r} \, dr 
\]

The amplitude function of a group of electrons is

\[
f_e \rho(r) 
\]

Substituting into \( F(\Delta k) \) gives

\[
F(\Delta k) = \int_{all\ r} f_e \rho(r)e^{i\Delta k \cdot r} \, dr 
\]
Thomson Scattering by a Group of Electrons (III) or the Motif

\[ F(\Delta k) = \int \rho(r) e^{i\Delta k \cdot r} \, dr \]

\[ F(\Delta k) = \int_{\text{unit cell}} \rho(r) e^{i\Delta k \cdot r} \, dr \quad \text{or} \quad F_{\text{rel}}(\Delta k) = \int_{\text{unit cell}} \rho(r) e^{i\Delta k \cdot r} \, dr \]

Let's define coordinates of the unit cell as follows:

\[ 0 \leq X \leq a, \ 0 \leq Y \leq b, \ 0 \leq Z \leq c \]

\[ x = \frac{X}{a}, \ y = \frac{Y}{b}, \ z = \frac{Z}{c} \quad \text{and} \ 0 \leq x \leq 1, \ 0 \leq y \leq 1, \ 0 \leq z \leq 1 \]

\[ X, \ Y \] and \[ Z \] represent absolute coordinates and \[ x, \ y \] and \[ z \] represent fractional coordinates.

\[ r = xa + yb + zc \]

\[ dr = dx \ dy \ dz \quad a \cdot b \wedge c = V \quad dx \ dy \ dz \]

\[ \rho(r) \] becomes \[ \rho(x, y, z) \]
Bragg’s Law

\[ |\Delta k| = 2k \sin \theta \]

\[ k = \frac{2\pi}{\lambda} \]

\[ |\Delta k| = 2\pi S_{hkl} \]

\[ 2\pi S_{hkl} = 2 \frac{2\pi}{\lambda} \sin \theta \]

\[ S_{hkl} = \frac{2\sin \theta}{\lambda} \]

\[ S_{hkl} = \frac{1}{d_{hkl}} \]

\[ \frac{1}{d_{hkl}} = \frac{2\sin \theta}{\lambda} \]

\[ \lambda = 2d_{hkl} \sin \theta \]

Let us increase \( \theta \) starting from \( \theta = 0 \) when

\( \lambda = 1.5418 \text{ Å} \) and \( d_H = 5.2 \text{ Å} \).
Thomson Scattering by a Group of Electrons (IV) or the Motif

\[ F_{rel}(\Delta k) = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x, y, z)e^{i\Delta k \cdot (xa + yb + zc)} \, dx \, dy \, dz \]

\[ \Delta k = 2\pi S_{hk} \]

\[ S_{hk} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

\[ \Delta k \cdot \mathbf{r} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c}) \]

\[ = 2\pi(hx + ky + lz) \]

\[ F_{rel}(\Delta k) = F_{hk} = V \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} \rho(x, y, z)e^{2\pi i(hx + ky + lz)} \, dx \, dy \, dz \]

\[ F_{hk} = |F_{hk}|e^{i\phi_{hk}} \]

\[ I_{hk} = |F_{hk}|^2 \]
The Electron Density Function

\[ F_{rel}(\Delta k) = F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x, y, z)e^{i\Delta k \cdot (xa+yb+zc)} \, dx \, dy \, dz \]

\[ F_{hkl} \] is the Fourier transform of \( \rho(x, y, z) \)

\[ \rho(x, y, z) = \frac{1}{V} \int_{all \Delta k} F_{rel}(\Delta k)e^{-i\Delta k \cdot (xa+yb+zc)} \, d(\Delta k) \]

\[ \rho(x, y, z) = \frac{1}{V} \int_{all \Delta k} F_{rel}(\Delta k)e^{-2\pi i (hx+ky+lz)} \, d(\Delta k) \]

But the \( hkl \) values are discrete so we can rewrite this as

\[ \rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i (hx+ky+lz)} \]
The Structure Factor

\[ F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x, y, z) e^{i\Delta k(xa+yb+zc)} \, dx \, dy \, dz \]

\[ F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

- In the first equation the coordinates \((x, y, z)\) refer to any position within the unit cell, whereas \((x_j, y_j, z_j)\) in the second equation define the position of the atoms.
- \(\rho(x, y, z)\) is a continuous function describing the overall electron density, \(f_j\), is a property of each atom.
- The first equation requires an integration over the entire unit cell, but the second equation requires a summation over the positions of the atoms within the unit cell.
What does $F_{hkl} = \sum_{j} f_{j} e^{2\pi i (hx+ky+lz)} = |F_{hkl}| e^{i\phi}$ mean?

- The **amplitude** of scattering depends on the number of electrons in each atom.
- The **phase** depends on the **fractional** distance it lies from the lattice plane.

Scattering from lattice planes add as **complex numbers**, or **vectors**.
The Atomic Scattering Factor

\[ d \mathbf{R} = R^2 \sin \phi \ dR \ d\phi \ d\psi \] and \[ S_{hkl} \cdot \mathbf{R} = S_{hkl} R \cos \phi \]

\[ f_j = \int_{\psi=0}^{\psi=2\pi} \int_{\phi=0}^{\phi=\pi} \int_{R=0}^{R=\infty} \rho_j(R) e^{2\pi i S_{hkl} R \cos \phi} R^2 \sin \phi \ dR \ d\phi \ d\psi \]

\[ f_j = \int_{\psi=0}^{\psi=2\pi} \int_{\phi=0}^{\phi=\pi} \int_{R=0}^{R=\infty} \rho_j(R) e^{2\pi i S_{hkl} R \cos \phi} R^2 \sin \phi \ dR \ d\phi \ d\psi \]

\[ f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left( \frac{e^{2\pi S_{hkl} R} - e^{-2\pi S_{hkl} R}}{2\pi S_{hkl} R} \right) dR \]

\[ f_j = 4\pi \int_0^\infty R^2 \rho_j(R) \left( \frac{\sin 2\pi S_{hkl} R}{2\pi S_{hkl} R} \right) dR \]

\[ S_{hkl} = \frac{2 \sin \theta}{\lambda} \]

\[ f_j = 4\pi \int_0^\infty R^2 \rho_j(R) \left( \frac{\sin \left( \frac{4\pi \sin \theta}{\lambda} R \right)}{\frac{4\pi \sin \theta}{\lambda} R} \right) dR \]
Correction for Thermal Motion (I)

\[ F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

\[ F_{hkl} = \sum_j f_j e^{2\pi i S_{hkl} \cdot r_j} \]

Consider a small random displacement about \( r_j \)

\[ F_{hkl} = \sum_j f_j e^{2\pi i S_{hkl} \cdot (r_j + u_j)} \]

\[ F_{hkl} = \sum_j f_j e^{2\pi i S_{hkl} r_j} e^{2\pi i S_{hkl} u_j} \]

Let us define \( u_j \) as motion in the direction of \( S_{hkl} \) that is perpendicular to the plane \( hkl \):

\[ S_{hkl} \cdot u_j \text{ becomes } S_{hkl} u_j \text{ and} \]

\[ F_{hkl} = \sum_j f_j e^{2\pi i S_{hkl} r_j} e^{2\pi i S_{hkl} u_j} \]

\( F_{hkl} \) is measured over a long time

\[ F_{hkl} = \sum_j f_j e^{2\pi i S_{hkl} r_j} \frac{e^{2\pi i S_{hkl} u_j}}{e^{2\pi i S_{hkl} u_j}} \]

\[ e^{2\pi i S_{hkl} u_j} \approx 1 + 2\pi i S_{hkl} u_j - 2\pi^2 (S_{hkl} u_j)^2 \]

\[ e^{2\pi i S_{hkl} u_j} \approx 1 + 2\pi i S_{hkl} u_j - 2\pi^2 (S_{hkl} u_j)^2 \]

\[ e^{2\pi i S_{hkl} u_j} \approx e^{2\pi^2 S_{hkl}^2 u_j^2} \]
Correction for Thermal Motion (II)

\[-2\pi^2 S_{hkl}^2 u_j^2 = -2\pi^2 \left( \frac{2 \sin \theta}{\lambda} \right) u_j^2 \]

\[-2\pi^2 S_{hkl}^2 u_j^2 = -8\pi^2 \left( \frac{\sin \theta}{\lambda} \right)^2 u_j^2 \]

Let us define \( B_j = 8\pi^2 u_j^2 \)

\[ e^{2\pi i S_{hkl} u_j} \approx e^{-B_j (2 \sin \theta / \lambda)^2} \]

\[ (f_j)_T = f_j e^{-B_j (2 \sin \theta / \lambda)^2} \]

\[ (F_{hkl})_T = \sum_j (f_j)_T e^{2\pi i (hx_j + ky_j + lz_j)} \]

\[ (F_{hkl})_T = \sum_j f_j e^{-B_j (2 \sin \theta / \lambda)^2} e^{2\pi i (hx_j + ky_j + lz_j)} \]
Let's consider two centrosymmetrically disposed reflections:

\[ F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

\[ F_{\bar{h}k\bar{l}} = \sum_j f_j e^{2\pi i (\bar{h}x_j + \bar{k}y_j + \bar{l}z_j)} = \sum_j f_j e^{-2\pi i (hx_j + ky_j + lz_j)} \]

\[ F_{hkl}^* = F_{\bar{h}k\bar{l}} \quad \text{and thus} \quad |F_{hkl}| = |F_{hkl}^*| = |F_{\bar{h}k\bar{l}}| \]

\[ I_{hkl} = I_{\bar{h}k\bar{l}} = |F_{hkl}|^2 = |F_{\bar{h}k\bar{l}}|^2 \]

Furthermore:

\[ \phi_{\bar{h}k\bar{l}} = -\phi_{hkl} \]
Dispersion

- Scattering is the result of an interaction of electromagnetic radiation with an electron.
  - Rayleigh or elastic scattering
  - Compton or inelastic scattering
- Dispersion occurs when electromagnetic radiation interacting with an electron in a shell has nearly the same frequency as the oscillator, i.e., resonates

\[
\frac{d^2 \bar{x}_j}{dt^2} + \kappa_j \frac{d\bar{x}_j}{dt} + \omega_j \bar{x}_j = -\frac{e}{m} E_0 e^{i\omega_0 t - i2\pi \bar{k}_0 \cdot \bar{r}_j}
\]

\[
\bar{x}_j = \frac{e}{m \omega_0^2} \frac{1}{1 - \frac{\omega_j^2}{\omega_0^2} - i \frac{\kappa_j}{\omega_0}} E_0 e^{i\omega_0 t - i2\pi \bar{k}_0 \cdot \bar{r}_j}
\]

\[
f = \sum_j \frac{\varphi_j}{\omega_j^2} = \sum_j \varphi_j \int \frac{w_j d\omega}{\omega} = f^0 + \sum_j \varphi_j (\xi_j + i \eta_j) = f^0 + f' + if''
\]
Effect on Diffraction Data

- **Form factor**
  \[ f = f^0 + \Delta f' + i\Delta f'' \]
  \[ f = f^0 + f' + if'' \]

- **Structure Factor**
  \[ F_{hkl} = \sum_j (f_j^0 + f_j' + if_j'') \cdot e^{2\pi i h \cdot r_j} \]
Breakdown of Freidel’s Law

\[ F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \]

\[ F_{hkl} = \sum_{j \neq A} f_j e^{2\pi i(hx_j + ky_j + lz_j)} + \left[ (f_A^0 + f'+if'') e^{2\pi i(hx_A + ky_A + lz_A)} \right] \]

\[ F_{hkl} = \sum_j f_j e^{2\pi i(\bar{hx}_j + \bar{ky}_j + \bar{lz}_j)} + \left[ (f_A^0 + f'+if'') e^{2\pi i(\bar{hx}_A + \bar{ky}_A + \bar{lz}_A)} \right] \]

\[ F_{hkl}^* \neq F_{hkl} \] and thus \[ |F_{hkl}| = |F_{hkl}^*| \neq |F_{hkl}| \]

\[ I_{hkl} \neq I_{hkl}^* \] and \[ |F_{hkl}|^2 \neq |F_{hkl}^*|^2 \]

Furthermore:
\[ \phi_{hkl}^* \neq -\phi_{hkl} \]
Systematic Absences (I)

Consider a body centered lattice. For a given atom at coordinates \((x, y, z)\) there will be a second atom at \((x+1/2, y+1/2, z+1/2)\) and \(F_{hkl}\) becomes

\[
F_{hkl} = \sum_{j=N/2}^{j=N/2} \left( f_j e^{2\pi i (hx_j+ky_j+lz_j)} + f_j e^{2\pi i [h(x_j+1/2)+k(y_j+1/2)+l(z_j+1/2)]} \right)
\]

\[
F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i (hx_j+ky_j+lz_j)} \left( 1 + e^{\pi i (h+k+l)} \right)
\]

If \(h+k+l\) is even: \(e^{\pi i (h+k+l)} = 1\) but

if \(h+k+l\) is odd: \(e^{\pi i (h+k+l)} = -1\)

For \(h+k+l = 2n\):

\[
F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i (hx_j+ky_j+lz_j)} (1+1) = 2 \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i (hx_j+ky_j+lz_j)}
\]

For \(h+k+l = 2n+1\):

\[
F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i (hx_j+ky_j+lz_j)} (1+(-1)) = 0
\]
Systematic Absences (II)

Let's consider a $2_1$ screw axis. For a given atom at coordinates $(x, y, z)$ there will be a second atom at $(-x, y + 1/2, -z)$ and $F_{hkl}$ becomes

$$F_{hkl} = \sum_{j=N/2}^{j=N/2} (f_j e^{2\pi i(hx_j + ky_j + lz_j)} + f_j e^{2\pi i[h(-x_j) + k(y_j + l/2) + l(-z_j)]})$$

For $h = 0$ and $l = 0$

$$F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i(hx_j + ky_j + lz_j)} (1 + e^{\pi ik})$$

When $k$ is even $e^{\pi ik} = 1$, thus:

$$F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i(hx_j + ky_j + lz_j)} (1+1) = 2 \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

For $h = 0$ and $l = 0$, when $k$ is odd: $e^{\pi ik} = -1$, thus

$$F_{hkl} = \sum_{j=N/2}^{j=N/2} f_j e^{2\pi i(hx_j + ky_j + lz_j)} (1 + (-1)) = 0$$

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Textbooks and Resources Used

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