XRD – 6
Diffraction

XRD-6 READ

Sherwood & Cooper, Chap 4.13, 5.6, 6.1~6.7, 6.14

Sherwood & Cooper, Chap 6.8~6.14

Ott, Chapter 13.4

Sherwood & Cooper, Chap 4.1~4.3, 4.11, 5.1~5.3

Sherwood & Cooper, Chap 4.4~4.10, 5.4, 5.7~5.10

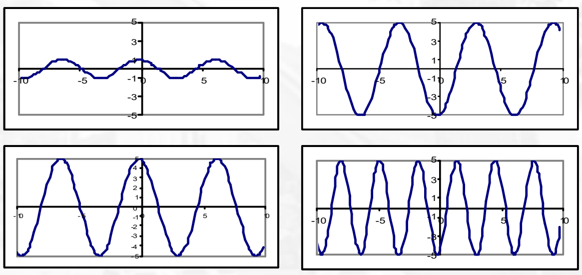
www.ruppweb.org/Xray/101index.html

Waves

- Plane wave
  - ✓ direction of propagation is left to right
  - ✓ wave fronts are a series of parallel lines
- Circular wave
  - ✓ direction of propagation is radial
  - ✓ wave fronts are a set of concentric circles
- Transverse wave
  - ✓ local motion is ⊥ to the direction of propagation
  - ✓ water waves, waves on a string, X-ray
- Longitudinal wave
  - ✓ local motion is // to the direction of propagation
  - ✓ sound wave

$$f(x) = A \cos (kx + \varphi)$$

Amplitude Frequency Phase



Sherwood & Cooper, Chapter 4

Waves

➢ 1-D Wave equations $\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi(x,t)}{\partial t^2}$

$$\psi(x,t) = \sum_n \psi_n \cos(k_n x - \omega_n t + \phi_n) + \sum_m \psi_m \cos(k_m x - \omega_m t + \phi_m)$$

$$\psi(x,t) = \psi_0 \cos(kx - \omega t)$$

➢ 3-D

$$\psi(\mathbf{r},t) = \sum_n \psi_n \cos(k_n \cdot \mathbf{r} - \omega_n t + \phi_n) + \sum_m \psi_m \cos(k_m \cdot \mathbf{r} - \omega_m t + \phi_m)$$

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

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

Wave vector $|\mathbf{k}| = k = \frac{2\pi}{\lambda}$

Phase velocity $v = \frac{\omega}{k}$

Wave frequency $\omega = \frac{2\pi}{\tau} = 2\pi\nu$

Group velocity $g = \frac{d\omega}{dk}$

Intensity $I = |\psi(\mathbf{r},t)|^2$

Sherwood & Cooper, Chapter 4

Fourier transform

➢ Joseph Fourier

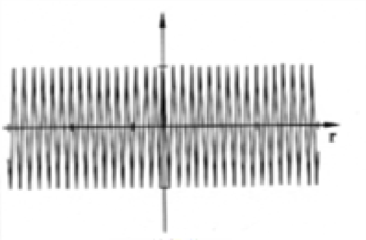
- ✓ Joined Napoleon's army as a scientific adviser
- ✓ Developed the theory on heat propagation using expanded series of sinusoids
- ✓ A periodic function can be described as the sum of simple sine and cosine functions that have wavelengths as integrals of the function

➢ Fourier transform; integral of a set of periodic (imaginary) primitive functions

➢ Fourier transforms are used in:

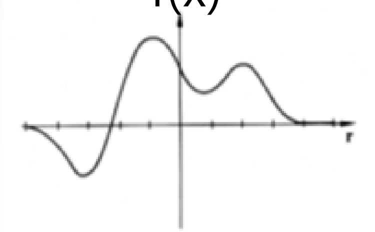
- ✓ crystallography; image analysis; (NMR) spectroscopy
- ✓ electron microscopy; optics & light-microscopy
- ✓ communication

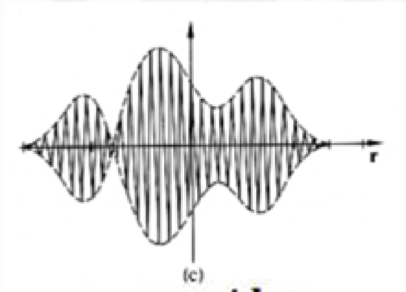
$f(x)e^{ikx}$



e^{ikx}

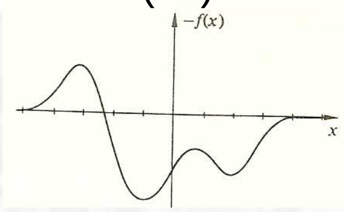
f(x)





$f(x)\, e^{ikx}$

f(-x)



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

Fourier transform

- Fourier transform of f(x)

$$F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} = \mathcal{T} f(\mathbf{r})$$

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

$$F(k) = \mathcal{T} f(x)$$

- Inverse Fourier transform of F(k)

$$f(\mathbf{r}) = \int_{\text{all } \mathbf{k}} F(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k} = \mathcal{T}^{-1} F(\mathbf{k})$$

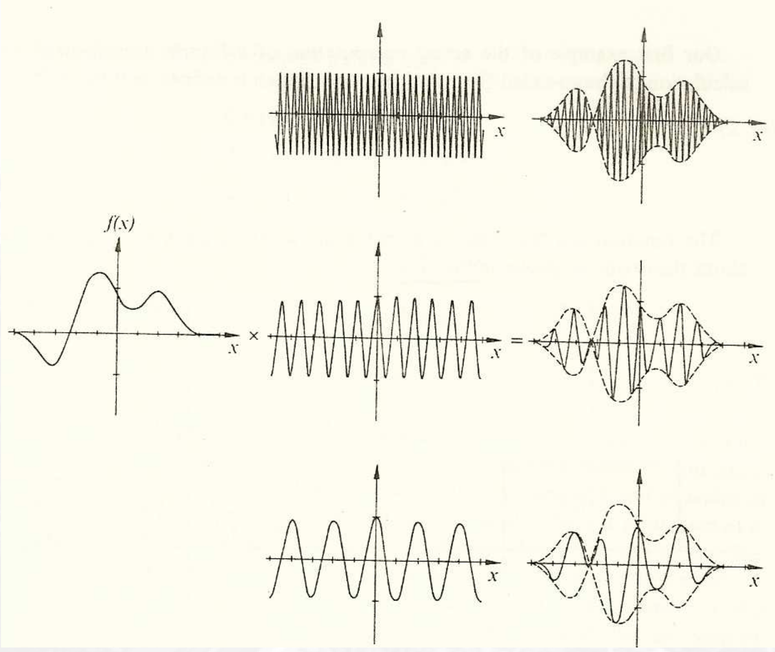
$$f(x) = \int_{-\infty}^{\infty} F(k) e^{-ikx} dk$$

$$f(x) = \mathcal{T}^{-1} F(k)$$

Fourier mates $f(x) \leftrightarrow F(k)$

- Space defined by ***r*** → real space
- Space defined by ***k*** → ***k*** space, reciprocal space, Fourier space

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



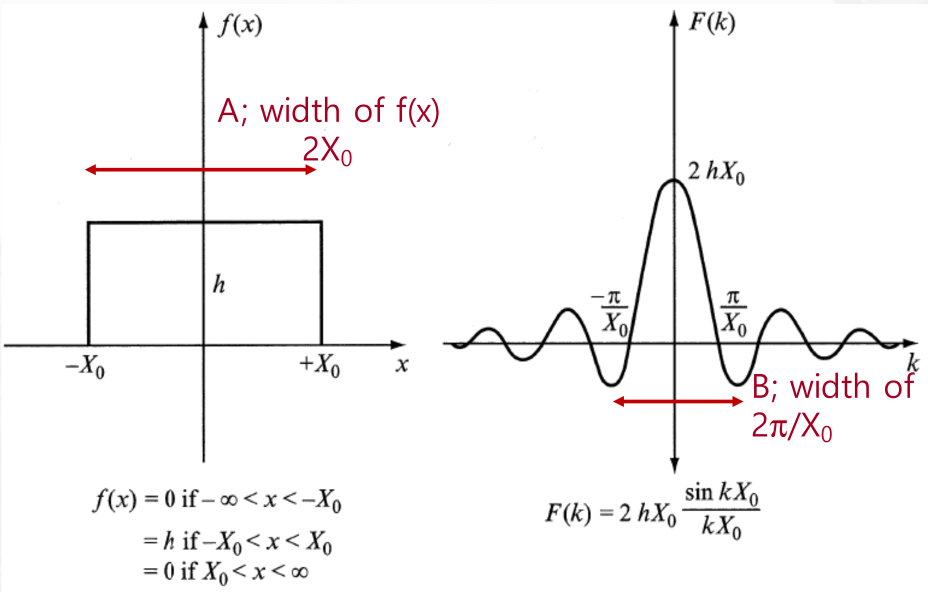
k large

k small

$f(x)$ x e^{ikx} = $f(x)e^{ikx}$

Sherwood & Cooper Chap 5.3

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



As A ↗, B ↘

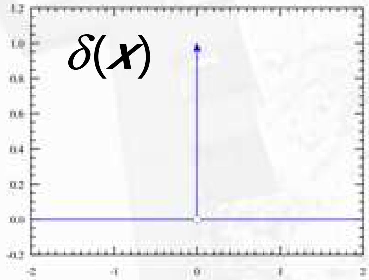
The narrower the f(x), the wider the F(k)

Dirac delta function

- Unit impulse function
- $\delta(x-x_0) = \infty$, when $x = x_0$

  $= 0$, elsewhere

$$\int_0^{\infty} \delta(x-x_0)\,dx = 1$$



an infinitely high, infinitely thin spike at the origin, with total area one under the spike, and physically represents an idealized point mass or point charge.

Crystal Lattice; 3D array of points in space

Crystal Lattice can be described using an array of delta function

- Lattice point $\mathbf{r} = p\,\mathbf{a} + q\,\mathbf{b} + r\,\mathbf{c}$
- Lattice = array of $\delta(\mathbf{r}-[p\,\mathbf{a} + q\,\mathbf{b} + r\,\mathbf{c}])$
- Lattice function $l(\mathbf{r}) = \sum_{\text{all } p,q,r} \delta(\mathbf{r} - [p\mathbf{a} + q\mathbf{b} + r\mathbf{c}])$

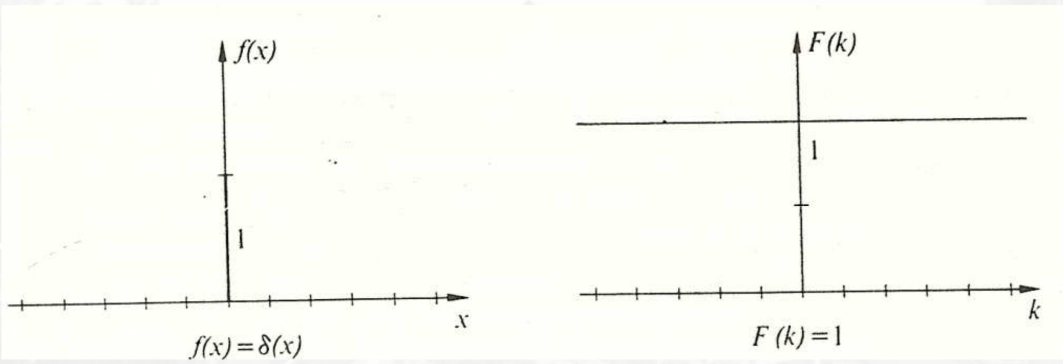
Fourier transform > 1 delta function

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

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

$$= e^0$$

$$= 1$$



$$f(x) = \delta(x) \qquad F(k) = 1$$

Fourier transform > 2 delta functions

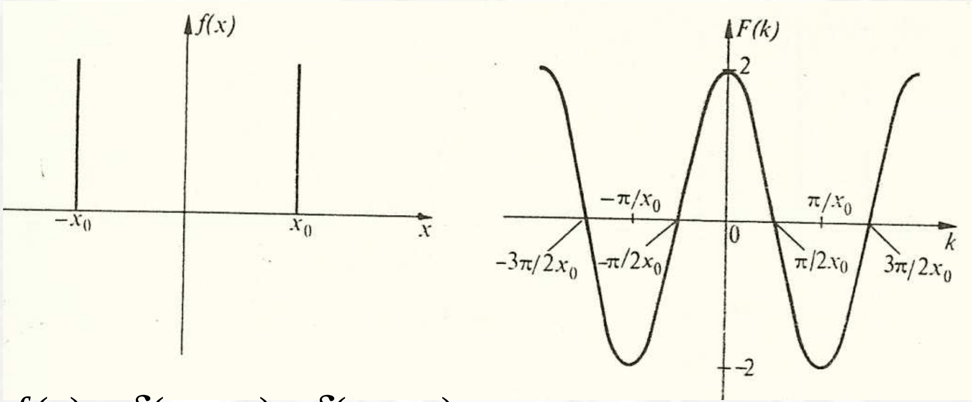
$$F(k) = \int_{-\infty}^{\infty} f(x)\, e^{ikx}\, dx$$

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

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

$\delta = kx_0$

$F(x) = 2 \cos kx_0$



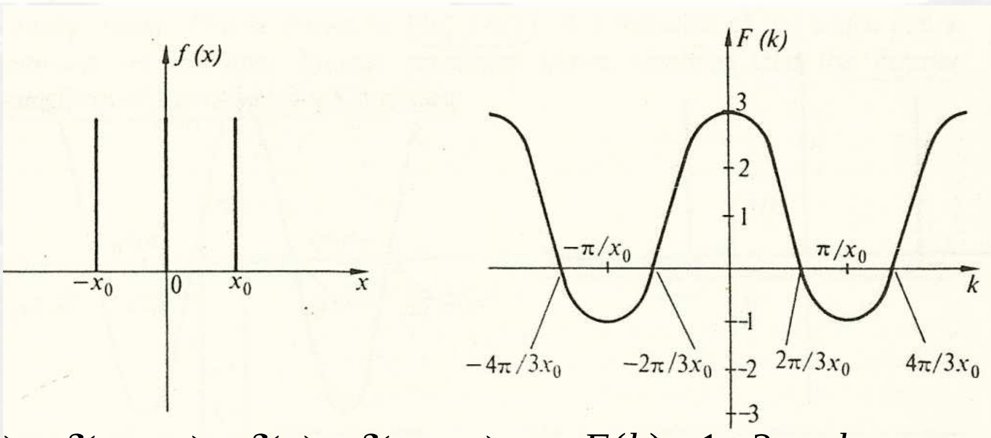
$$f(x) = \delta(x + x_0) + \delta(x - x_0) \qquad F(k) = 2\cos kx_0$$

Fourier transform > 3 delta functions

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

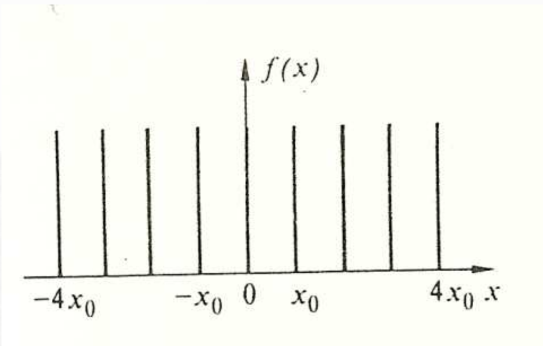
$$= \int_{-\infty}^{\infty} \delta(x + x_0)\, e^{ikx}\, dx + \int_{-\infty}^{\infty} \delta(x)\, e^{ikx}\, dx + \int_{-\infty}^{\infty} \delta(x - x_0)\, e^{ikx}\, dx$$

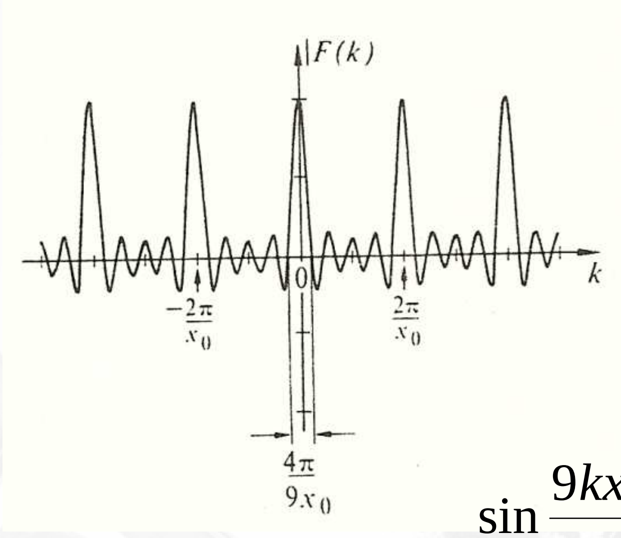
$$= e^{-ikx_0} + 1 + e^{ikx_0} \quad = 1 + 2\cos kx_0$$



$$f(x) = \delta(x + x_0) + \delta(x) + \delta(x - x_0) \qquad F(k) = 1 + 2\cos kx_0$$

Fourier transform > 9 delta functions

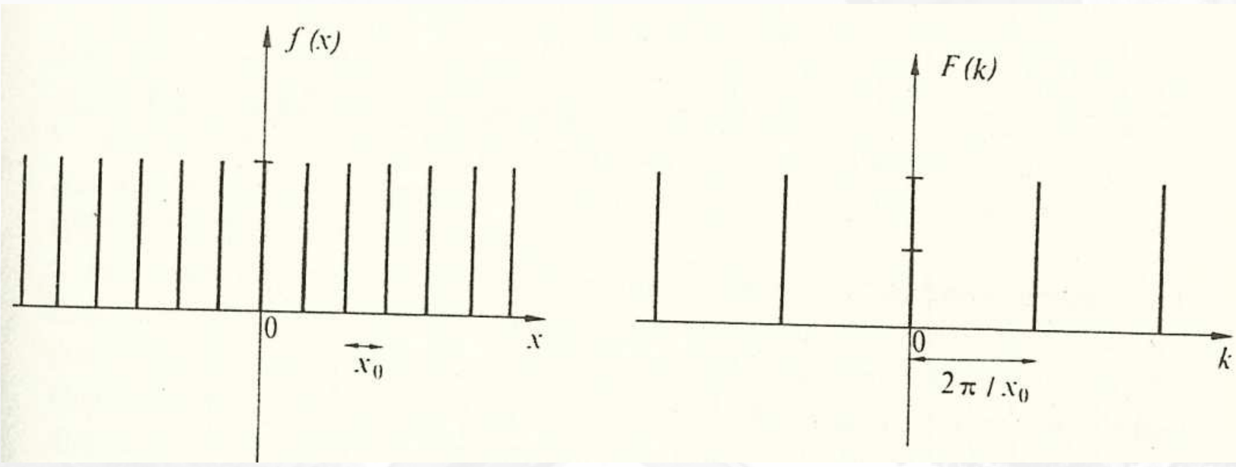




$$f(x)=\sum_{n=-4}^{n=4}\delta(x-nx_0)$$

$$F(k)=\frac{\sin\frac{9kx_0}{2}}{\sin\frac{kx_0}{2}}$$

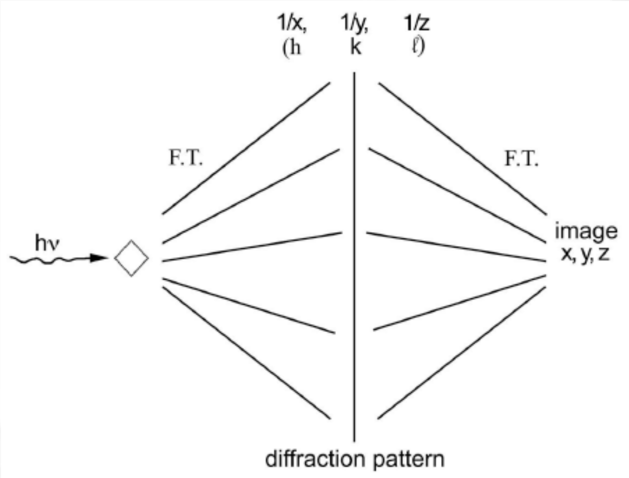
Fourier transform > infinite number of delta functions



$$f(x)=\sum_{n=-\infty}^{n=\infty}\delta(x-nx_0)$$

$$F(k)=\sum_{n=-\infty}^{n=\infty}\delta(k-2n\frac{\pi}{x_0})$$

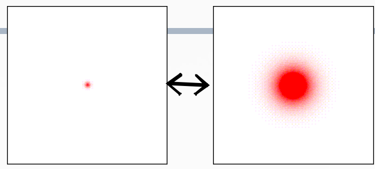
How can we describe diffraction pattern of a xtal?



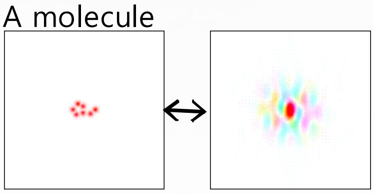
- The Fourier transform decomposes or separates a periodic function into sinusoids of different frequency which sum to the original function.
- Decompose f(x) into a series of cosine waves. That when summed, reconstruct f(x).

$$F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{r} = \mathcal{T} f(\mathbf{r})$$

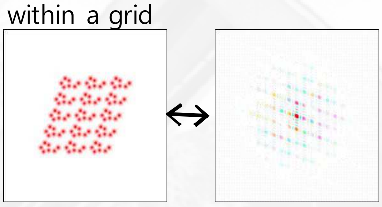
Fourier transform



An atom is a sharp feature, whereas its transform is a broad smooth function.

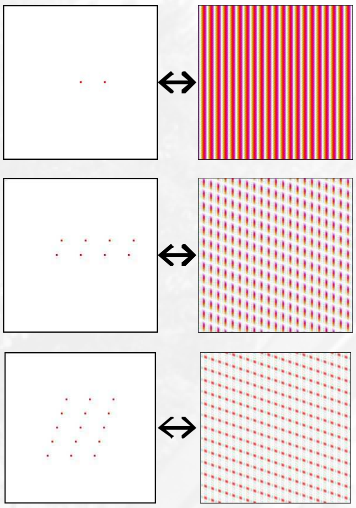


A molecule can be considered as the convolution of the *point atom structure and the atomic shape.* → *Its transform is* the product of the *point atom transform and the atomic transform.*



A crystal can be built up by convoluting the *molecule with the grid.* → crystal structure

The Fourier transform of the crystal is the product of the *molecular transform and* the *reciprocal lattice.* → *diffraction pattern*



The Fourier transform of a grid is a grid with reciprocal *directions and spacings.* → the origin of the reciprocal lattice

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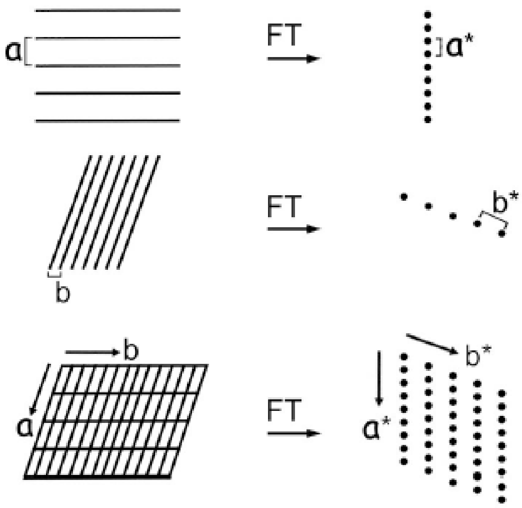
Fourier transform & convolution



- Diffraction pattern of a set of lines is a row of dots perpendicular to the lines
- The separation between the dots is proportional to the inverse of the separation between the lines

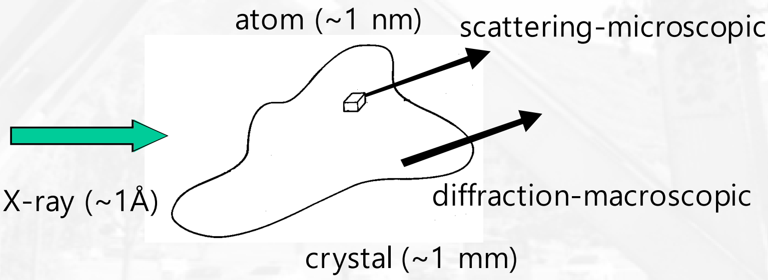
Form lattice by multiplying the two functions

The diffraction pattern of the lattice is a convolution of the diffraction patterns of the two sets of lines

Interaction of waves with obstacles

- Infinite plane wave with wave vector ***k*** and frequency ***w;*** $\psi = \psi_0 \, e^{i(\mathbf{k} \cdot \mathbf{r} - wt)}$
- What happens when a wave motion interacts with an obstacle placed in its path?
- How is the wave equation modified to take account of the interaction of the wave with the obstacle?

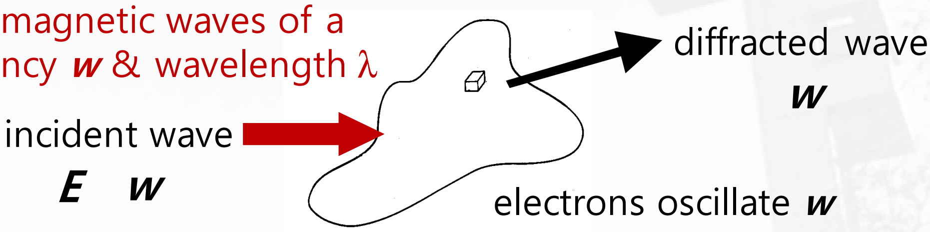
- Scattering; wave-obstacle interaction such that the dimensions of obstacles and wavelength are comparable
- Diffraction; wave-obstacle interaction such that the dimensions of obstacles are much larger than the wavelength



Sherwood & Cooper Chap 6

Mathematics of Diffraction

plane electromagnetic waves of a single frequency ***w*** & wavelength λ



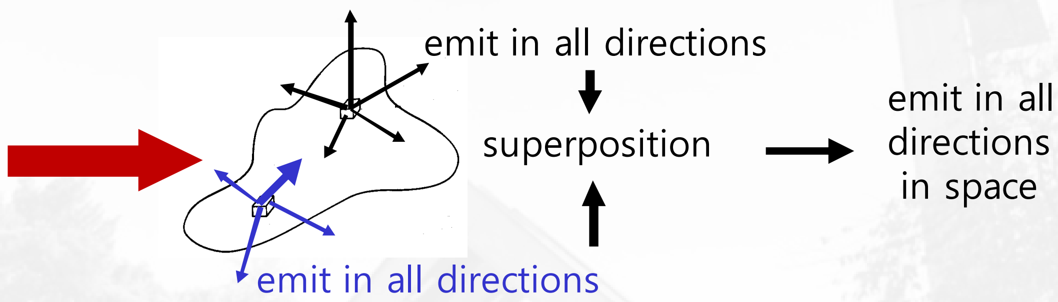
- In any medium, velocity of electromagnetic radiation is constant → λ unchanged. → diffracted waves have the same ***w*** and λ as the incident waves.
- Electrons behave as if it were free,

  when ***w*** of orbital motion of e' <<< ***w*** of incident wave (See page 194, 195 of Sherwood)

  ✓ ***w*** (electron) = 10^{16}Hz, ***w*** (X-ray) = 10^{19}Hz

Mathematics of Diffraction (continued)

- ***w*** & λ unchanged → there should be some other effect of diffracting obstacle.



- plane wave → spatially different wave
- Information of the wave is somehow contained in the way in which they are spread out in space. → direction → only ***k*** has spatial info among ψ_0, w, ***k.***

Mathematics of Diffraction (continued)

- significance of the wave vector ***k*** $|\mathbf{k}| = k = \frac{2\pi}{\lambda}$

$$\psi(\mathbf{r},t) = \psi_0 \exp i(\mathbf{k}\cdot\mathbf{r} - \omega t)$$

- ***k*** of diffracted wave has the same magnitude as the incident wave, but has different direction.

- Total set of diffracted waves = set of wave vectors all of which have same magnitude (equal to that of incident wave), but different directions.

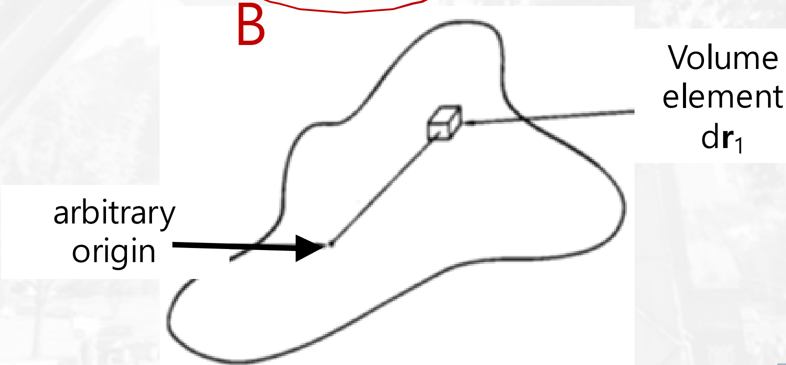
Mathematics of Diffraction (continued)

- mathematical description
  - ✓ Waves are propagated thru obstacle.
  - ✓ Obstacle perturbs these waves.
- Perturbing effect; f(**r**)
- The effect of d$\mathbf{r}_1$ on the wave motion; $f(\mathbf{r}_1)d\mathbf{r}_1$ A
- Wave in d$\mathbf{r}_1$ centered on $\mathbf{r}_1$;

$$e^{i(\mathbf{k}\cdot\mathbf{r}_1 - \omega t)}$$

B

Diffracted wave must be represented by some mathematical combination of A & B.

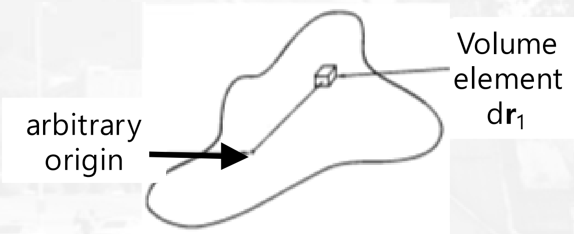


Mathematics of Diffraction (continued)

- The effect of $d\mathbf{r}_1$ on the wave motion; $f(\mathbf{r}_1)d\mathbf{r}_1$ A
- Wave in $d\mathbf{r}_1$ centered on $\mathbf{r}_1$; $e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}$ B

- Wave diffracted from $d\mathbf{r}_1$ = AB = $f(\mathbf{r}_1)e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}d\mathbf{r}_1$
- Wave diffracted from $d\mathbf{r}_2$ = $f(\mathbf{r}_2)e^{i(\mathbf{k}\cdot\mathbf{r}_2-\omega t)}d\mathbf{r}_2$

- Diffraction pattern = $\int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}d\mathbf{r}$



Mathematics of Diffraction (continued)

- Diffraction pattern = $\int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}d\mathbf{r} = e^{-i\omega t}\int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r})}d\mathbf{r}$
- Intensity, not amplitude, is recorded.
- XRD experiment measures time average of the I of the diffracted wave.
  → result obtained is independent of time.
- We need info on space, not info on time. →

Diffraction pattern = $\int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r})}d\mathbf{r} = \int_{\text{all } \mathbf{r}} f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r})}d\mathbf{r}$

Fourier transform of $f(\mathbf{r})$

Mathematics of Diffraction (continued)

- Diffraction pattern = $\int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r})}d\mathbf{r}$ = $\int_{\text{all } \mathbf{r}} f(\mathbf{r})e^{i\,\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$

Fourier transform of f(**r**)

- To compute the diffraction pattern of any obstacle for which f(**r**) is known, we can compute the Fourier transform of f(**r**).
- f(**r**); amplitude function

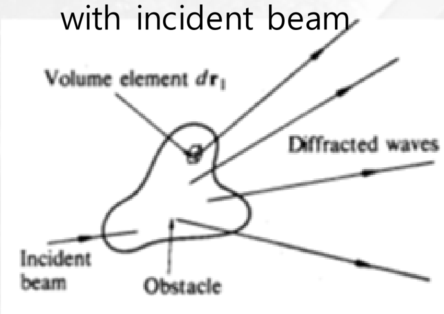
- Diffraction pattern of any obstacle = Fourier transform of amplitude function

Significance of Fourier Transform

- Diffraction pattern = $F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r})e^{i\,\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$

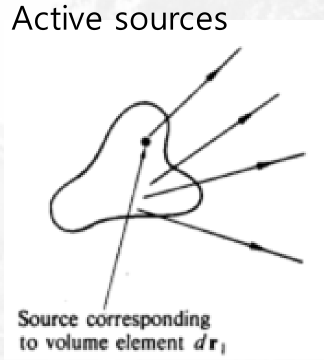
- Info in the diffraction pattern is essentially spatial.
- The only way waves can contain spatial info is by means of their wave vector ***k*.**

Passive scatterer with incident beam



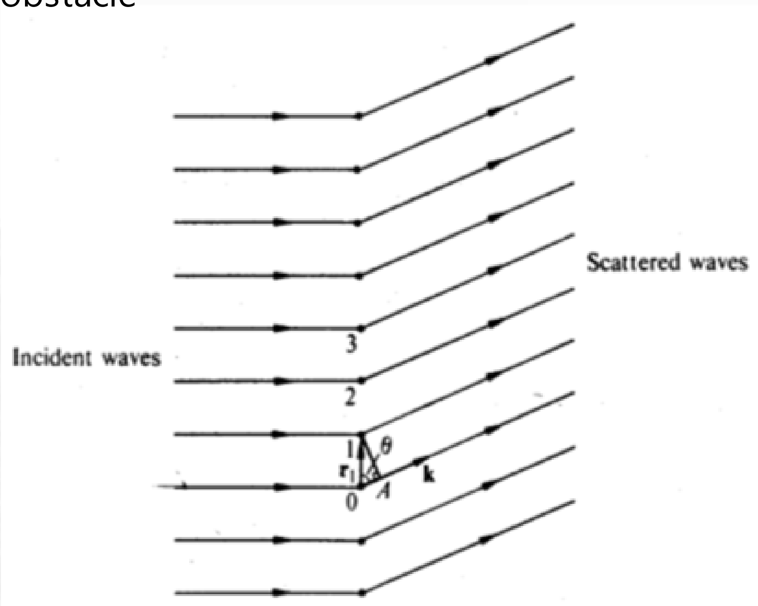
Identical effect

Active sources



Page 202

- Phase relationships b/w waves scattered by various scattering centers in an obstacle

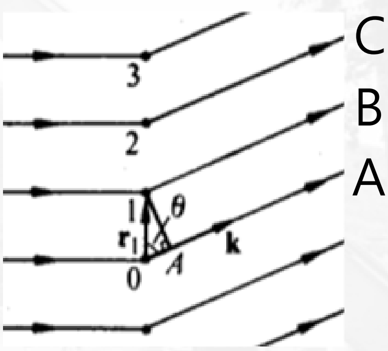


- Path difference b/w A & B = $r_1 \cos\theta$
- Phase difference b/w A & B = $(2p/l)\, r_1 \cos\theta = \boldsymbol{k \cdot r_1}$
- Phase difference b/w A & C = $(2p/l)\, r_2 \cos\theta = \boldsymbol{k \cdot r_2}$
- Wave scattered from point 0 = $f(\mathbf{r}_0)d\mathbf{r}_0$
- Wave scattered from point 1 = $f(\mathbf{r}_1)e^{i\mathbf{k}\cdot\mathbf{r}_1}d\mathbf{r}_1$
- Wave scattered from point 2 = $f(\mathbf{r}_2)e^{i\mathbf{k}\cdot\mathbf{r}_2}d\mathbf{r}_2$
- Total scattered wave

$$= \int_{\text{obstacle}} f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$$

$$= \int_{\text{all } \mathbf{r}} f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$$

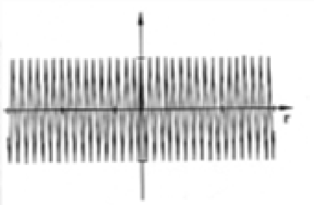
$$|\mathbf{k}| = k = \frac{2\pi}{\lambda}$$



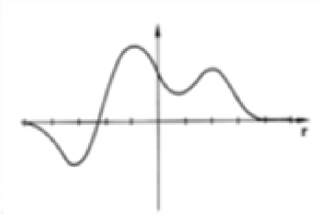
Fourier Transform and Information

- How is information transmitted in general? see chap 6.11

Diffraction pattern = $\mathrm{F}(\mathbf{k}) = \int_{\text{all } \mathbf{r}} \mathrm{f}(\mathbf{r}) e^{i\,\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$



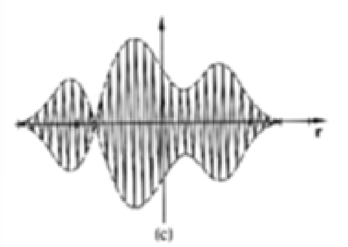
$e^{i\,\mathbf{k}\cdot\mathbf{r}}$



$\mathrm{f}(\mathbf{r})$

amplitude function

Describes behavior of the obstacle



$\mathrm{f}(\mathbf{r})\, e^{i\,\mathbf{k}\cdot\mathbf{r}}$

Constant w & λ
Different amplitudes
amplitude modulated wave

Fourier Transform & diffraction

Diffraction pattern = Fourier transform of f(**r**)

$$\mathrm{F}(\mathbf{k}) = \int_{\text{all } \mathbf{r}} \mathrm{f}(\mathbf{r}) e^{i\,\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$$

Inverse transform $\mathrm{f}(\mathbf{r}) = \int_{\text{all } \mathbf{k}} \mathrm{F}(\mathbf{k}) e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}$

F(**k**) ; contains info on the spatial distribution of diffraction pattern.

f(**r**) ; contains info on the structure of obstacle.

XRD experiment → intensity $|\mathrm{F}(\mathbf{k})|^2$ → $\mathrm{F}(\mathbf{k})$ → $\mathrm{f}(\mathbf{r})$ → Crystal structure

f(**r**) vs. F(**k**)

If the structure is known,
→ f(**r**) is known.
→ diffraction pattern F(**k**) can be computed.

If the diffraction pattern is known,
→ F(**k**) is known.
→ f(**r**) can be computed.

The act of diffraction = taking Fourier transform of the obstacle

Diffraction pattern of an obstacle described by f(**r**) is the Fourier transform of f(**r**), which is F(k).

Experimental Limitation

- Information is contained in all space.
  - ✓ It is impossible to scan all space to collect all the information.
    - → some info is lost.
    - → reconstruction of the obstacle from the diffraction data will be incomplete.
- PHASE PROBLEM
  - ✓ Only the intensity is measured.
  - ✓ The phase of diffraction pattern is not measured.

$$F(\vec{k}) = \left|F(\vec{k})\right| e^{i\delta}$$

observe $\left|F(\vec{k})\right|^2$

Info on δ is lost.

intensity

$F(\mathbf{k}) \rightarrow |F(\mathbf{k})|^2$ — Phase info is lost.

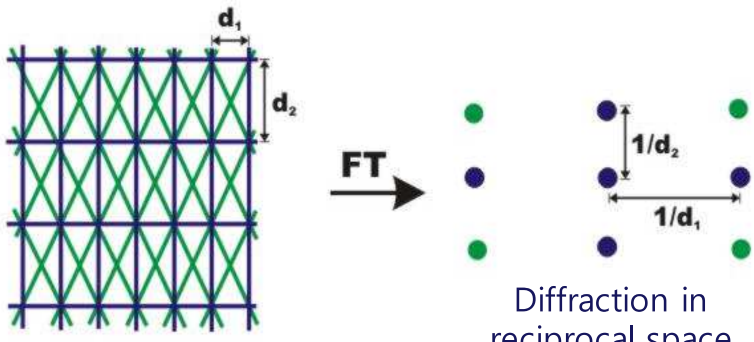
$|F(\mathbf{k})|^2 \rightarrow F(\mathbf{k})$ — Phase info is needed.

Phase problem

- What is measured is INTENSITY, not the COMPLEX AMPLITUDE of the diffraction pattern.
- F(**k**) is complex $F(\mathbf{k}) = |F(\mathbf{k})|e^{i\delta}$ δ; phase factor
- What is measured is $|F(\mathbf{k})|^2$.
- $|F(\mathbf{k})|^2$ contains no info on δ.
- A lot of info is lost because we can record only intensity (not the amplitude).
- The problem caused by the loss of info contained in δ. → PHASE PROBLEM

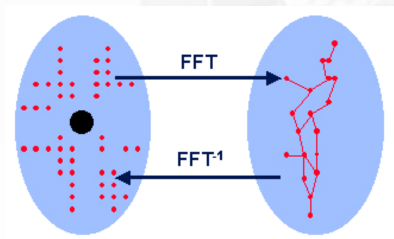
Sherwood & Cooper Chap 6.14

Reciprocal lattice vs Crystalline lattice in real space



Crystal structure in real space

Diffraction in reciprocal space



X-ray pattern

Crystal structure

The crystal structure can be deduced by performing a FT on the resultant diffraction pattern once the phase is known.

Phase problem can be solved by direct method, isomorphous replacement method, heavy atom method, etc.

Crystal Lattice vs. Diffraction Pattern

Fourier transform

crystal structure	⟷	diffraction pattern
"Real space"		"Reciprocal space"
periodic		Discrete & complex
ρ(x, y, z)		F(h, k, l)

F(h, k, l) → I(h, k, l) intensity; δ(h, k, l) phase

$$F_{hkl} = \int_V \rho_{xyz} \exp[2\pi i(hx + ky + lz)] dV$$

$$\rho_{xyz} = \frac{1}{V} \sum |F_{hkl}| \exp(i\varphi_{hkl}) \exp[-2\pi i(hx + ky + lz)]$$

todos

➢ XRD-6 READ

- Sherwood & Cooper, Chap 4.13, 5.6, 6.1~6.7, 6.14
- Sherwood & Cooper, Chap 6.8~6.14
- Ott, Chapter 13.4
- Sherwood & Cooper, Chap 4.1~4.3, 4.11, 5.1~5.3
- Sherwood & Cooper, Chap 4.4~4.10, 5.4, 5.7~5.10

No problem solving homeworks, only reading homeworks