Basic Principles of Scattering and Diffraction

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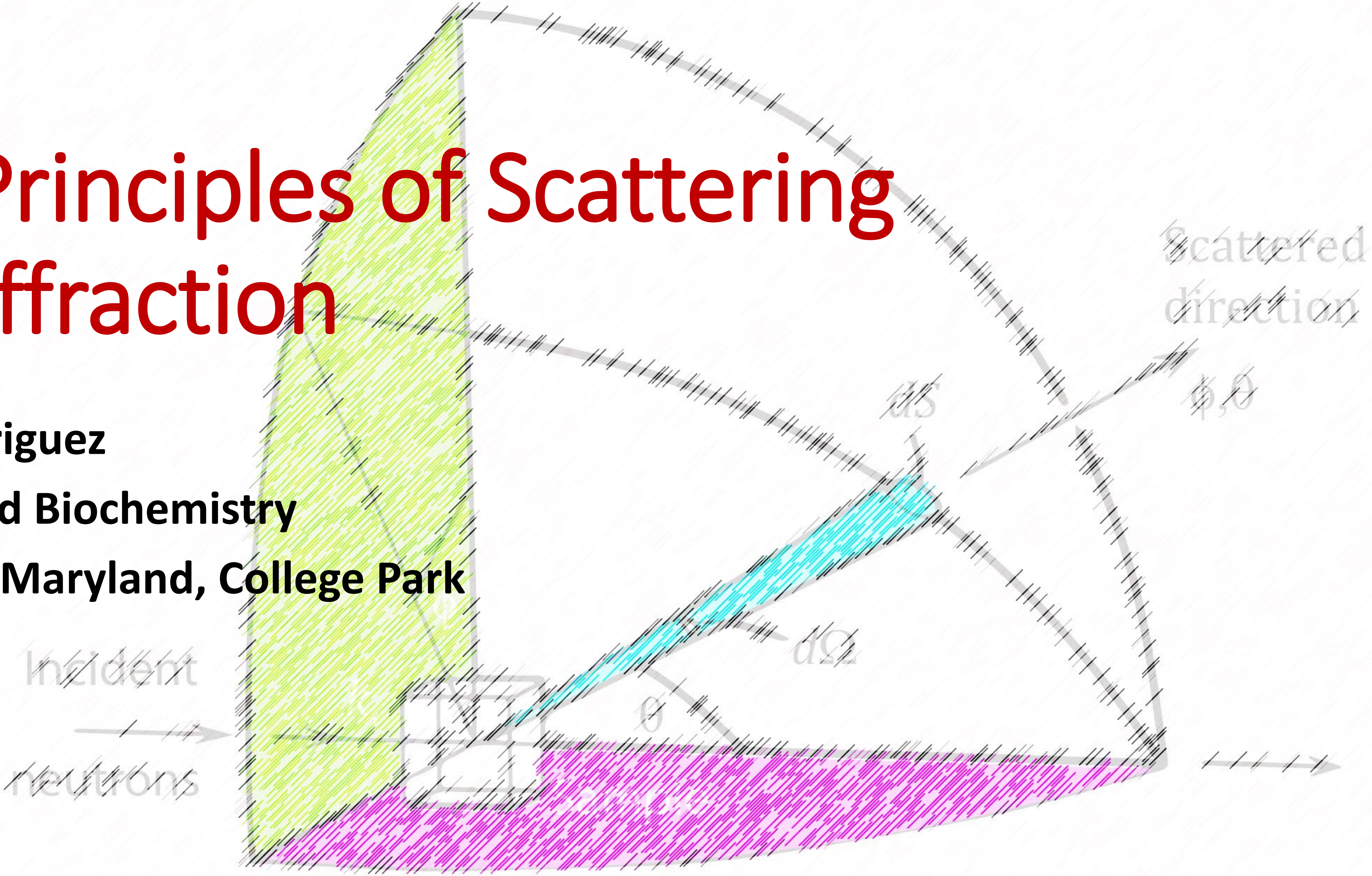

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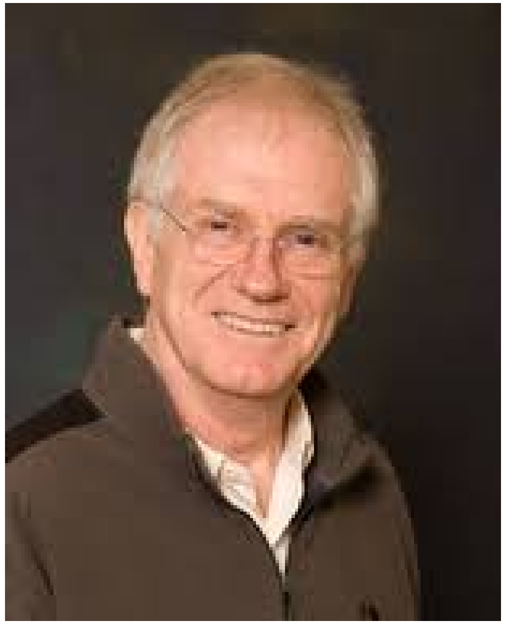

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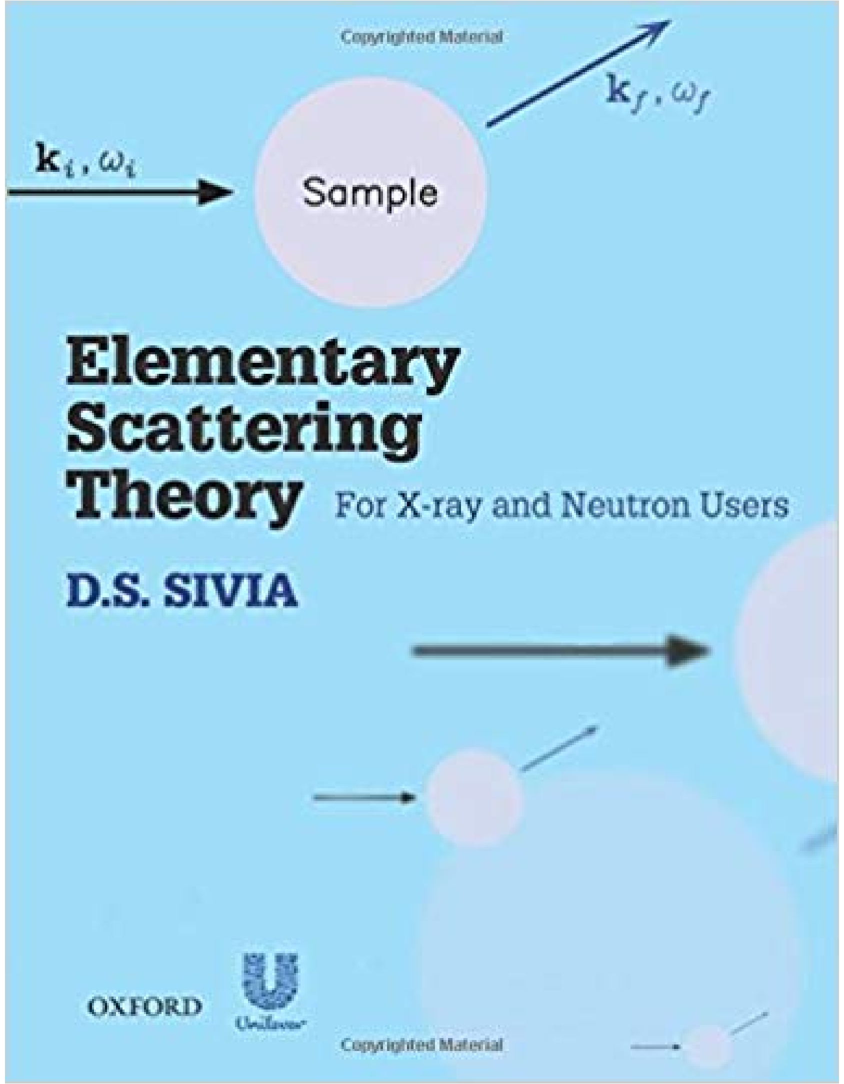
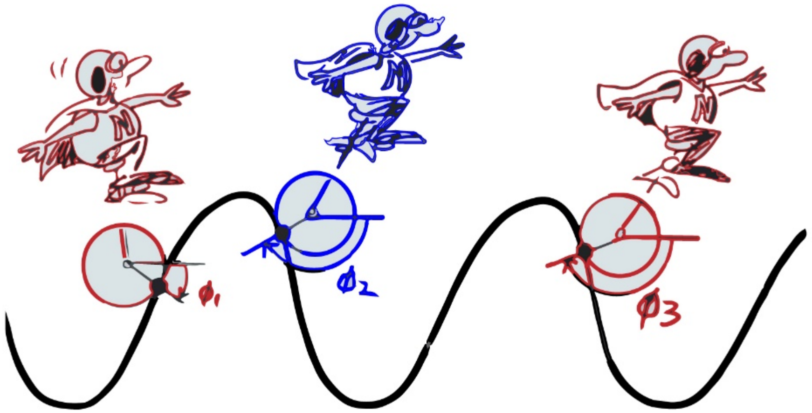


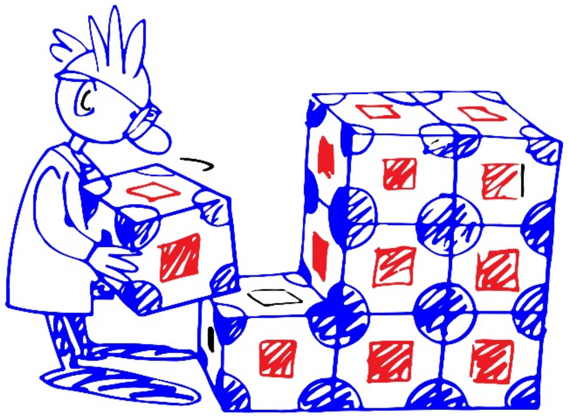
Outline

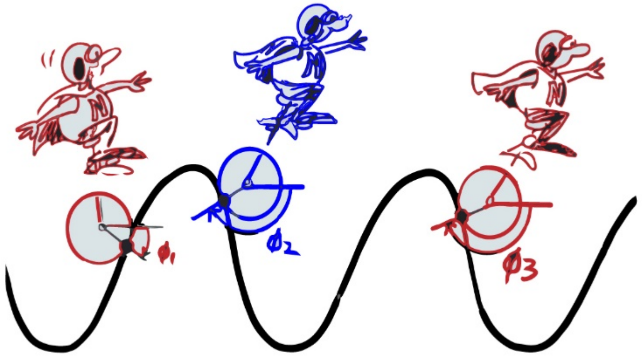
1. Scattering geometry basics: Plane waves and Fourier transforms

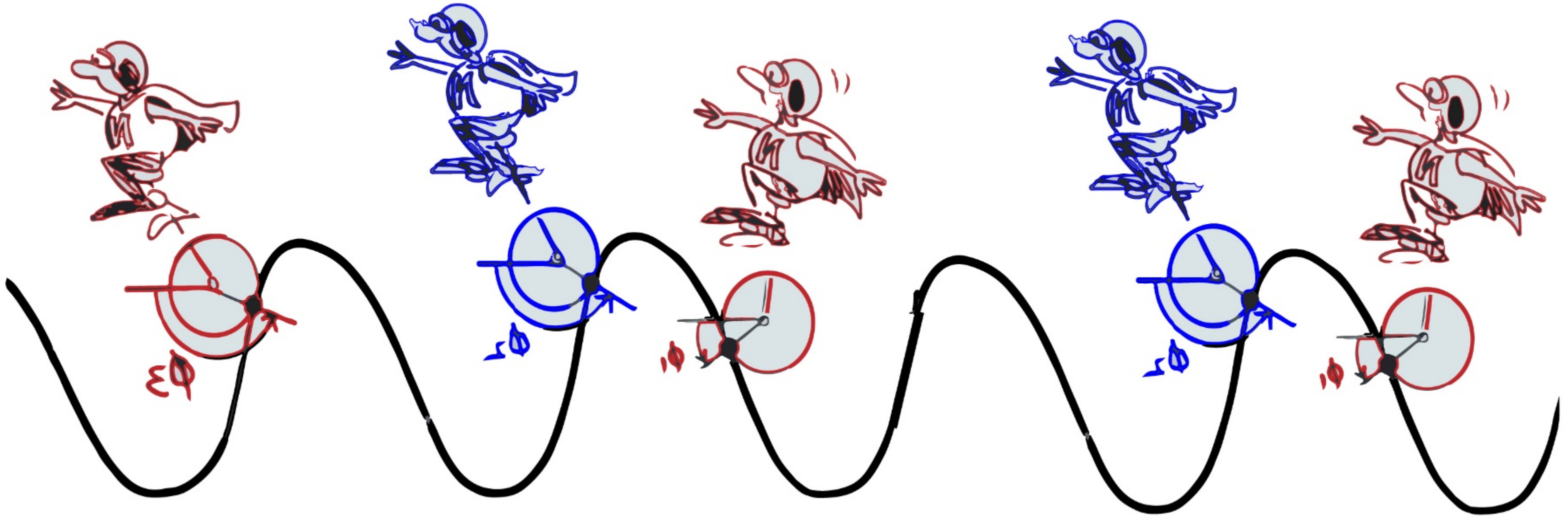


2. Scattering cross sections for neutrons and x-rays

3. Scattering from ensemble of atoms and diffraction



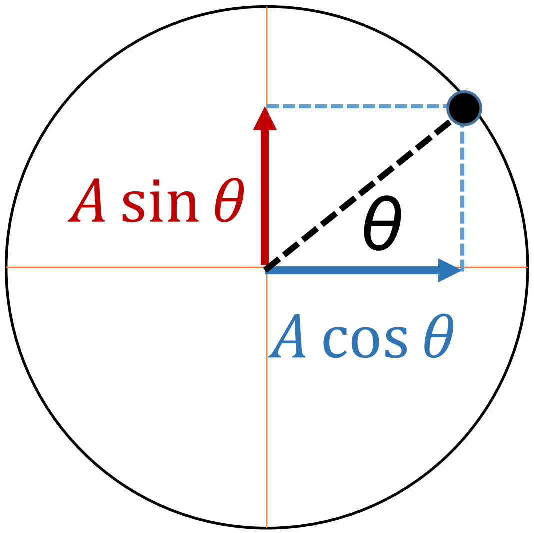




Scattering geometry basics

Plane waves and Fourier transforms

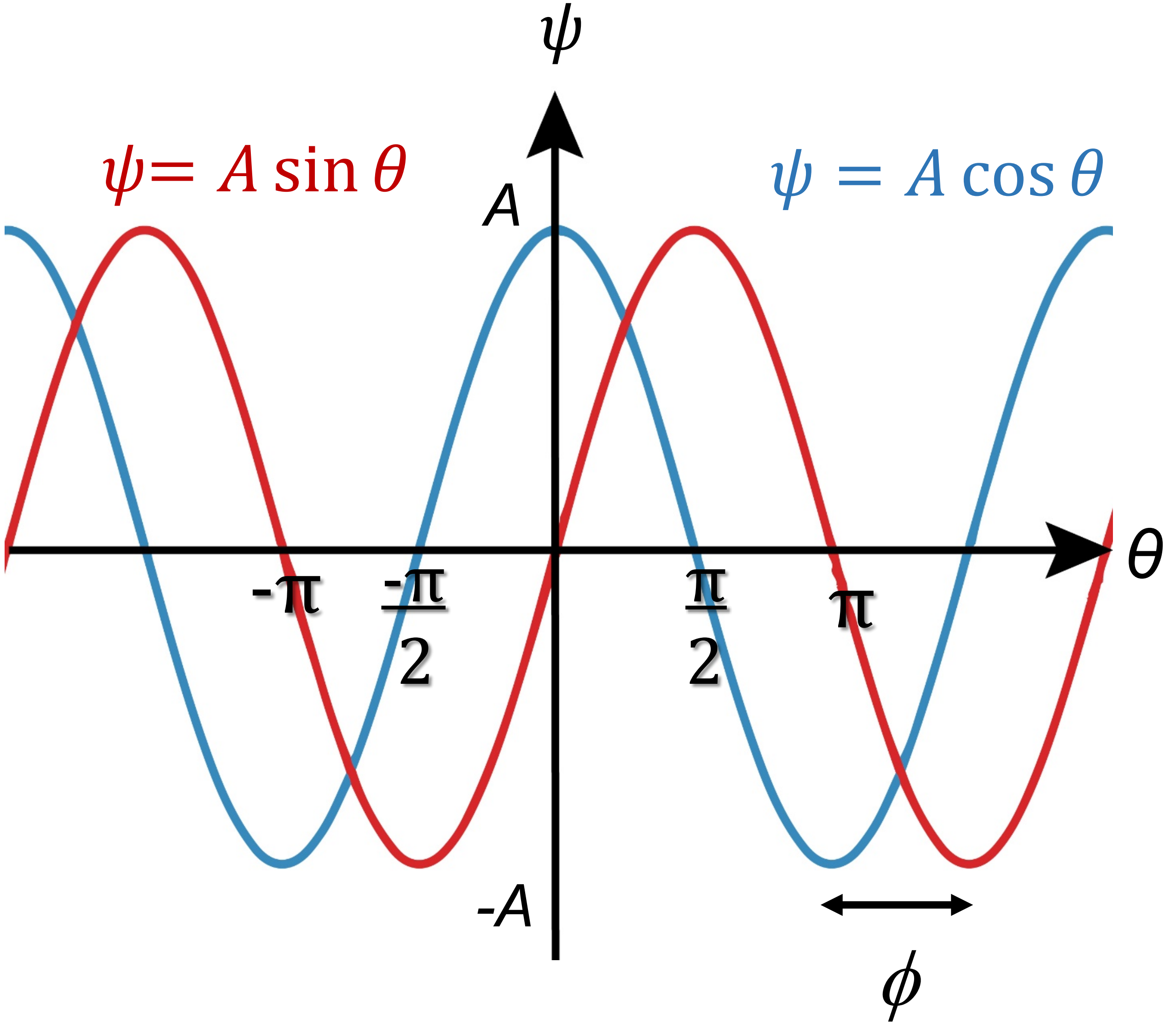
Scattering geometry basics: The sinusoidal wave



A = amplitude
θ = angle
ϕ = phase difference

$$\cos\theta = \sin(\theta + \pi/2)$$

$$\psi = A\sin(\theta + \phi)$$



Scattering geometry basics: The wavenumber *k*

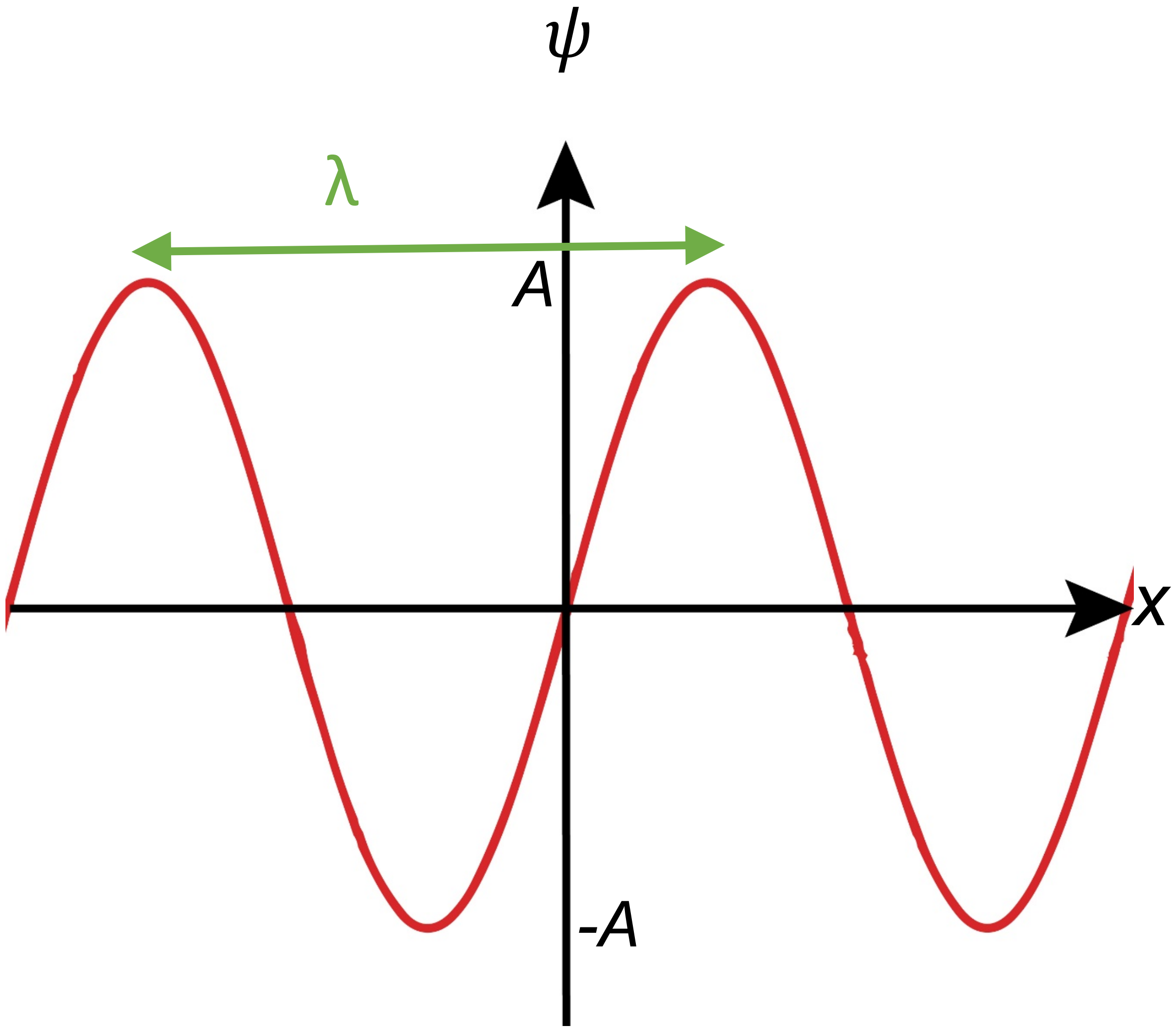
$$\psi = A\sin(\theta + \phi)$$

k = wavenumber
x = position
λ = wavelength

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

k has SI units of rad m^{-1}

$$\boxed{\psi = A\sin(kx + \phi)}$$



Scattering geometry basics: The travelling wave

Wave moves in *x*-direction with time, *t*

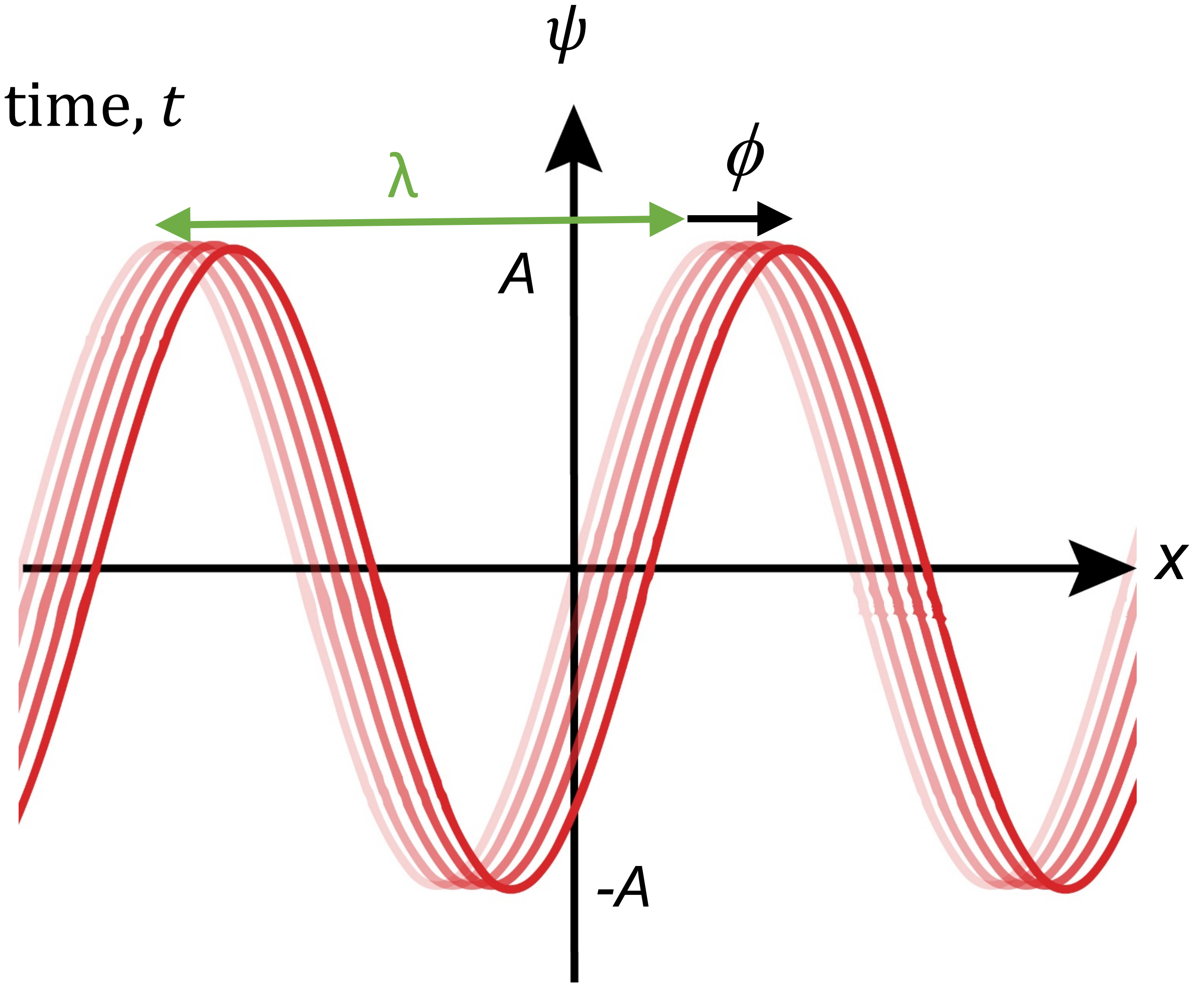
$$\psi = A\sin(kx + \phi)$$

ϕ_0 = initial phase angle
ϕ = phase after time t
ω = angular frequency

$$\omega = 2\pi\nu$$

$$\phi = \phi_0 - \omega t$$

$$\psi = A\sin(kx - \omega t + \phi_0)$$



Scattering geometry basics: The plane wave

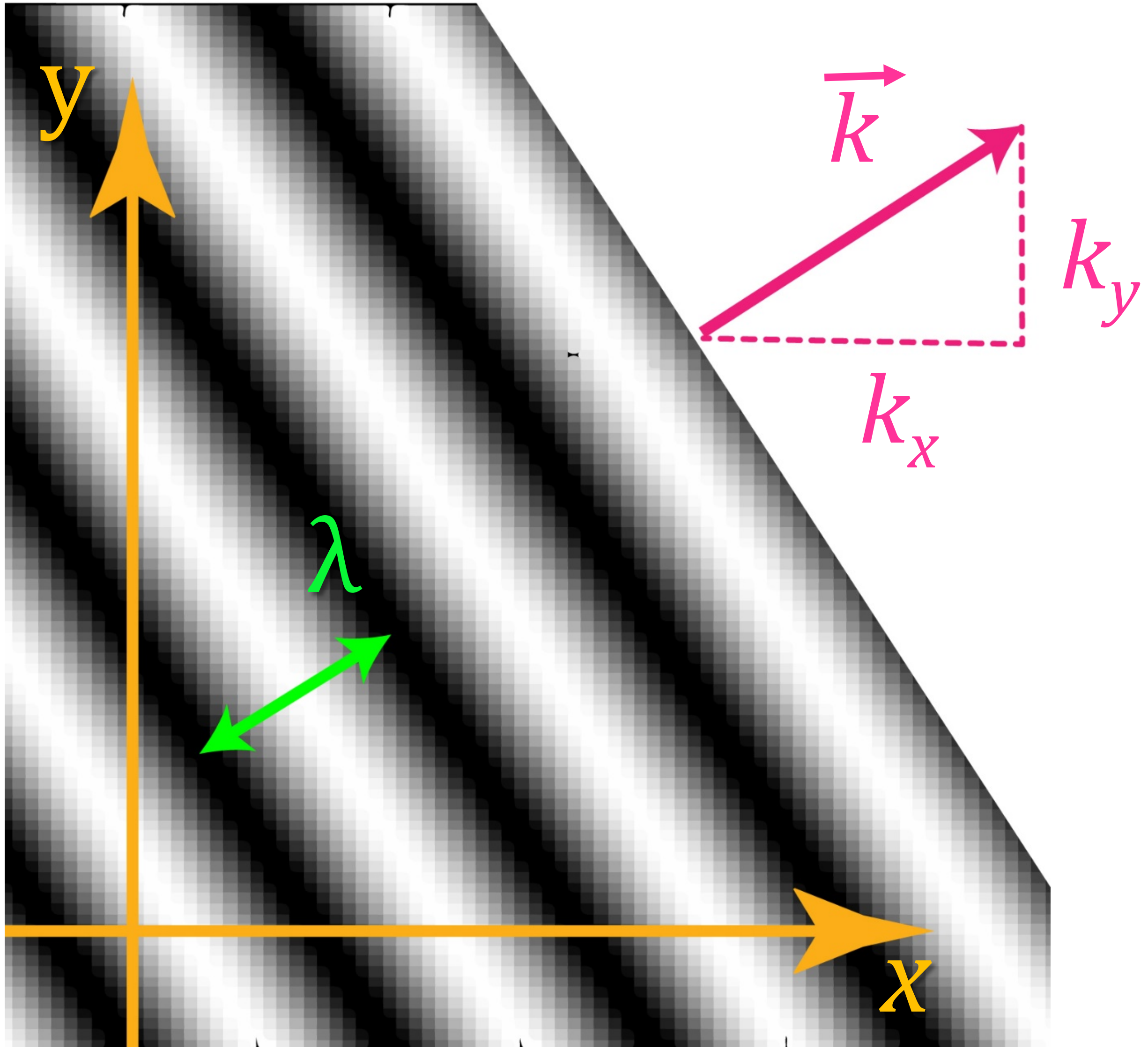
We define a plane wave:
Amplitude in the *z*-direction,
Propagates in *y*- and *x*-directions.

$\vec{r}$ = direction of propagation

$\vec{k}$ = wavevector

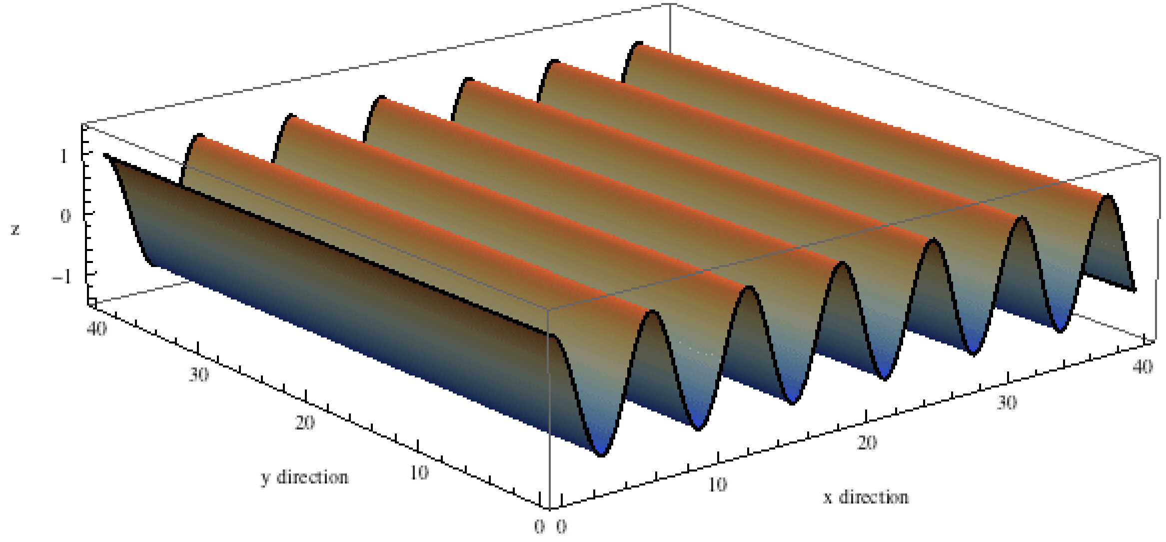
$$|\vec{k}| = \frac{2\pi}{\lambda}$$

$$\psi = A \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_0)$$

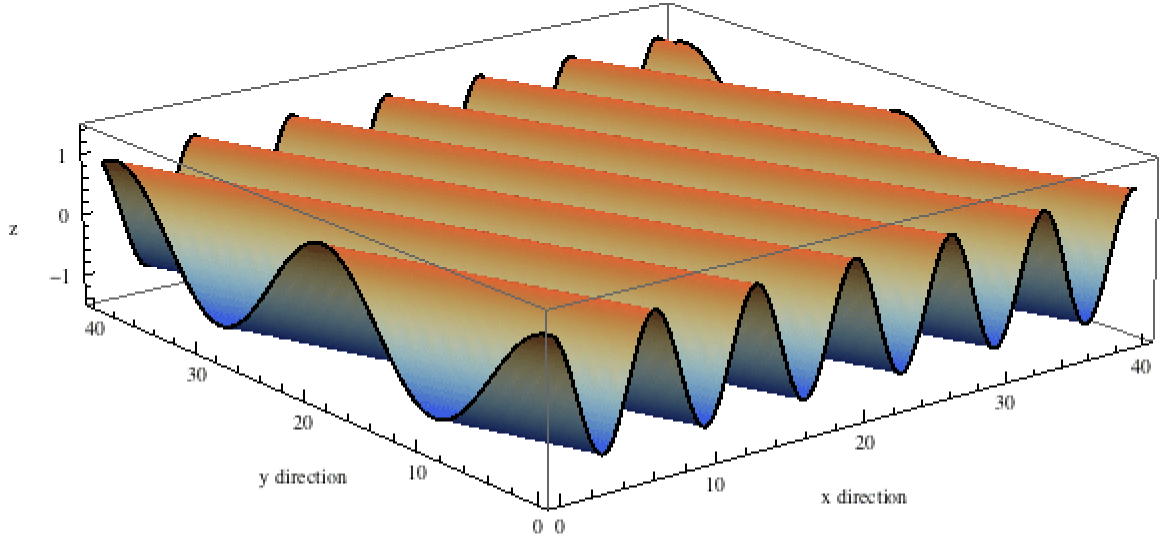


Scattering geometry basics: The traveling plane wave

Plane wave in *x*-direction only



Plane wave in *xy*-direction



Animation courtesy of Dr. Dan Russell, Grad. Prog. Acoustics, Penn State

Scattering geometry basics: Complex numbers

- Useful to work with exponential over sinusoidal waves
- Complex numbers allow us to simplify wavefunction equations

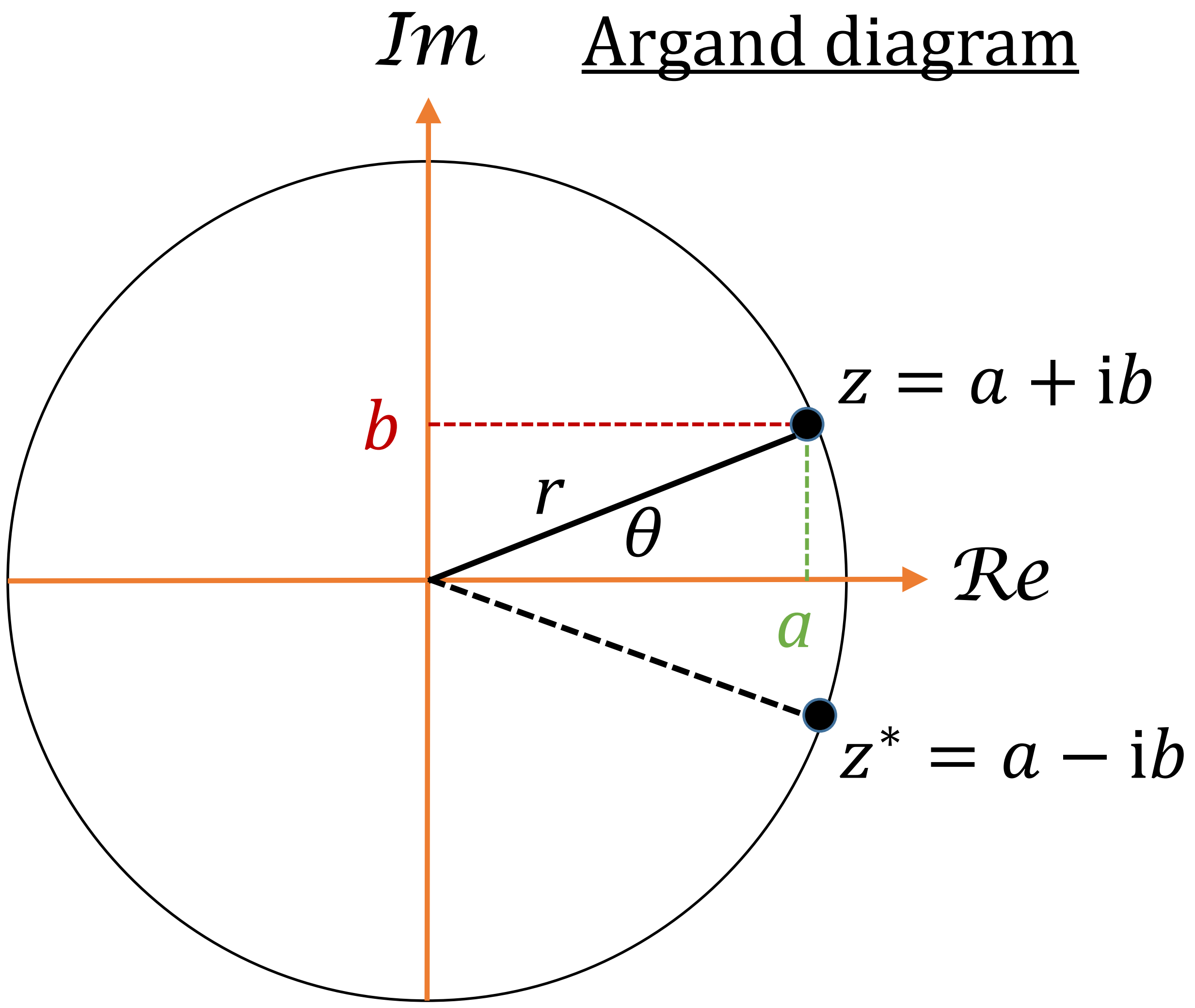
i = imaginary number

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$\psi = A\sin(\vec{k}\cdot\vec{r} - \omega t + \phi_0)$$

$$\boxed{\psi = Ae^{i(\vec{k}\cdot\vec{r} - \omega t)}}$$

<u>Argand diagram</u>



$\mathcal{Re}\{z\} = a$ $\mathcal{Im}\{z\} = b$

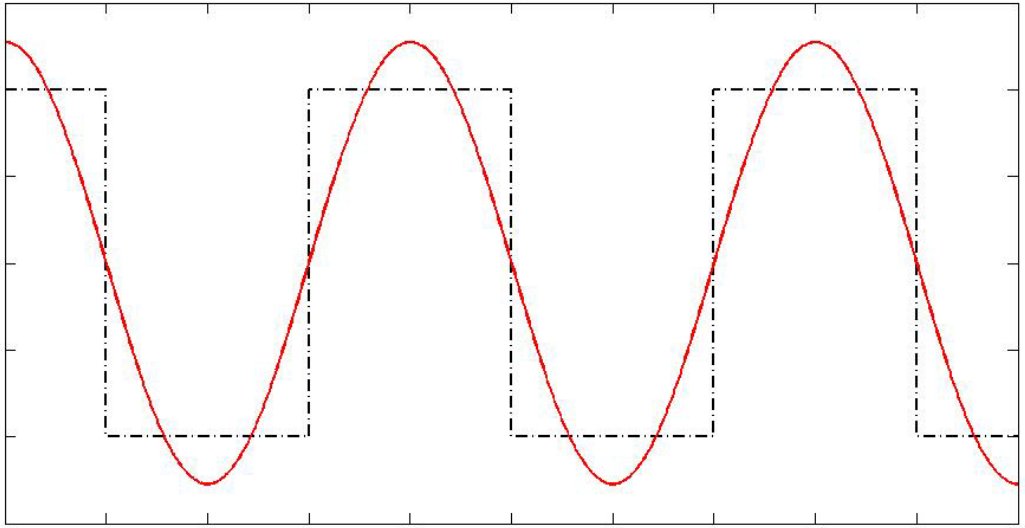
Scattering geometry basics: The Fourier series

- We approximate a periodic structure through a sum of cosines and sines.
- Let $f(x)$ be a function expanded by a Fourier series

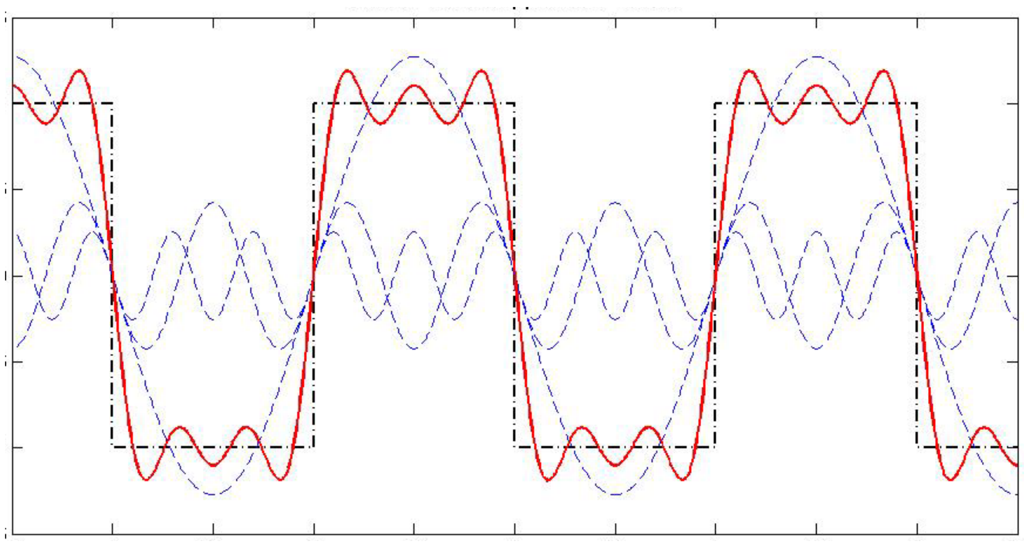
$$f(x) \approx a_0 + a_1\cos(kx) + a_2\cos(2kx) + a_3\cos(3kx) + \cdots$$
$$+ b_1\sin(kx) + b_2\sin(2kx) + b_3\sin(3kx) + \cdots$$

Goes to **zero** if $f(x) = f(-x)$

n = 1, fundamental harmonic



n = 3, higher harmonics included



The Fourier coefficients

- We write sum more efficiently if we pick the coefficients correctly.
- Now a definition and not approximation.

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \, e^{inkx}$$

where $c_{-n} = c_n^*$

$$c_n = \frac{1}{\lambda} \int_0^{\lambda} f(x) e^{-inkx} \mathrm{d}x$$

- We extend the analysis to a non-periodic function
- The Fourier coefficients become continuous functions we call $F(k)$

$$c_n = \frac{1}{\sqrt{2\pi}} F(k) \Delta k$$

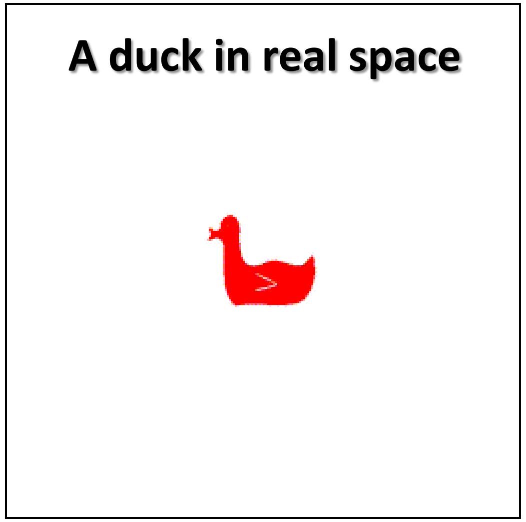
The Fourier transform

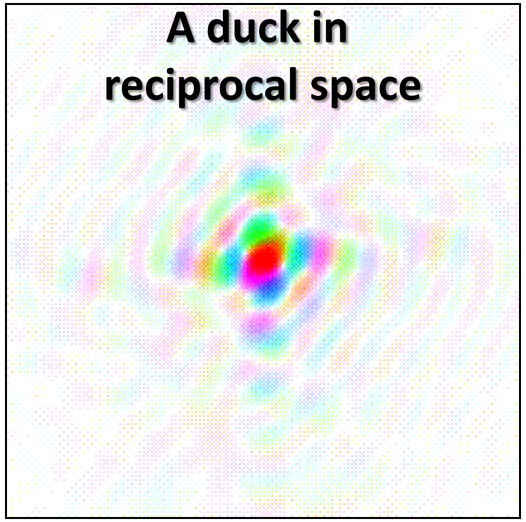
The limiting case is $\lambda \rightarrow \infty$ and $\Delta k \rightarrow 0$

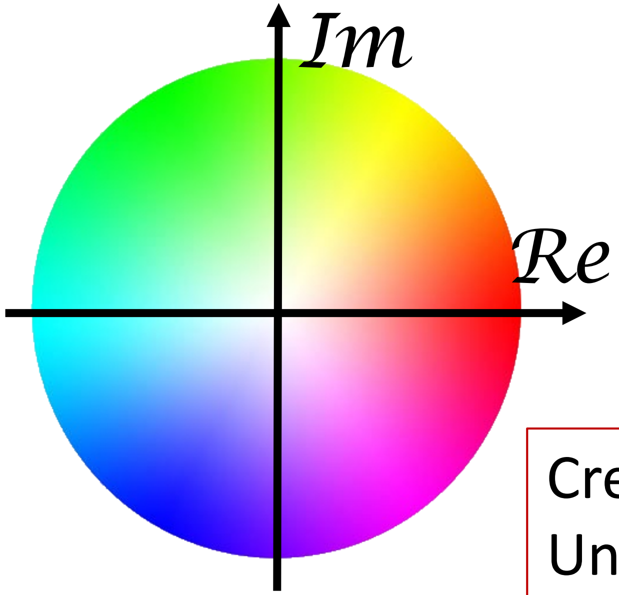
- We call $F(k)$ the Fourier transform of $f(x)$, and vice versa
- We can toggle between real space (x) and reciprocal space (k)

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{\mathrm{i}kx} \mathrm{d}k$$

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-\mathrm{i}kx} \mathrm{d}x$$



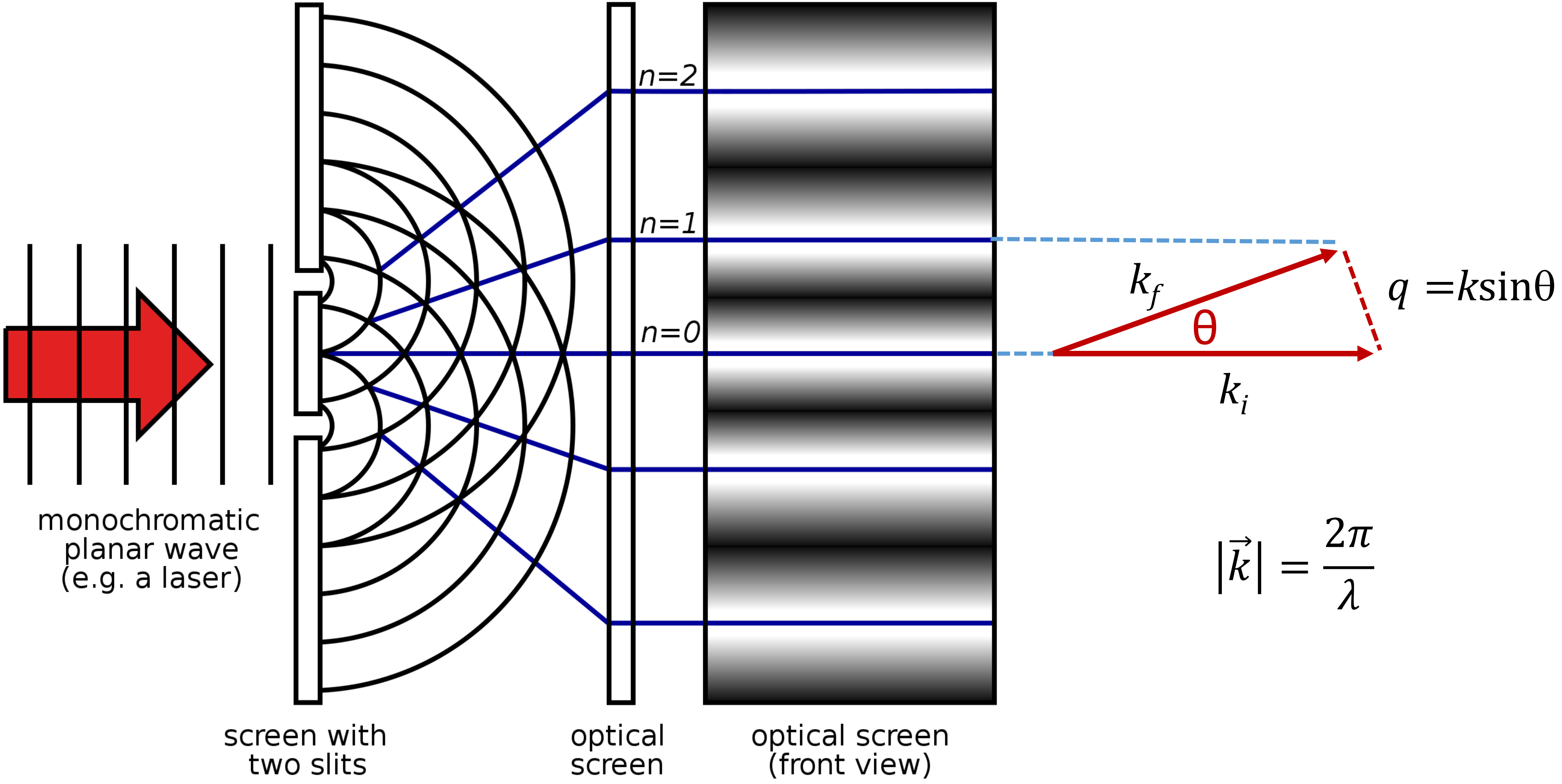




Argand diagram for real and imaginary components

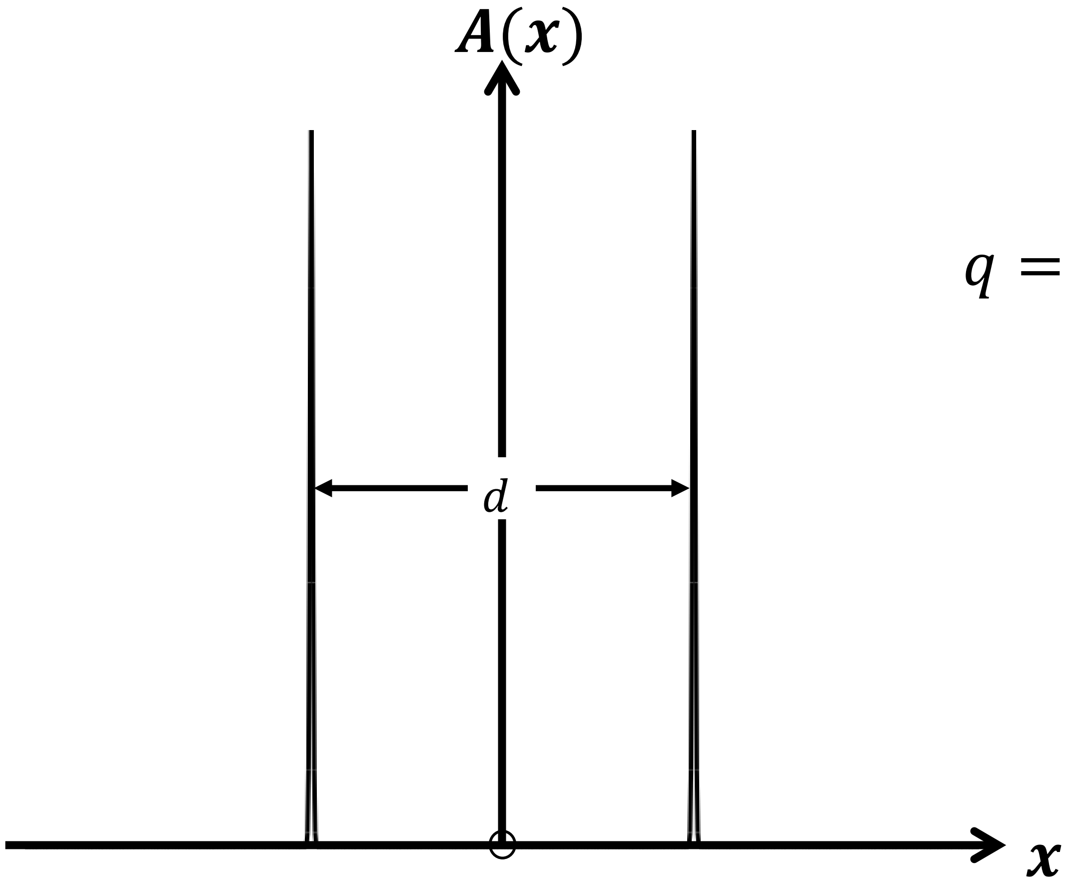
Credit: Dr. David Cowtan, University of York

Fourier optics: Young's double slit experiment



An important Fourier transform: Young's double slit

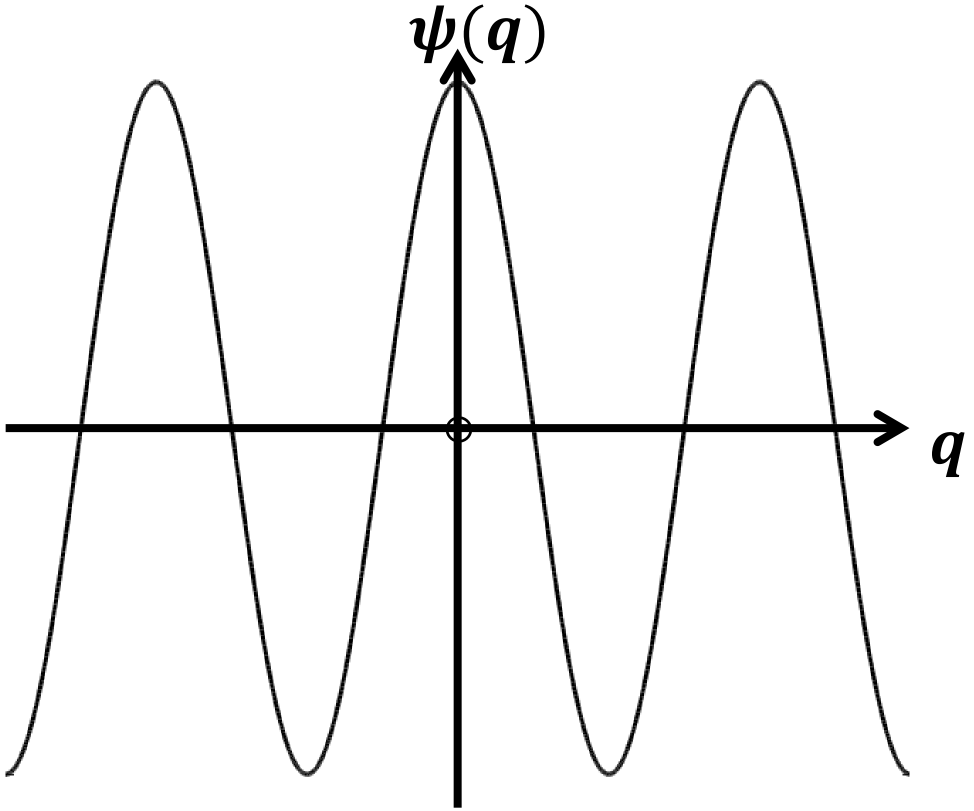
$$A(x) = \delta\left(x - \frac{d}{2}\right) + \delta\left(x + \frac{d}{2}\right)$$



$$q = \frac{2\pi \sin\theta}{\lambda}$$

$$\psi(q) = \psi_0\left(e^{iqd/2} + e^{-iqd/2}\right)$$

$$\psi(q) = \psi_0 2\cos\left(\frac{qd}{2}\right)$$

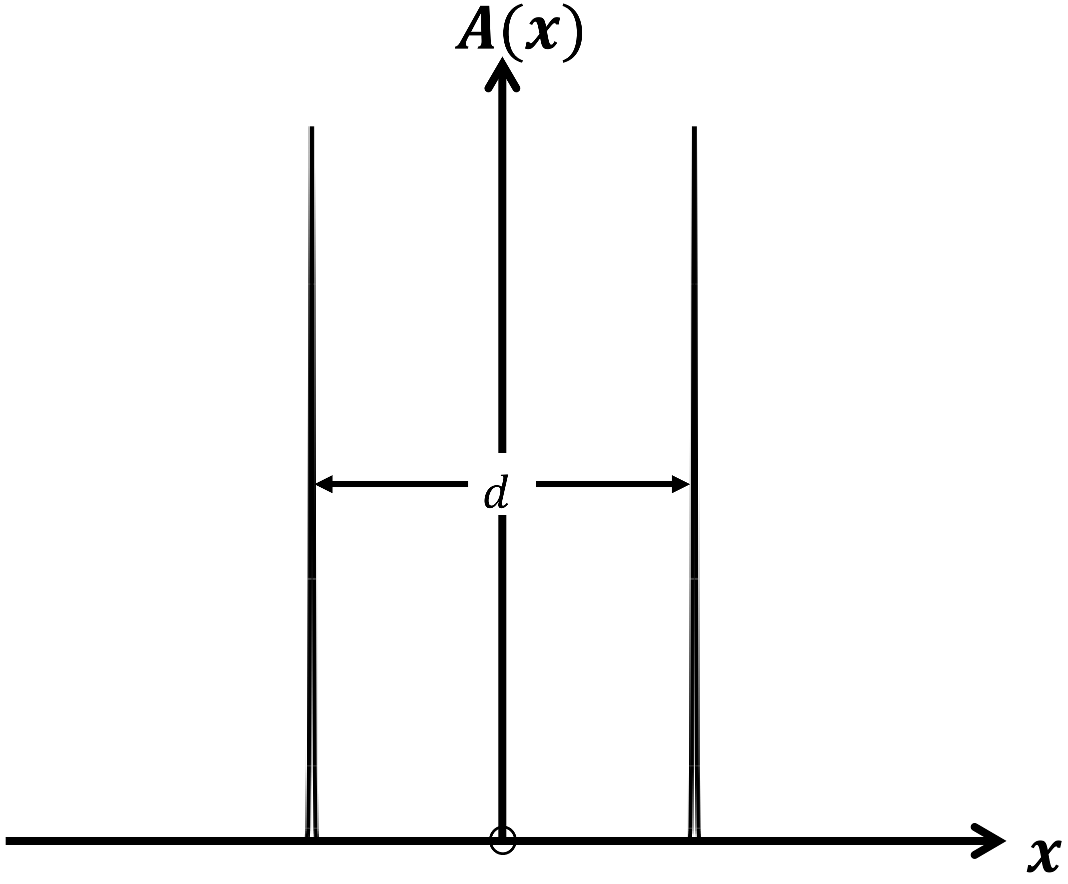


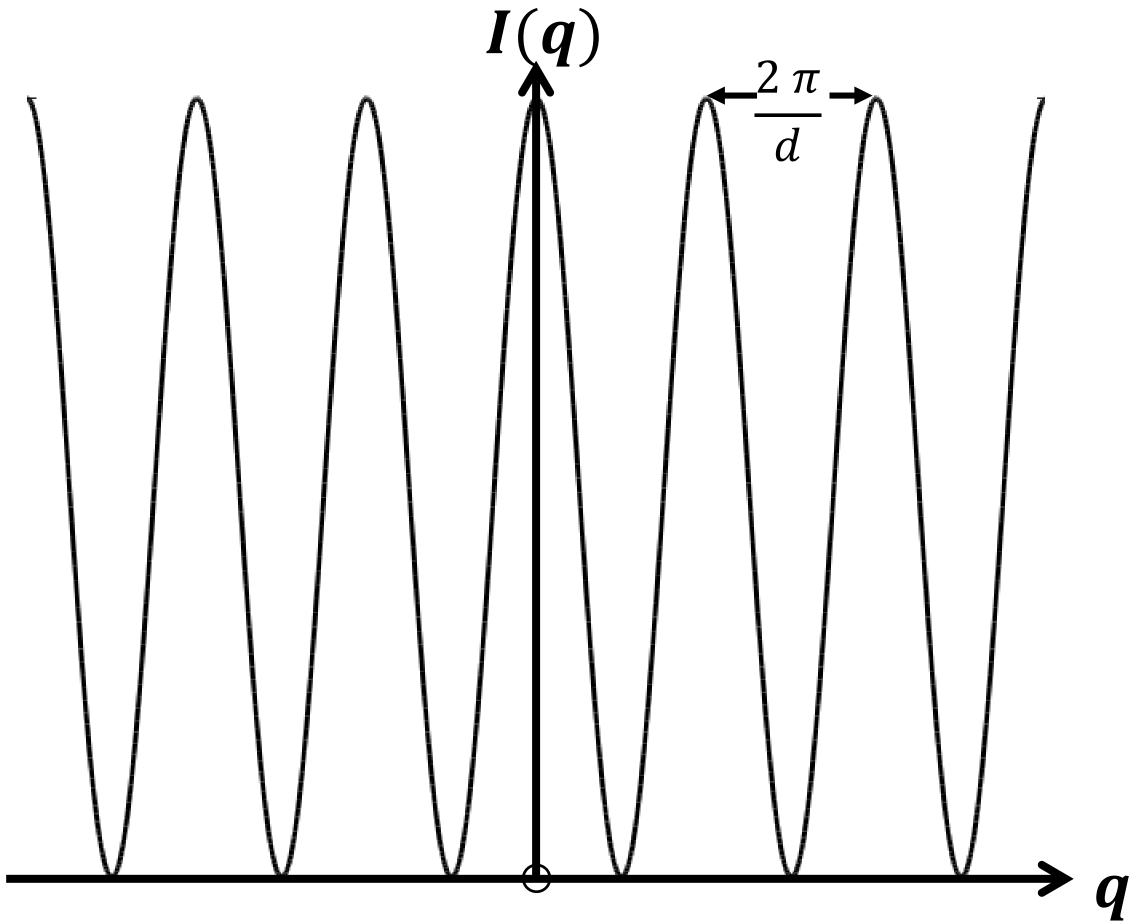
We don't see the transform, but its amplitude squared

$I(q)$ is our intensity or diffraction function

$$I(q) \propto \left[\cos\left(\frac{qd}{2}\right)\right]^2$$

$$I(q) \propto 1 + \cos(qd)$$





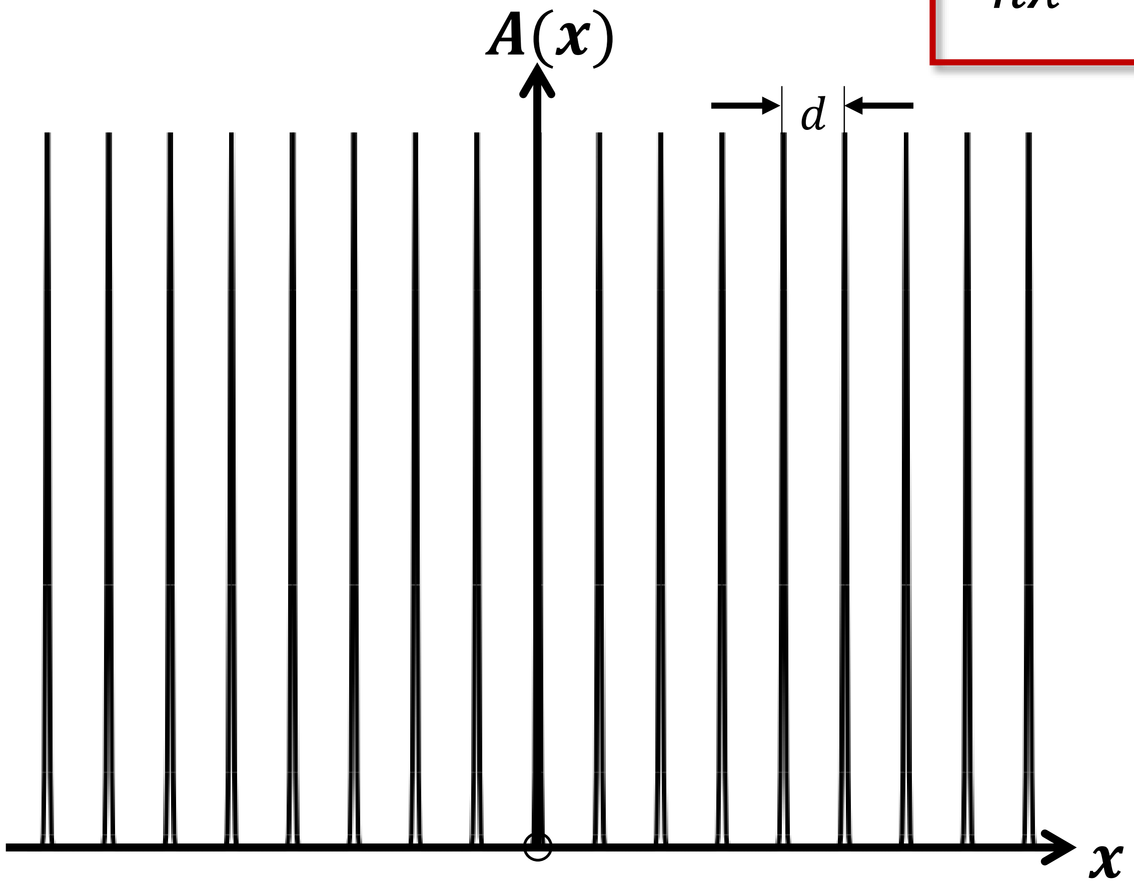
Bragg's law from Fourier transform of a diffraction grating

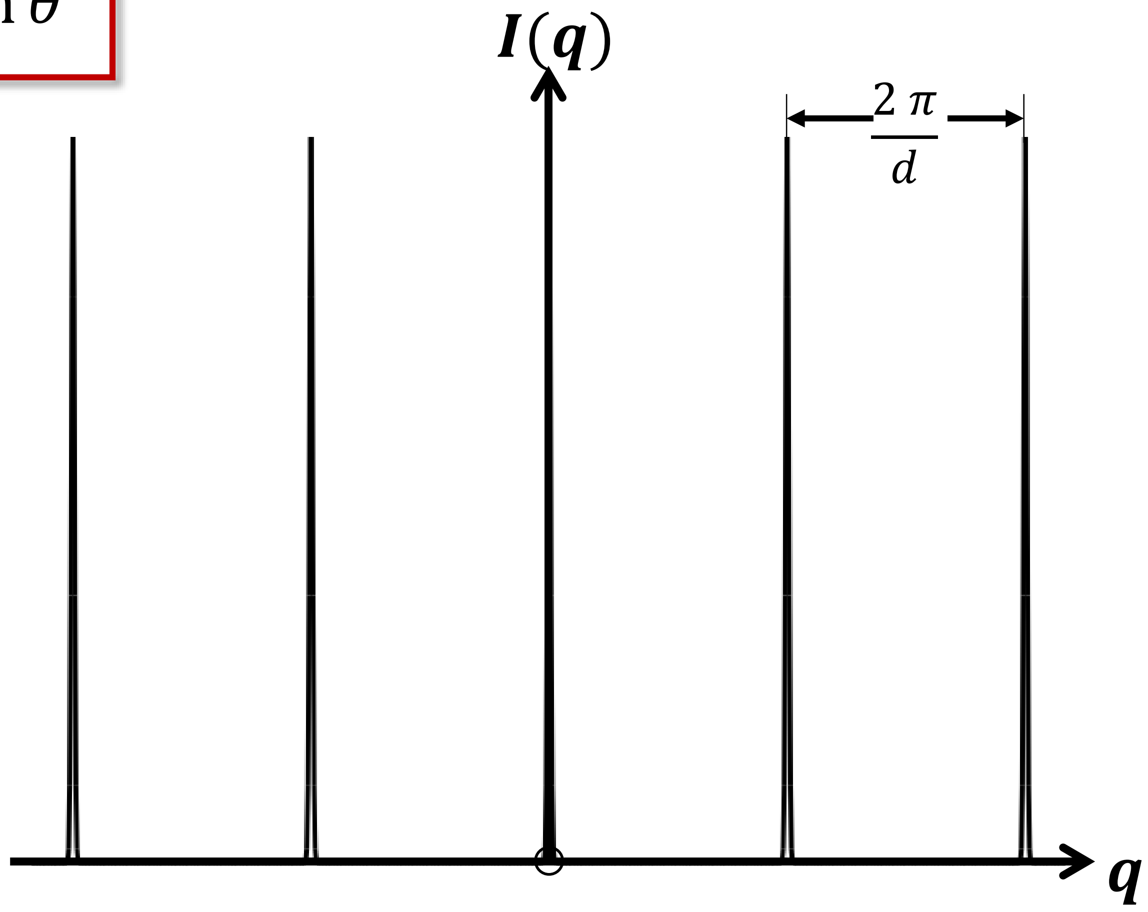
$$A(x) = \sum_{m=-\infty}^{\infty} \delta(x - md)$$

$$\frac{2\pi n}{d} = \frac{2\pi \sin\theta}{\lambda}$$

$$n\lambda = d \sin\theta$$

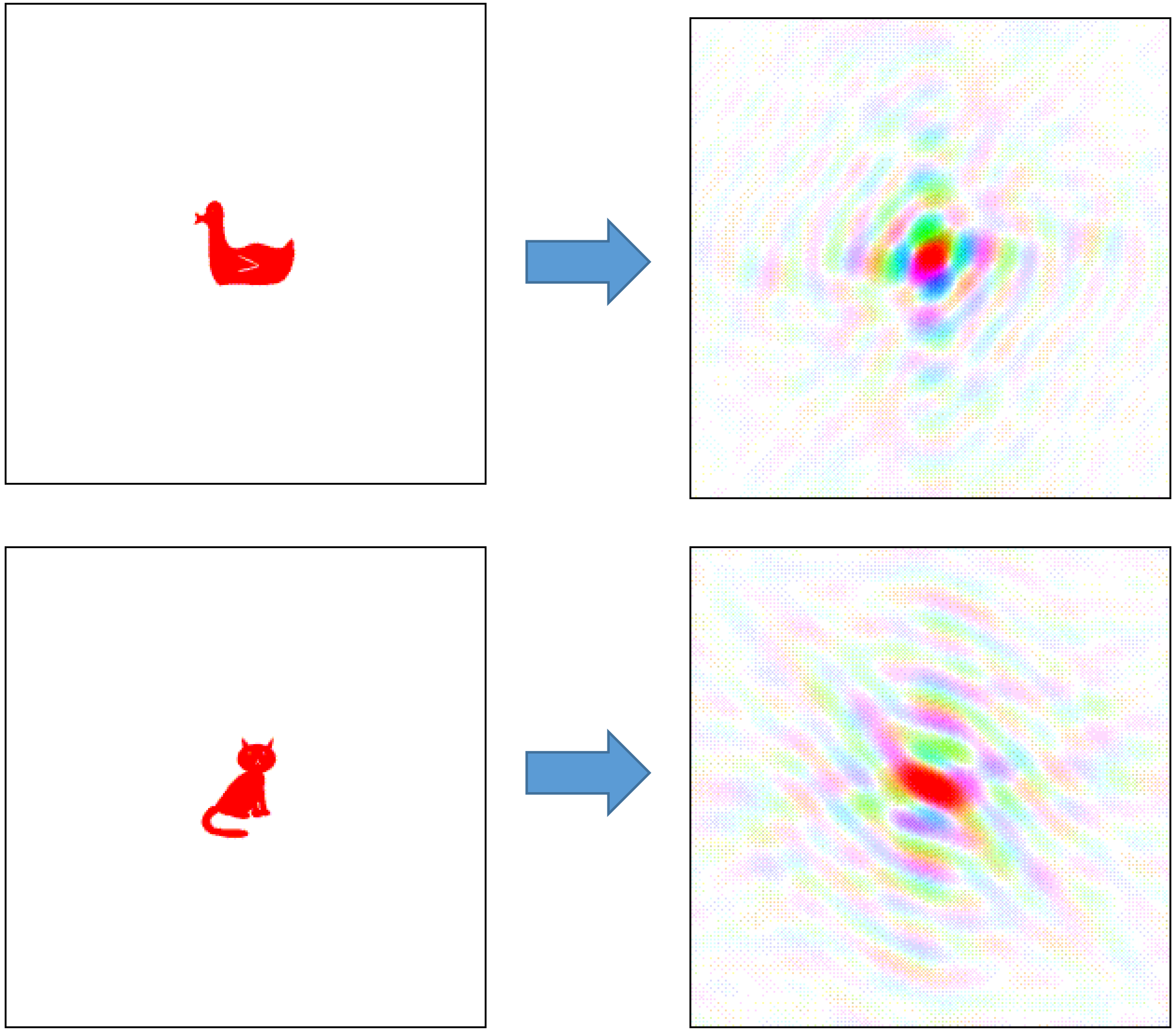
$$I(q) \propto \sum_{n=-\infty}^{\infty} \delta(q - nq_0)$$

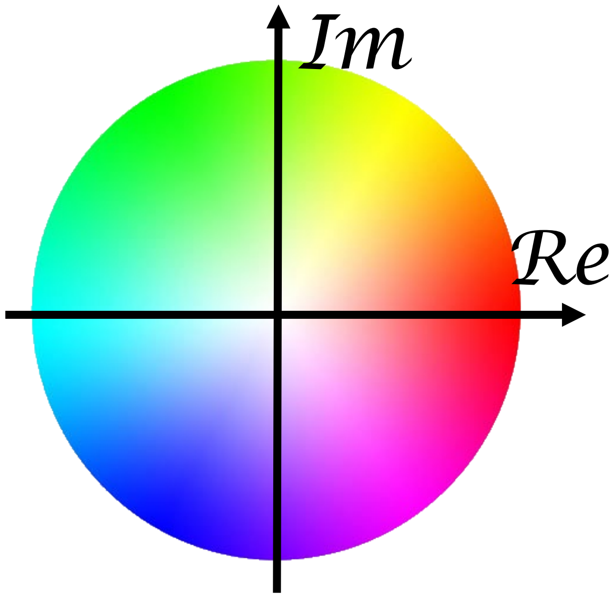




The phase problem with cats and ducks

animals in real space   animals in reciprocal space

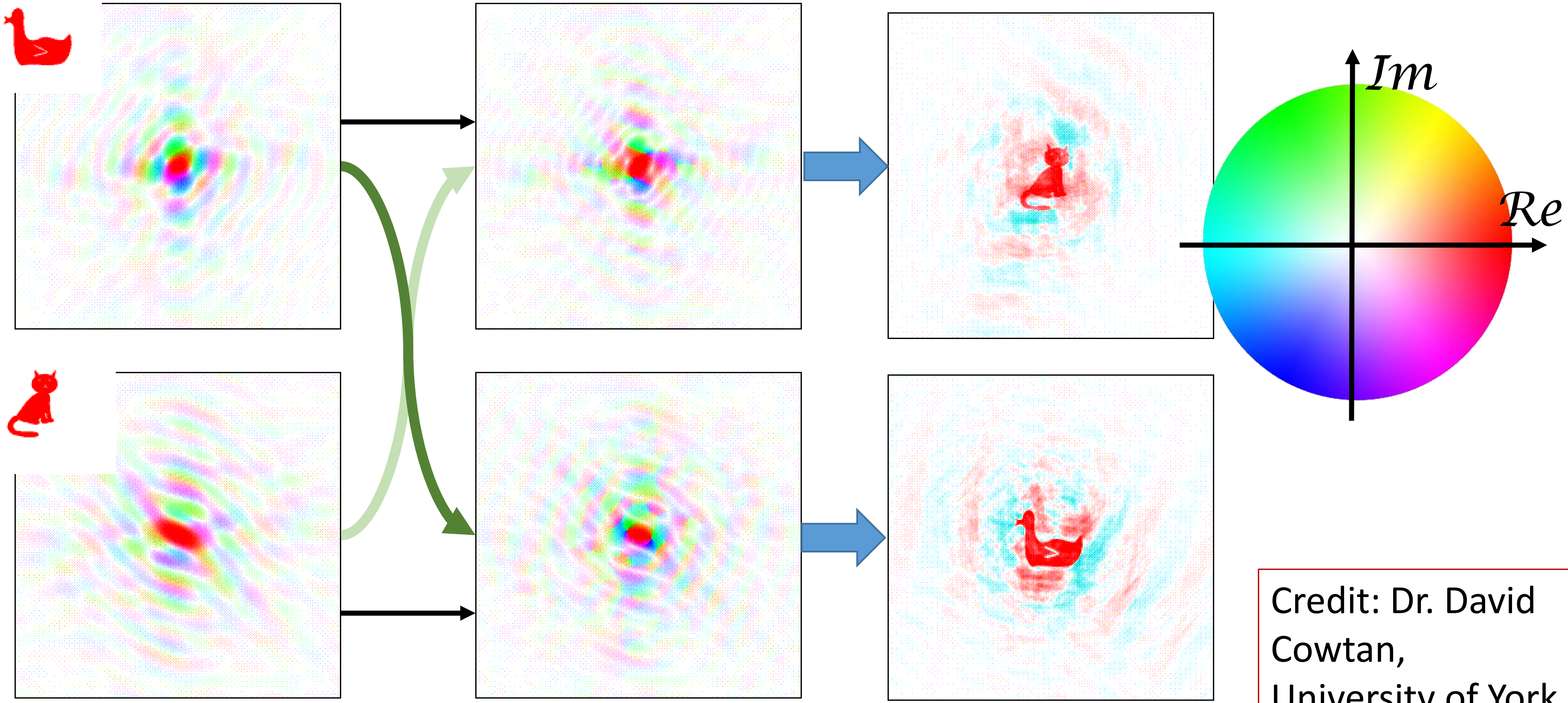




Credit: Dr. David Cowtan, University of York

The phase problem, mixing phases and amplitudes

amplitudes from original animal, but
phases from opposite animal



Credit: Dr. David Cowtan, University of York

Scattering cross sections

neutrons and x-rays

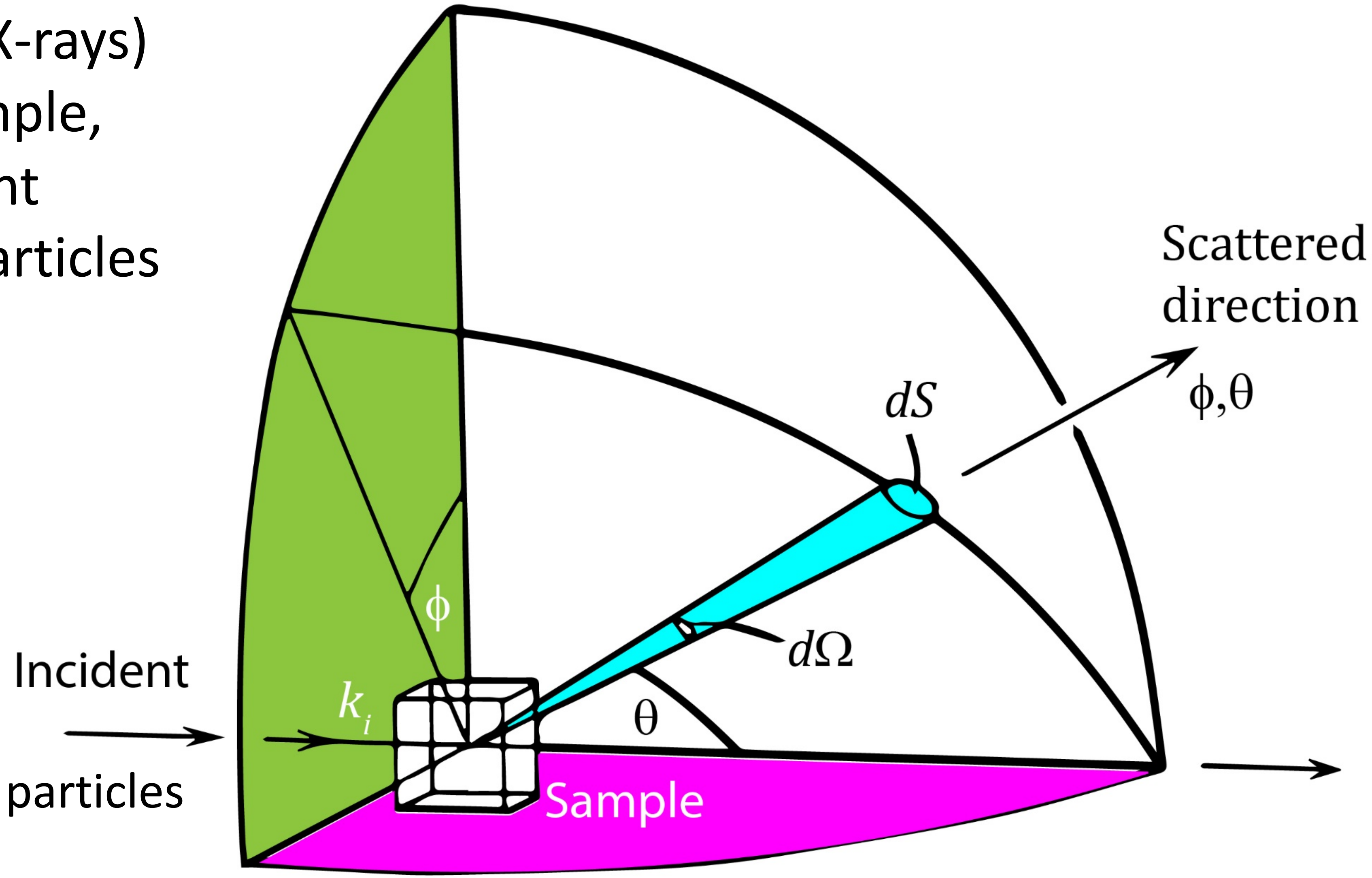
The differential cross-section

When neutrons (or X-rays) scattered by the sample, we use **σ** to represent number scattered particles

$$d\Omega = \frac{dS}{r^2}$$

We are after the **differential cross-section**

$$\frac{d\sigma}{d\Omega}$$



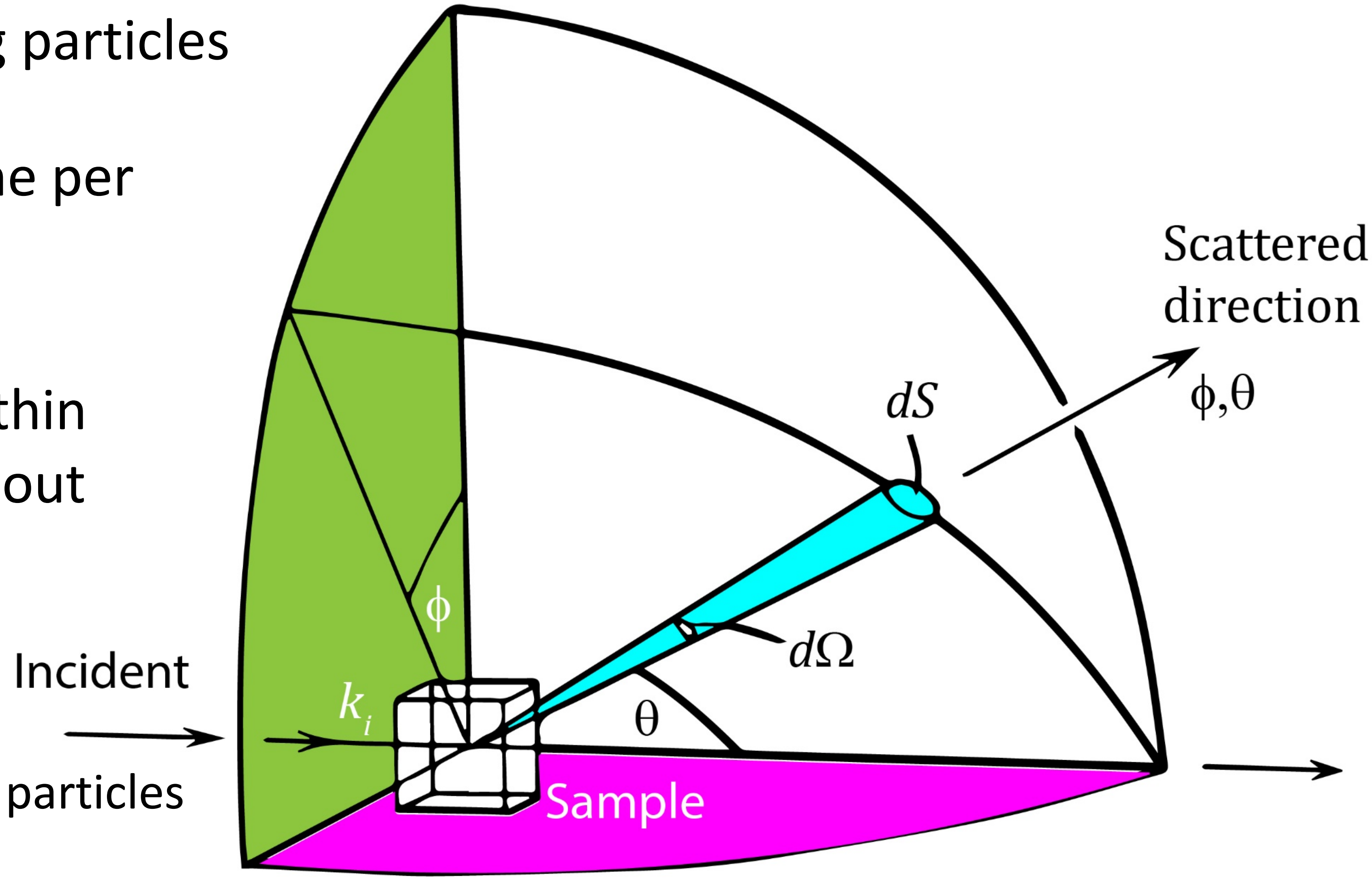
Flux of particles from beam and scattering at a solid angle

Φ = Flux of incoming particles

Number per unit time per unit area (s^{-1} cm^{-2})

Scattering occurs within the plane by 2θ and out by angle ϕ

We can define the solid angle as $\Delta\Omega$



The differential and double differential cross section

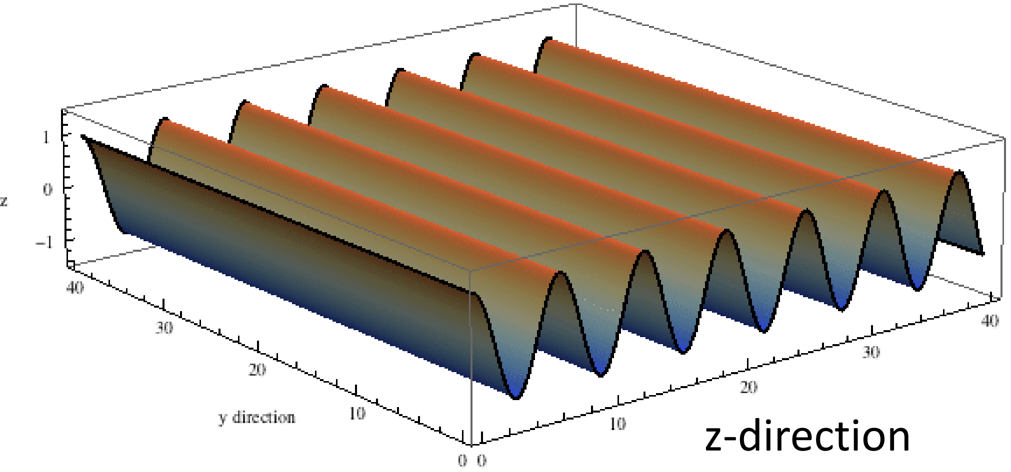
$$\Phi = \text{number of incident neutrons per cm}^2 \text{ per second}$$

$$\sigma = \text{total number of neutrons scattered per second} / \Phi$$

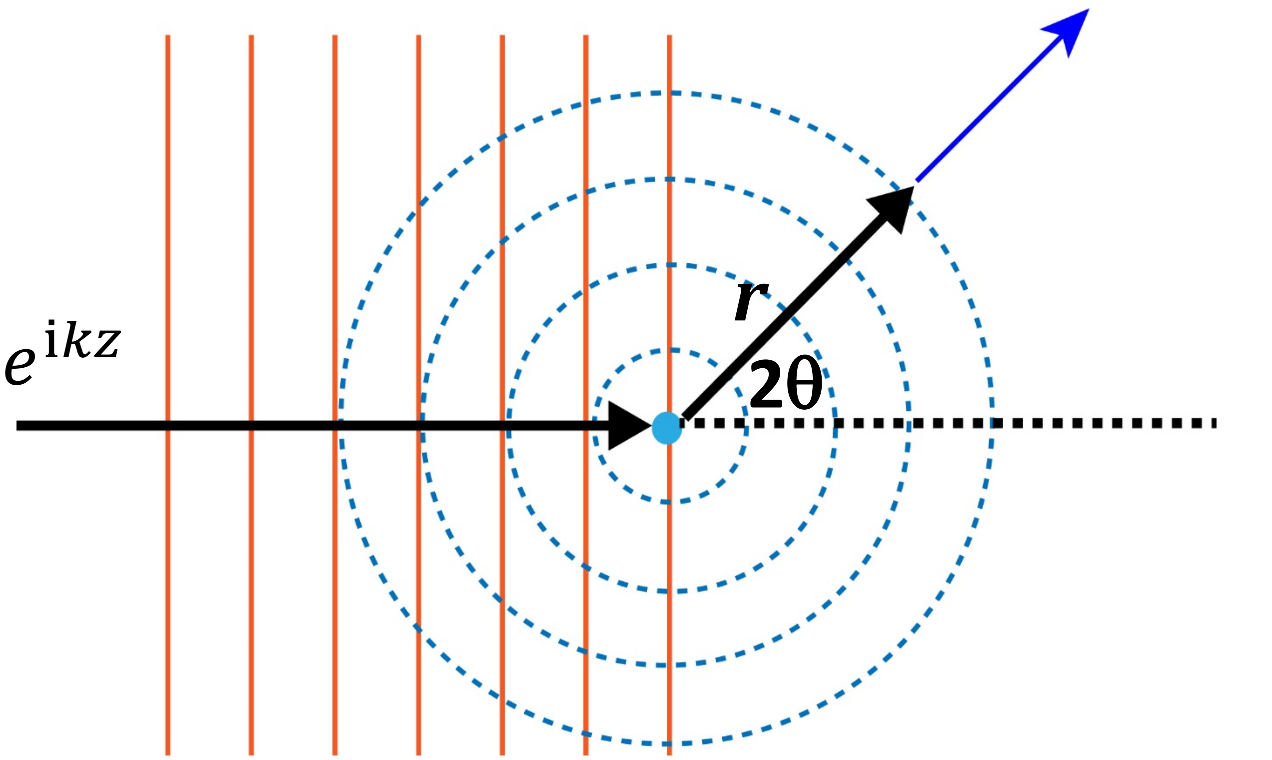
$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into d}\Omega}{\Phi \text{ d}\Omega}$$

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into d}\Omega \text{ \& dE}}{\Phi \text{ d}\Omega \text{ dE}}$$

Plane waves impinge on a single atom



$$\psi_f = \psi_0 f(\lambda, \theta)\,\frac{e^{ikx}}{r}$$



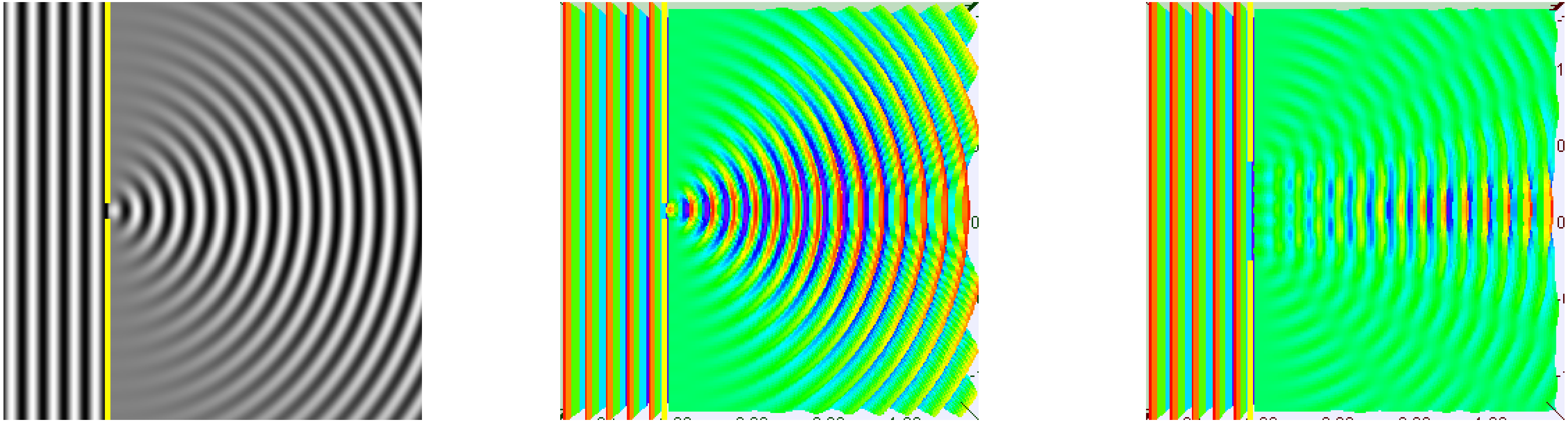
Top-down view of incident plane wave arriving at atomic center.

$$\psi_i = \psi_0 e^{ikz}$$

The ‘aperture’ function $f(\lambda,\theta)$ for scattering a plane wave

- We approximate $f(\lambda,\theta)$ as a constant for neutron scattering as a fixed point.
- For x-rays, we cannot make this approximation which affects $f(\lambda,\theta)$

Increasing slit-size means that the scattered wave has more 2θ-dependence
Intensity drops off at higher scattering angles



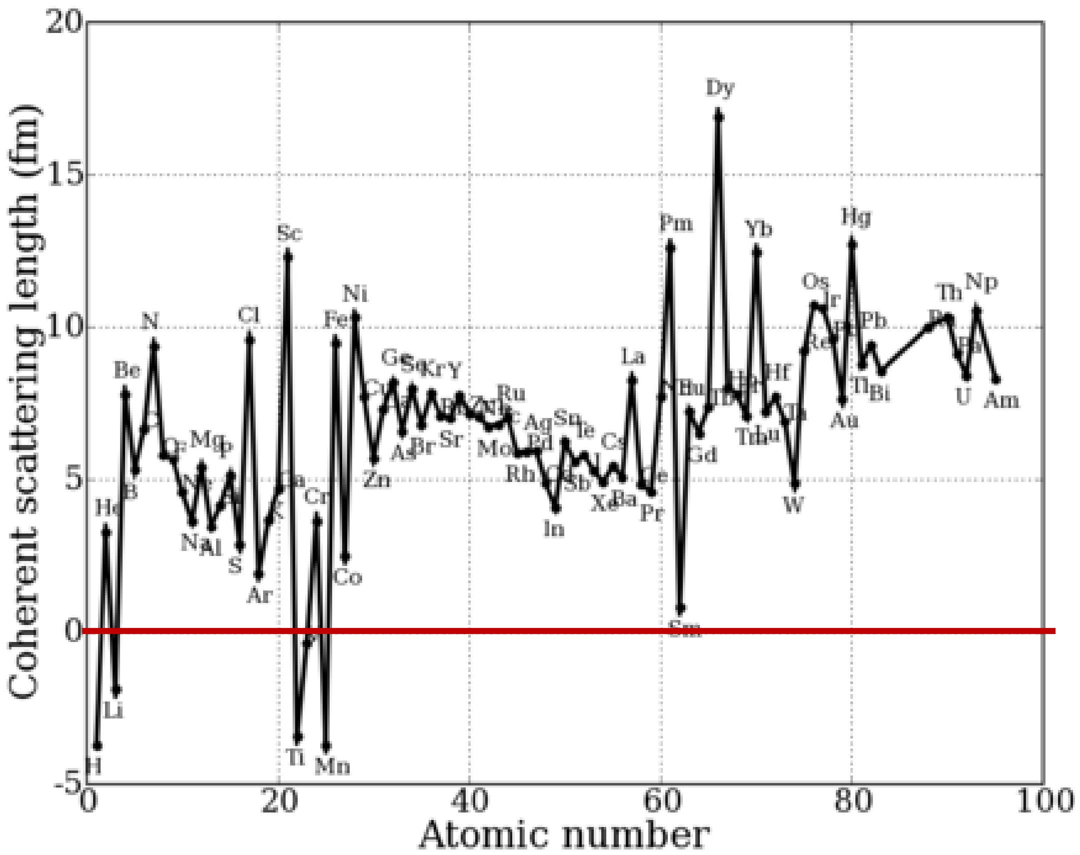
GIFs of plane wave arriving at a slit

The neutron scattering length

- In neutron scattering, the nucleus is a point source.
- *f*(λ,θ) is therefore a constant
- *f*(λ,θ) = *b* where *b* is known as **the scattering length**

$$\psi_f = \psi_0 f(\lambda,\theta)\frac{e^{ikx}}{r}$$

- Note that *f*(λ,θ) and *b* must have units of length since it is divided by *r*
- Typical *b* are in fm or 10^{-15} m
- Can be positive or negative!



The neutron scattering cross section

<u>*R*</u>   <u>Φ</u>   <u>d*S*</u>

<u>*Rate*</u> = <u>*incident flux*</u> x <u>*cross-sectional area*</u>

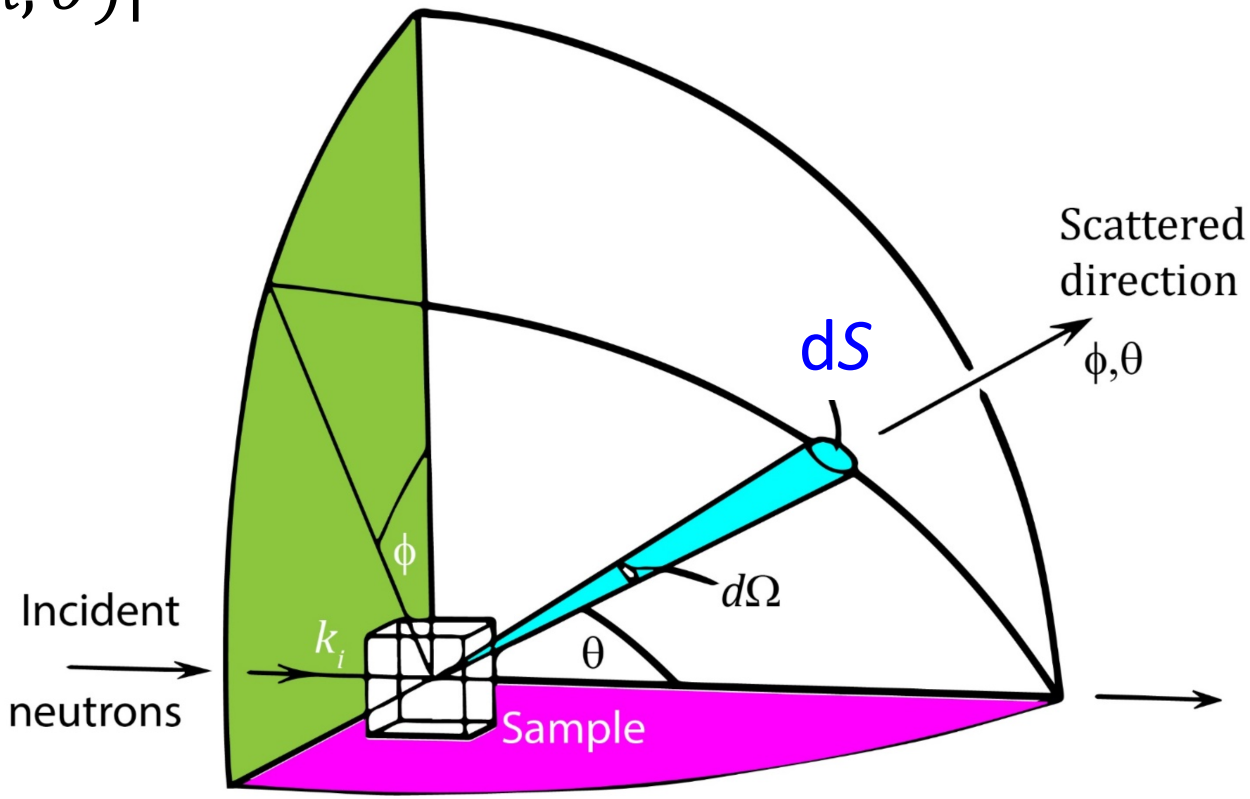
$$\sigma = 4\pi|b|^2$$

$$|\psi_0|^2 = \Phi$$

$$|\psi_f|^2 = \frac{\Phi}{r^2}|f(\lambda,\theta)|^2$$

$$R = \int_{2\theta=0}^{\pi}\int_{\phi=0}^{2\pi}|\psi_f|^2\, \mathrm{d}S$$

$$\sigma = 2\pi\int_{2\theta=0}^{\pi}|f(\lambda,\theta)|^2 \sin 2\theta \mathrm{d}2\theta$$



Neutron scattering length for hydrogen

- Units given in barns, where 1 barn = 10^{-28} m^2
- These are isotope specific and will depend on the orientation of nuclear spin with respect to the neutron
- Example hydrogen vs. deuterium
- H has triplet and singlet from proton

$$b^+ = 1.085 \times 10^{-14} m$$
$$b^- = -4.750 \times 10^{-14} m$$

$$\langle b \rangle = \frac{3}{4} b^+ + \frac{1}{4} b^-$$

$$\Delta b = \sqrt{\langle b^2 \rangle - \langle b \rangle^2}$$

$$\langle b \rangle = -0.374 \times 10^{-14} m$$

$$\Delta b = 2.527 \times 10^{-14}\ m$$

$$b = \langle b \rangle \pm \Delta b$$

Neutron scattering length for deuterium

- Deuterium has a quartet and doublet from proton and neutron in its nucleus
- 2/3 of states are quartet, 1/3 are doublet

$$\langle b \rangle = \frac{2}{3} b^{+} + \frac{1}{3} b^{-}$$

$$\langle b \rangle = 0.668 \times 10^{-14} m$$

$$\Delta b = 0.403 \times 10^{-14} m^2$$

$$\sigma = 4\pi |b|^2$$

$$\langle b^2 \rangle = \langle b \rangle^2 + (\Delta b)^2$$

$$\langle \sigma \rangle = \sigma_{coh} + \sigma_{inc}$$

(barns)	$\sigma_{coh} = 4\pi \langle b \rangle^2$	$\sigma_{incoh} = 4\pi (\Delta b)^2$
Hydrogen	1.76	80.27
Deuterium	5.59	2.05

The intrinsic cross section for x-rays

- The x-ray is a electromagnetic radiation with the electric field E_{in} oscillating normal to the wave's propagation.

$$\vec{E}_{\text{in}} = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

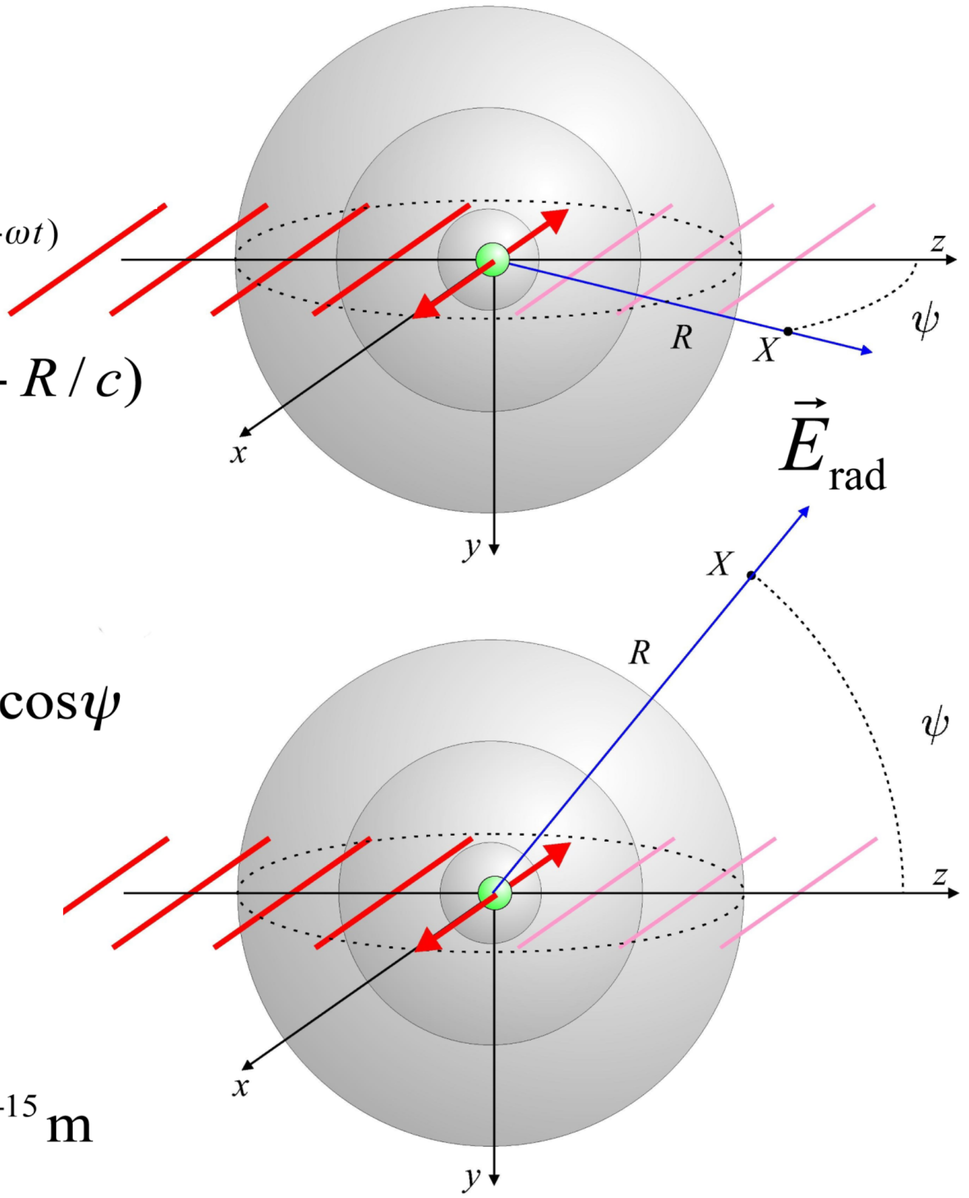
$$E_{\text{rad}}(R,t) = \frac{e}{4\pi\varepsilon_0 c^2 R}\ddot{x}(t - R/c)$$

- The electrons in the atomic center will oscillate with the x-ray and re-emit the x-ray with the oscillating field E_{rad}

$$\frac{E_{\text{rad}}(R,t)}{E_{\text{in}}} = -r_0\alpha(\omega)\frac{e^{ikR}}{R}\cos\psi$$

Thompson scattering length of the electron

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times10^{-15}\,\text{m}$$



The cross section for x-rays

$$\text{Measured intensity (i.e. number of x - ray photons)} \; \alpha \; \text{energy/sec}$$

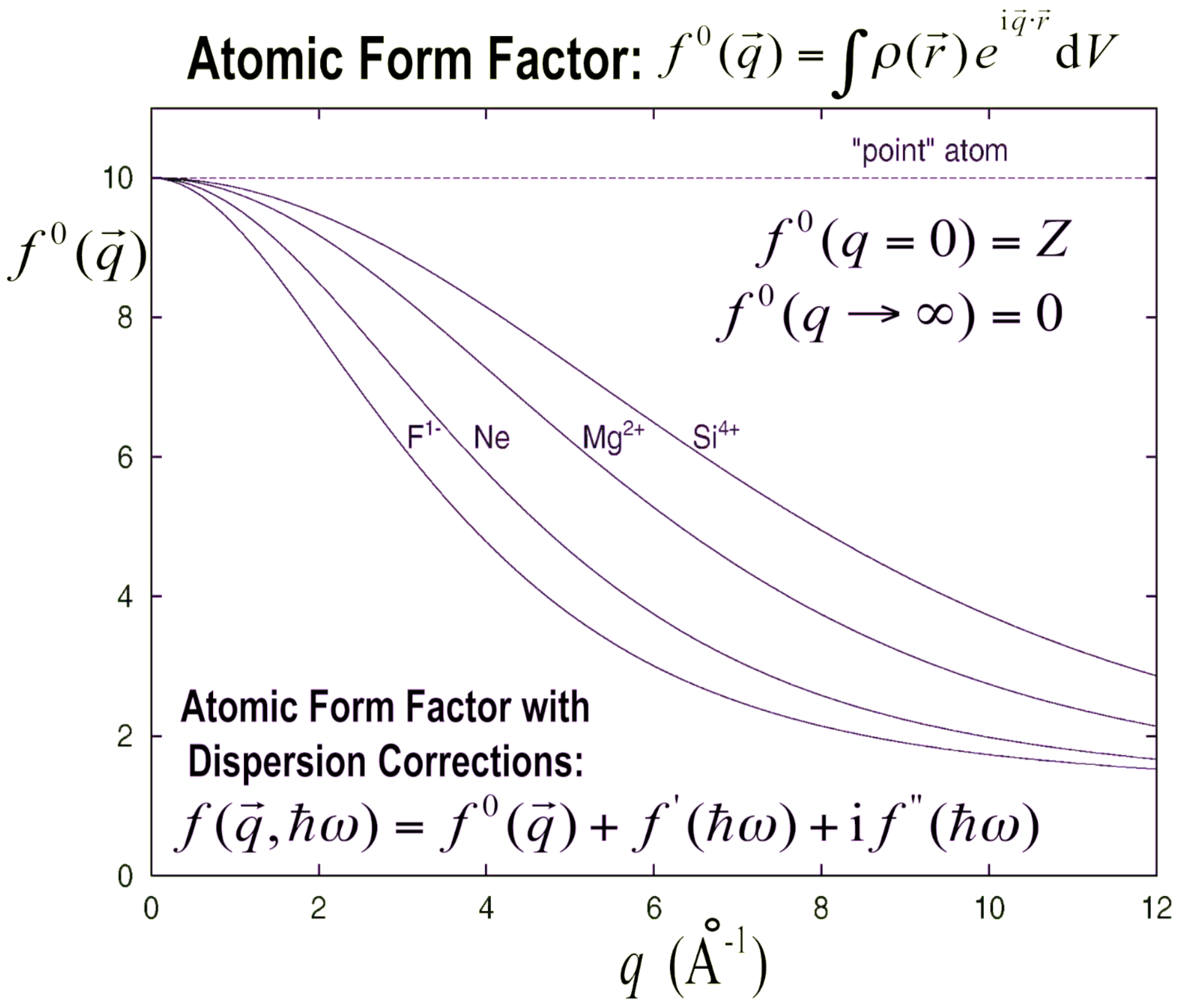
$$\text{Energy per unit area of beam} \; \alpha \; E^2 \; ;$$

$$\Rightarrow \frac{\text{intensity measured in detector}}{\text{incident intensity}} = \frac{I_{sc}}{I_0} = \frac{|E_{rad}|^2 R^2 \Delta\Omega}{|\mathrm{E}_{\mathrm{in}}|^2 A}$$

$$\text{differential cross section} = \frac{d\sigma}{d\Omega} = \frac{\text{number of xrays scattered per sec in } \Delta\Omega}{(\text{number of incident xrays per area}) * \Delta\Omega}$$

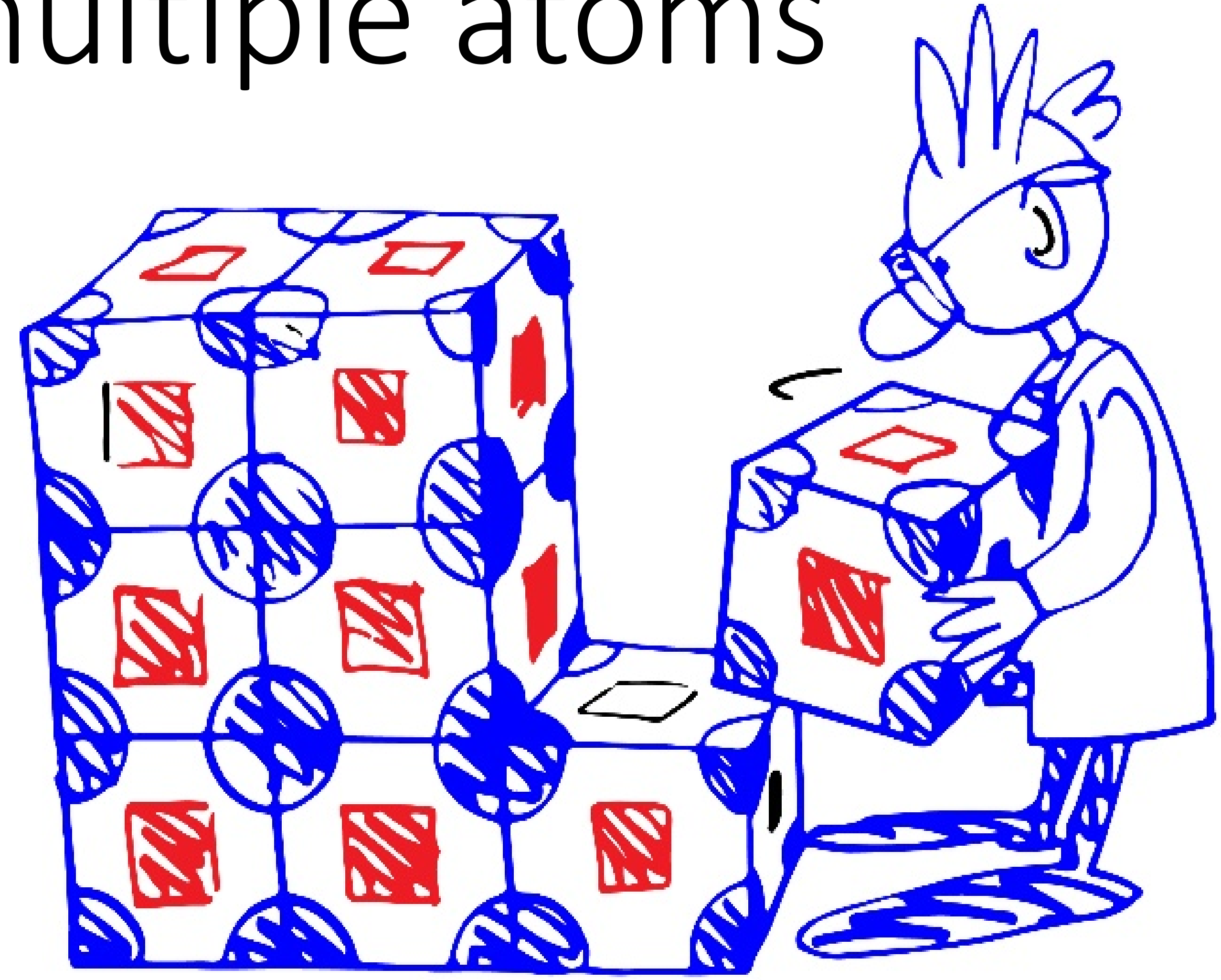
$$\frac{d\sigma}{d\Omega} = \frac{I_{sc}}{(I_0 / A)\Delta\Omega} = \frac{|E_{rad}|^2 R^2}{|\mathrm{E}_{\mathrm{in}}|^2} = r_0^2 \cos^2 \psi$$

The atomic form factor for x-rays



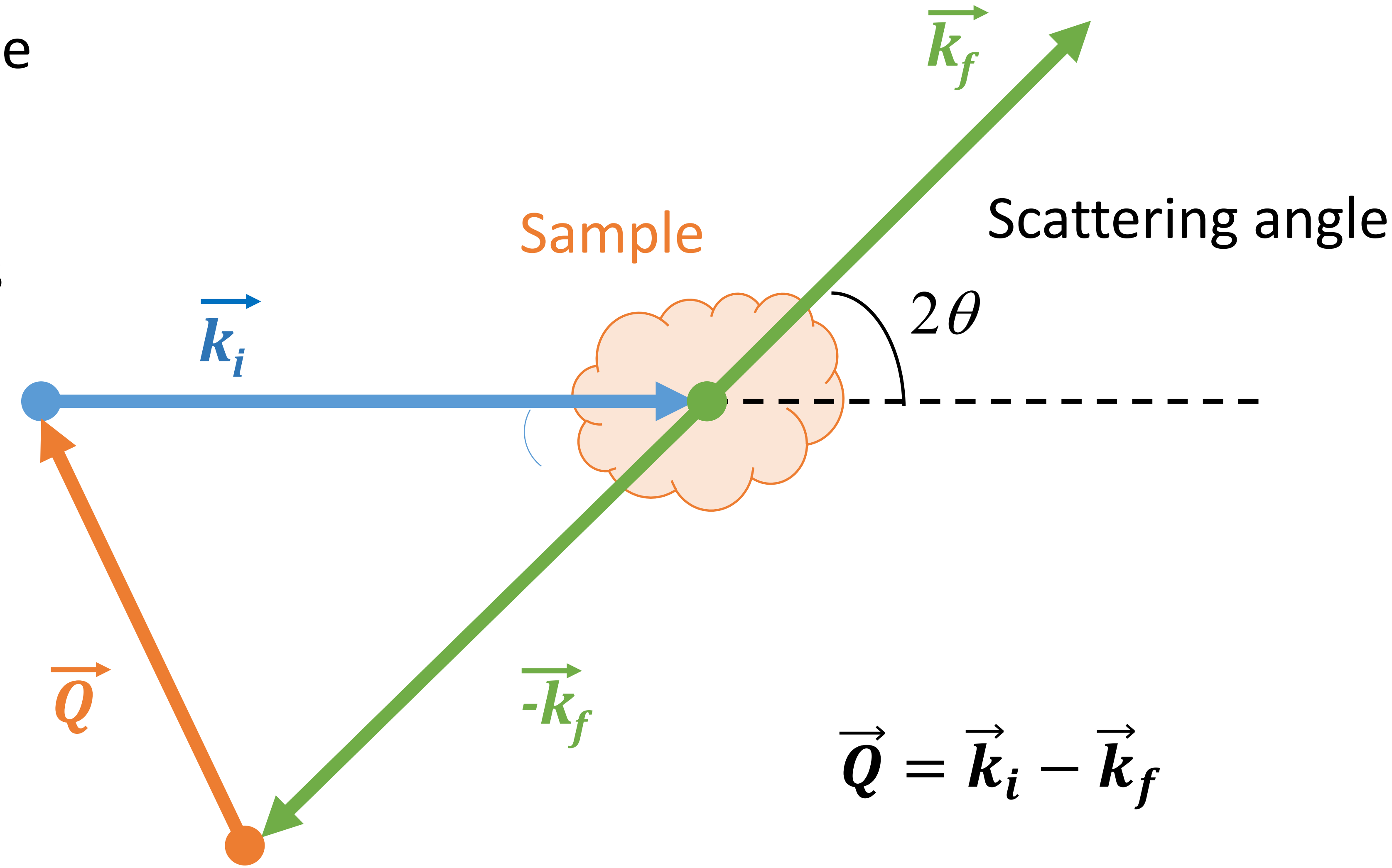
Scattering from multiple atoms

Diffraction from a crystal



The scattering triangle

- k_i is the incident wavevector and k_f is the scattered wavevector
- Useful to work with another vector besides k_i or k_f
- We define Q, as our **momentum transfer**



Momentum transfer, or Q-space

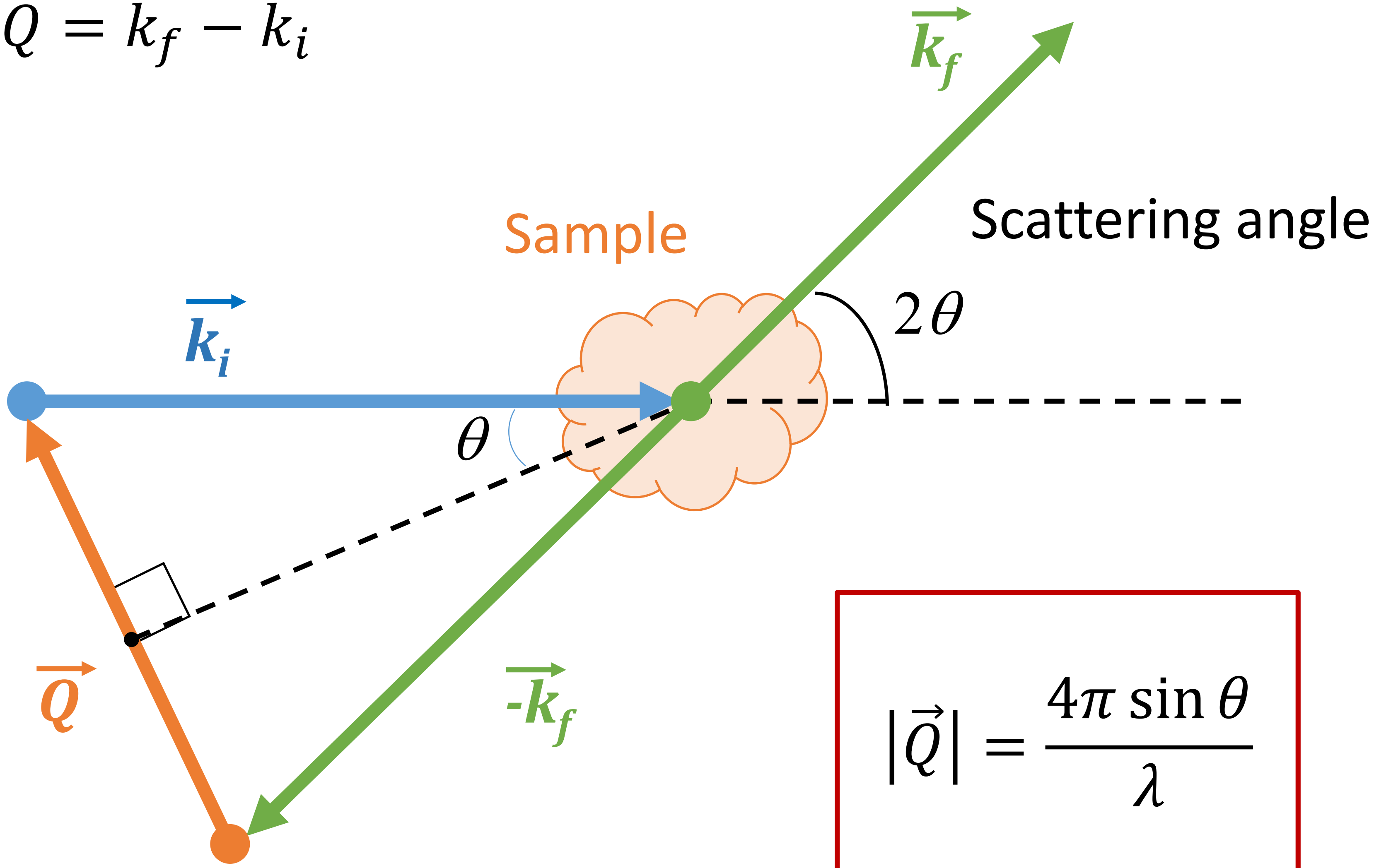
$\vec{Q} = \vec{k}_i - \vec{k}_f$ <u>or</u> $\vec{Q} = \vec{k}_f - \vec{k}_i$

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

For elastic scattering,
no energy transfer

$$|\vec{k}_i| = |\vec{k}_f|$$

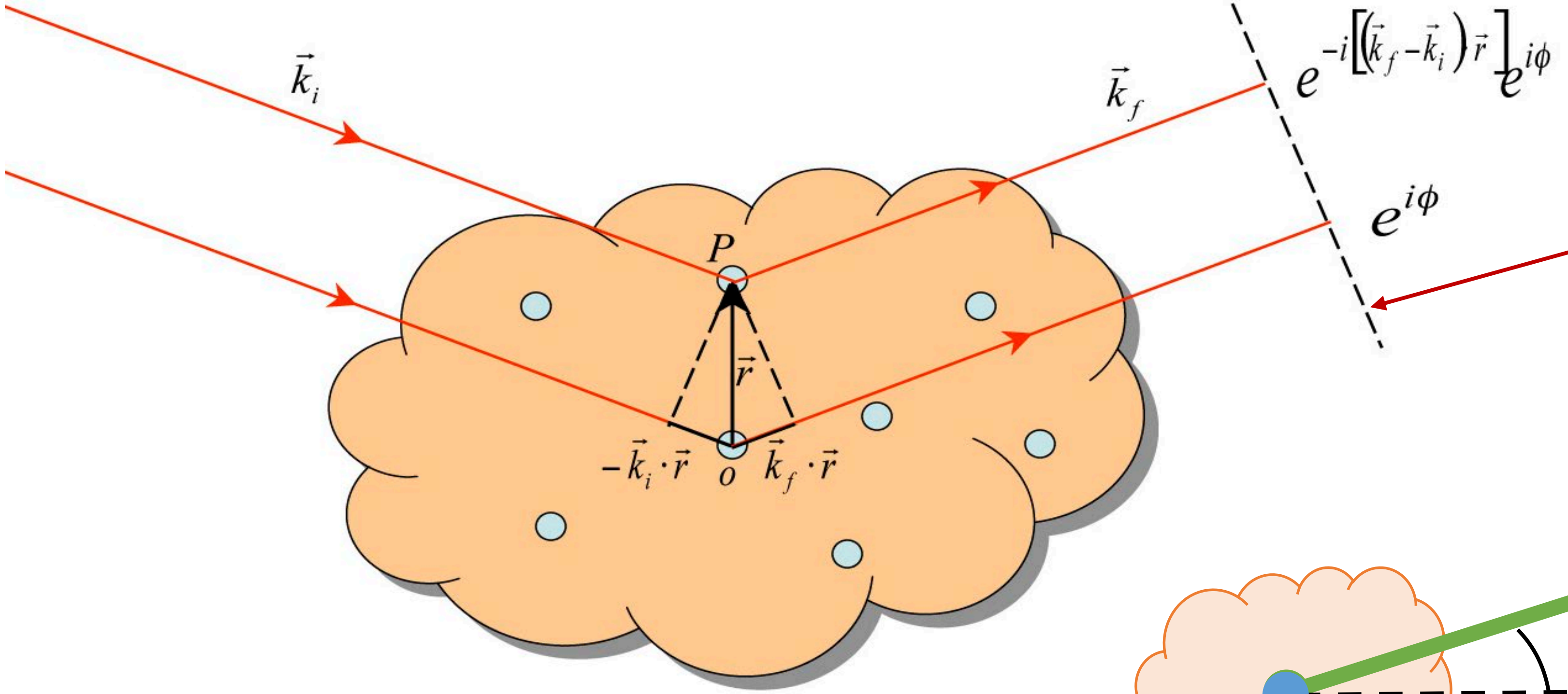
$$\frac{|\vec{Q}|}{2} = |\vec{k}| \sin\theta$$



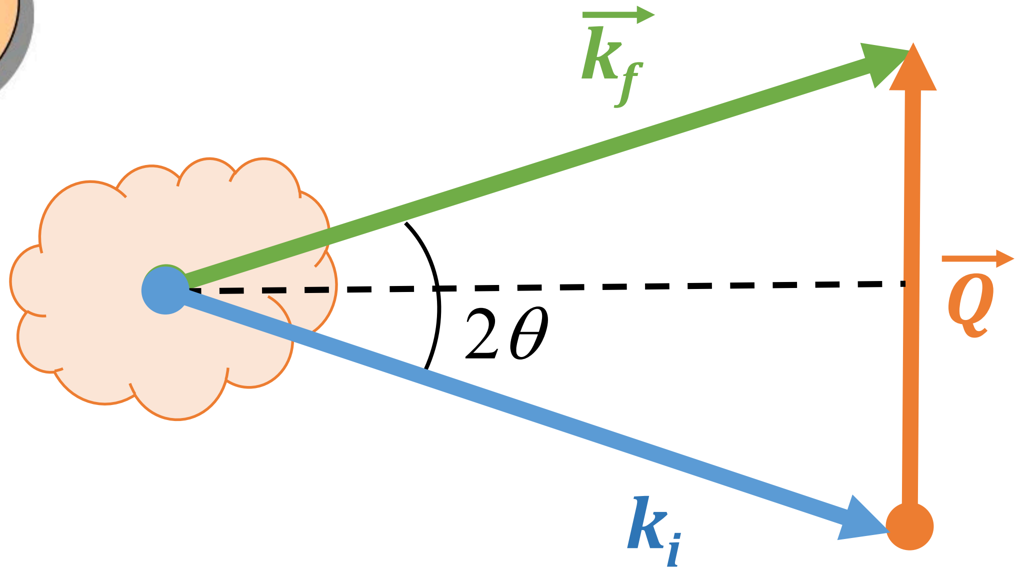
$$|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

Scattering from an ensemble of atoms

$$\vec{Q} = \vec{k}_f - \vec{k}_i$$



Waves scattered can add up in phase



$$|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

Adding up the waves scattered from different centers

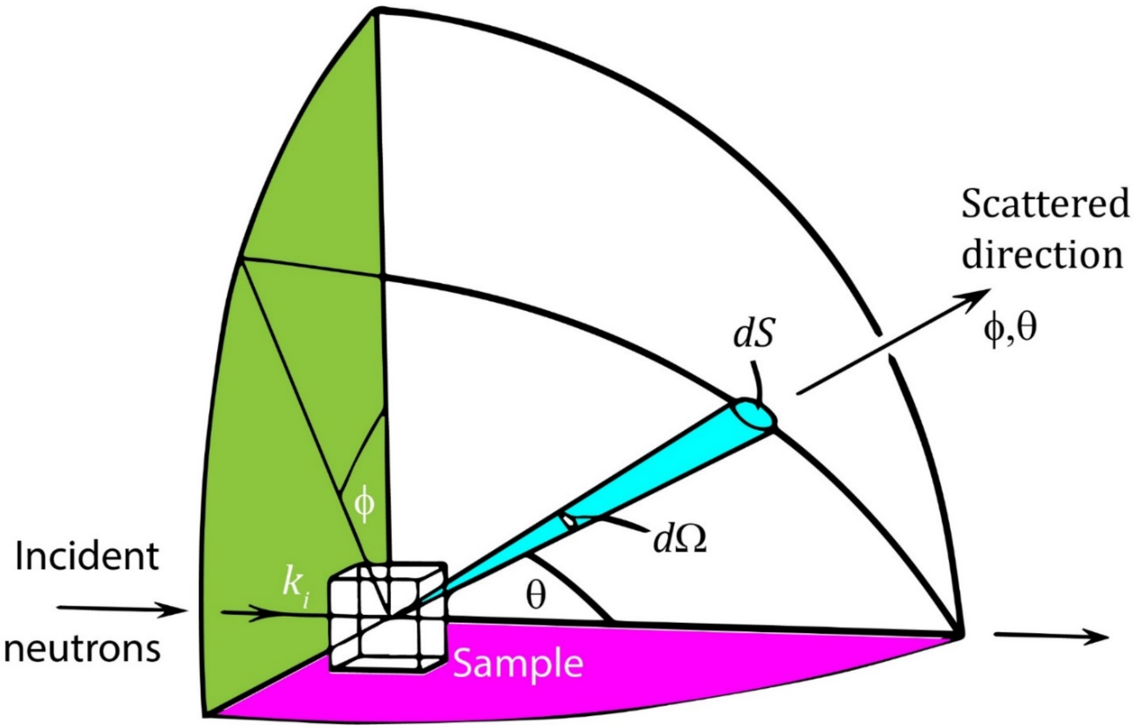
At a scattering center located at $\vec{R}_i$ the incident wave is $e^{i\vec{k}_0.\vec{R}_i}$

so the scattered wave at $\vec{r}$ is $\psi_{scat} = \sum e^{i\vec{k}_0.\vec{R}_i}\left[\frac{-b_i}{|\vec{r}-\vec{R}_i|}e^{i\vec{k}'.(\vec{r}-\vec{R}_i)}\right]$

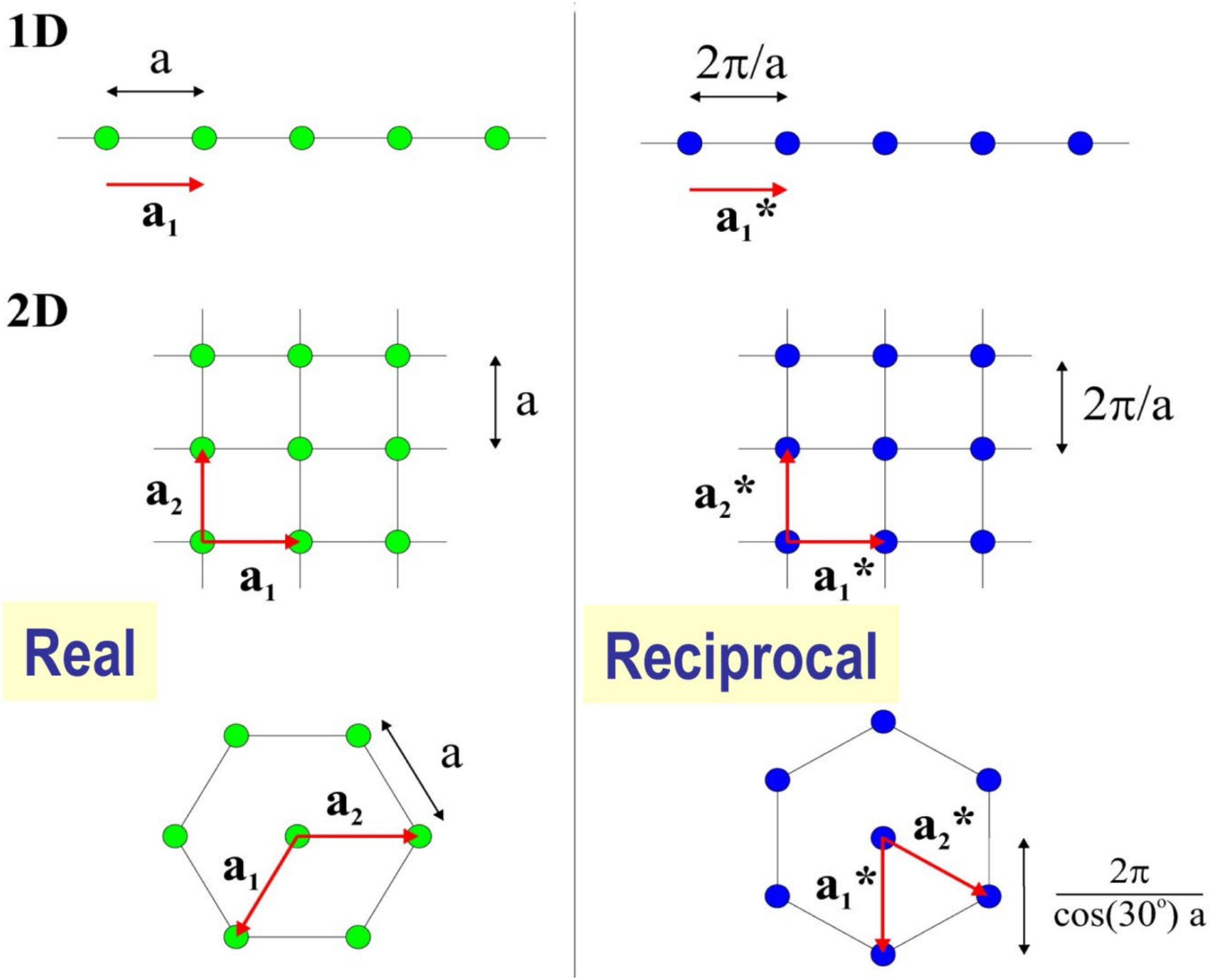
$$\therefore \frac{d\sigma}{d\Omega} = \frac{vdS|\psi_{scat}|^2}{vd\Omega} = \frac{dS}{d\Omega}\left|b_i e^{i\vec{k}'.\vec{r}}\sum\frac{1}{|\vec{r}-\vec{R}_i|}e^{i(\vec{k}_0-\vec{k}').\vec{R}_i}\right|^2$$

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{i(\vec{k}_0-\vec{k}').(\vec{R}_i-\vec{R}_j)} = \sum_{i,j} b_i b_j e^{-i\vec{Q}.(\vec{R}_i-\vec{R}_j)}$$

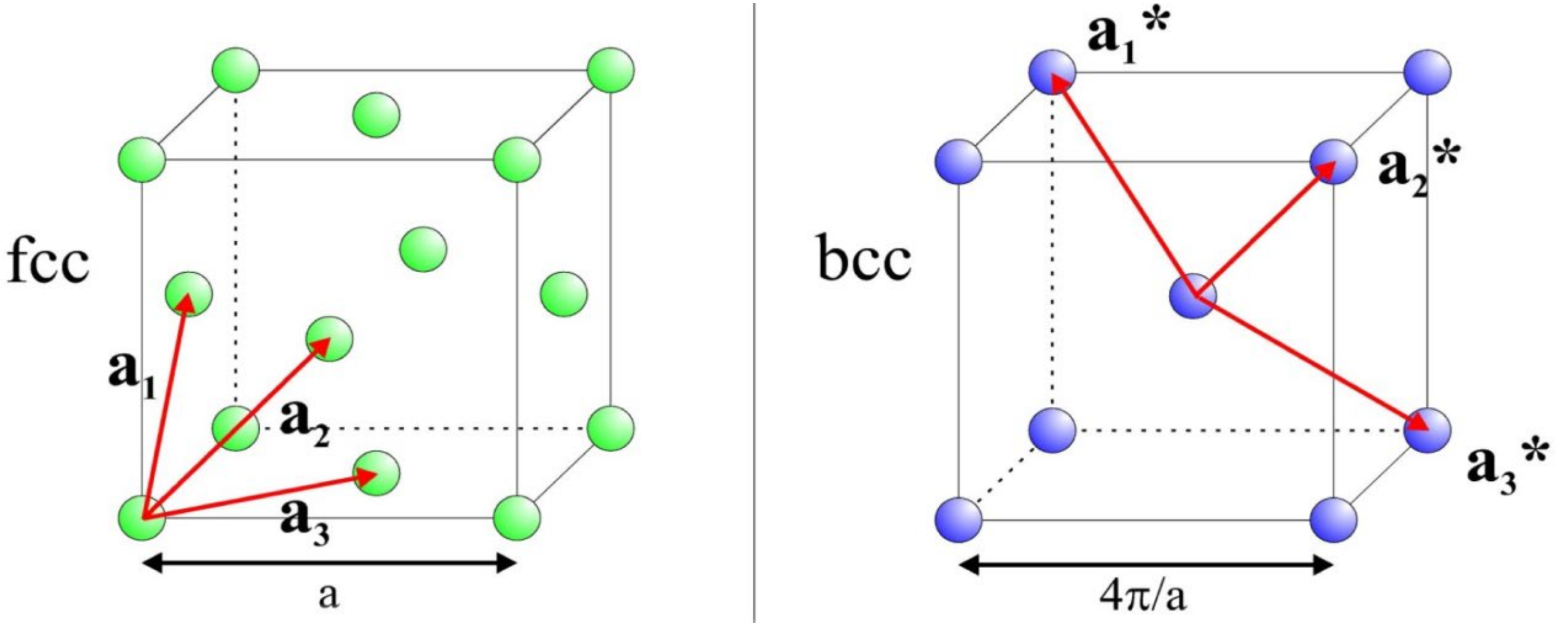
For x-rays: $\frac{d\sigma}{d\Omega} = r_0^2\sum_{i,j} e^{i(\vec{k}_0-\vec{k}').(\vec{R}_i-\vec{R}_j)}\left\{\frac{1-\cos^2 2\theta}{2}\right\}$



A crystal has translational symmetry



Relationship between real and reciprocal space in crystals



Reciprocal Lattice:

$$V_c = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

$$\vec{a}_1^* = \frac{2\pi}{V_c} \vec{a}_2 \times \vec{a}_3$$

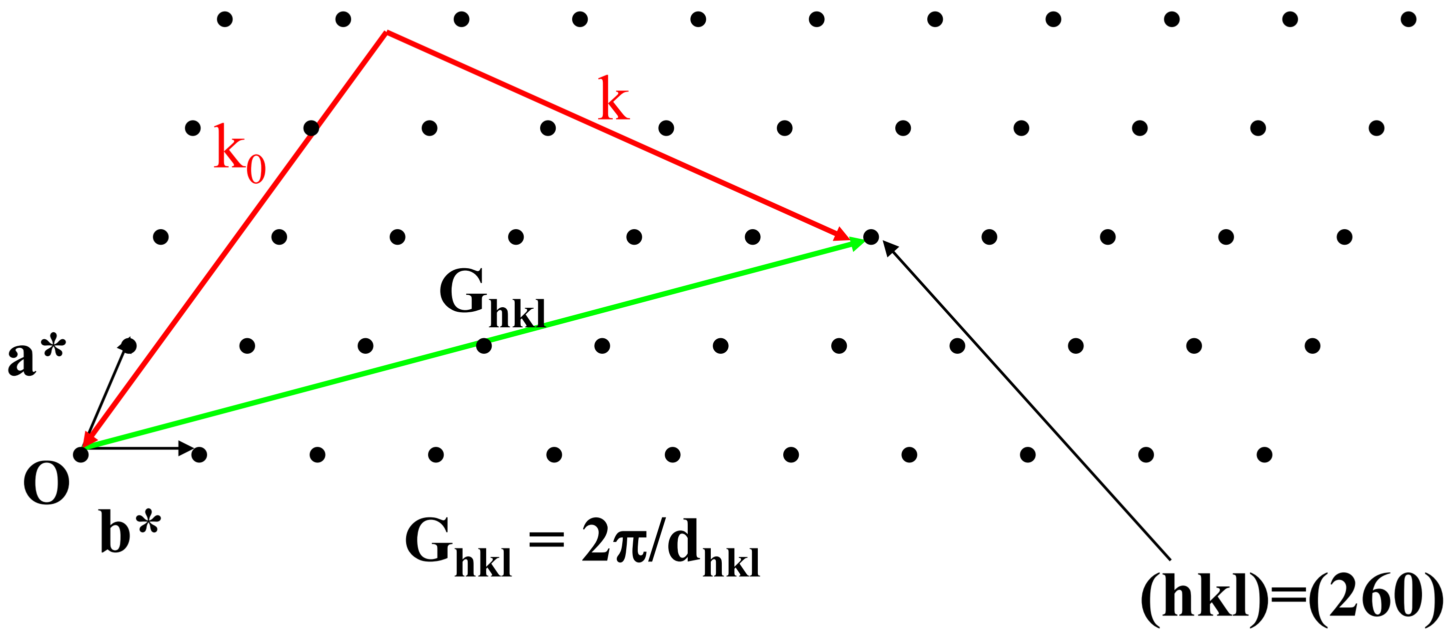
$$\vec{a}_2^* = \frac{2\pi}{V_c} \vec{a}_3 \times \vec{a}_1$$

$$\vec{a}_3^* = \frac{2\pi}{V_c} \vec{a}_1 \times \vec{a}_2$$

Diffraction and Bragg's law

G_{hkl} is called a reciprocal lattice vector (node denoted hkl)

h, k and l are called Miller indices



- (hkl) describes a set of planes perpendicular to G_{hkl}, separated by d_{hkl}

$$\vec{G}_{hkl} = \vec{Q}$$

- {hkl} represents a set of symmetry-related lattice planes

$$\frac{2\pi n}{d_{hkl}} = \frac{4\pi \sin\theta}{\lambda}$$

- [hkl] describes a crystallographic direction

$$n\lambda = 2d_{hkl}\sin\theta$$

- <hkl> describes a set of symmetry equivalent crystallographic directions

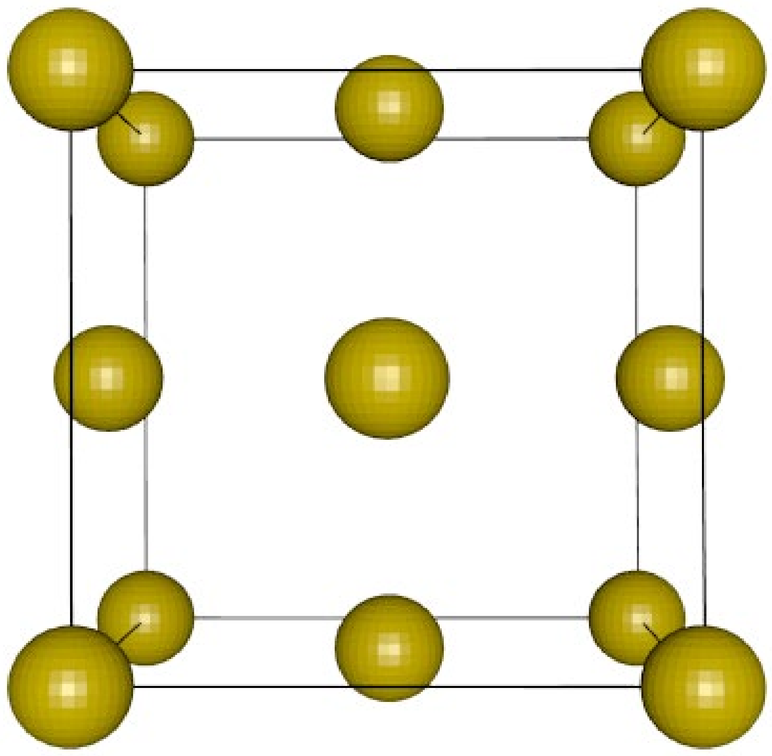
Example: diffraction from a crystal – the fcc lattice

- A monochromatic (single λ) neutron beam is diffracted by a single crystal only if specific geometrical conditions are fulfilled

- Useful λ are typically between 0.4 Å and 2.5 Å.

- These conditions can be expressed in several ways:
  - Laue's conditions: with h, k, and l as integers
  - Bragg's Law:
  - Ewald's construction

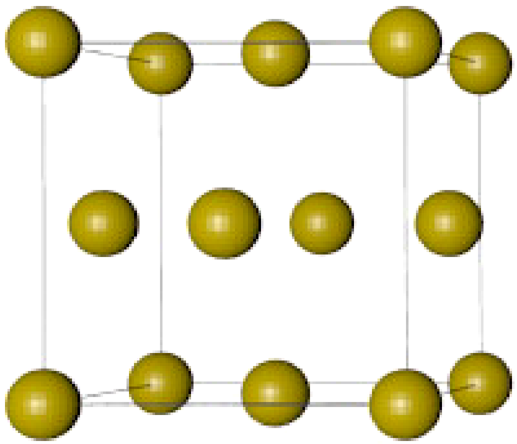
- Diffraction tells us about:
  - The dimensions of the unit cell
  - The symmetry of the crystal
  - The positions of atoms within the unit cell
  - The extent of thermal vibrations of atoms in various directions



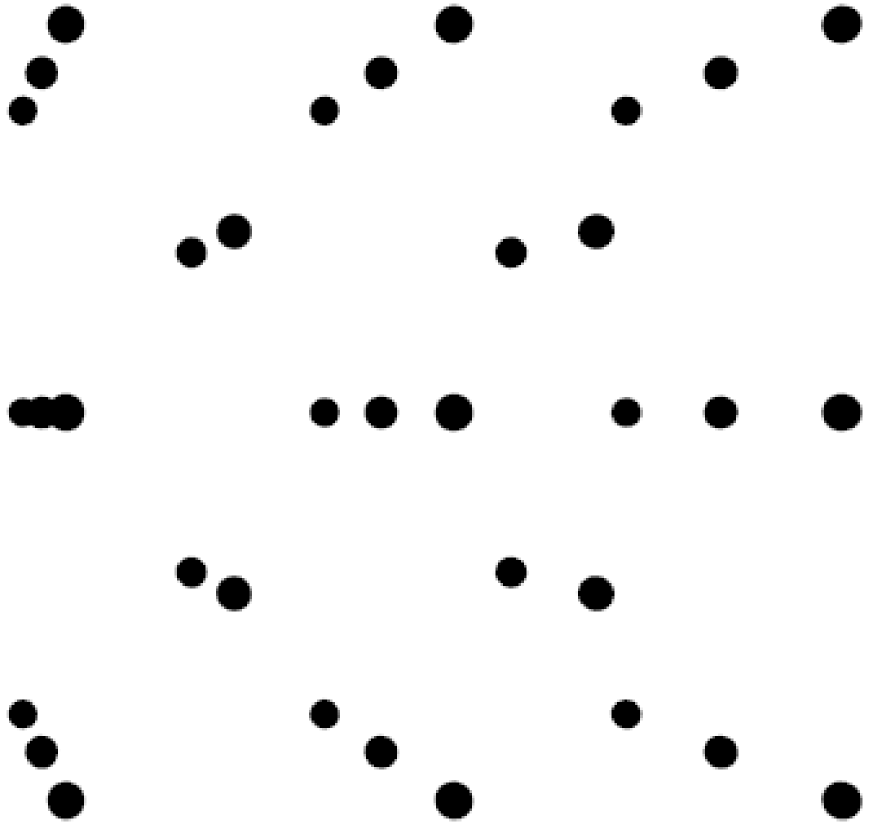
Lattice in real space

Relationship between real and reciprocal space

Real Space

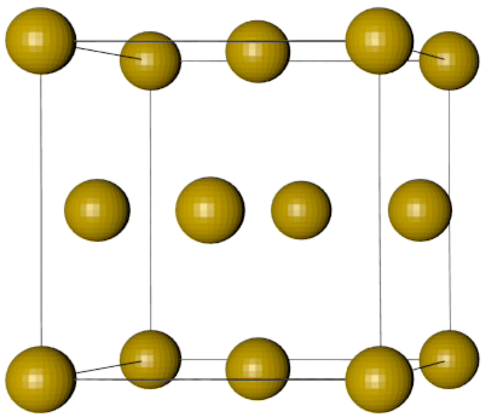


Reciprocal Space

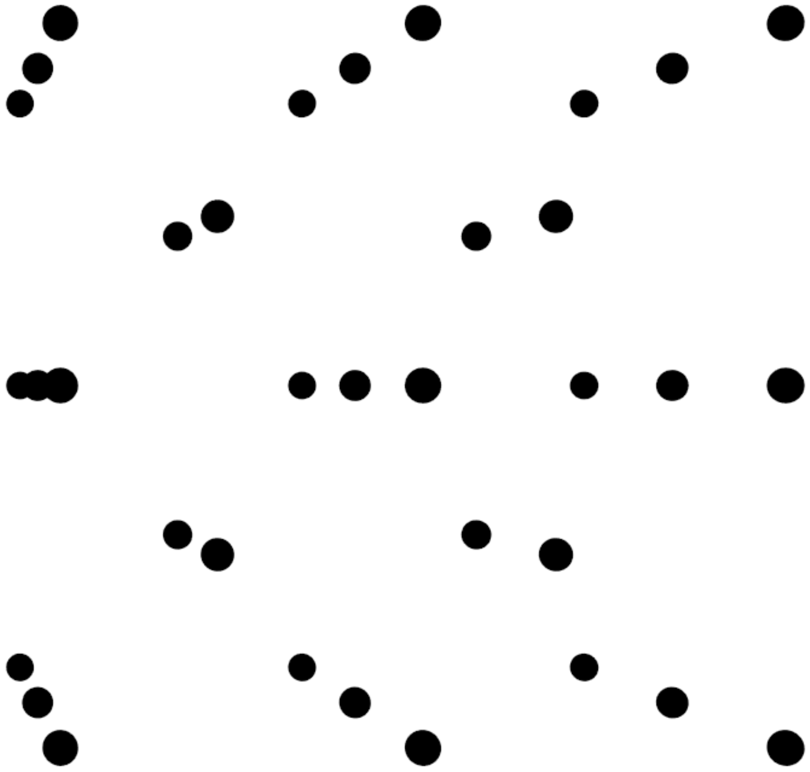


Beam of neutrons or x-rays scattered from planes

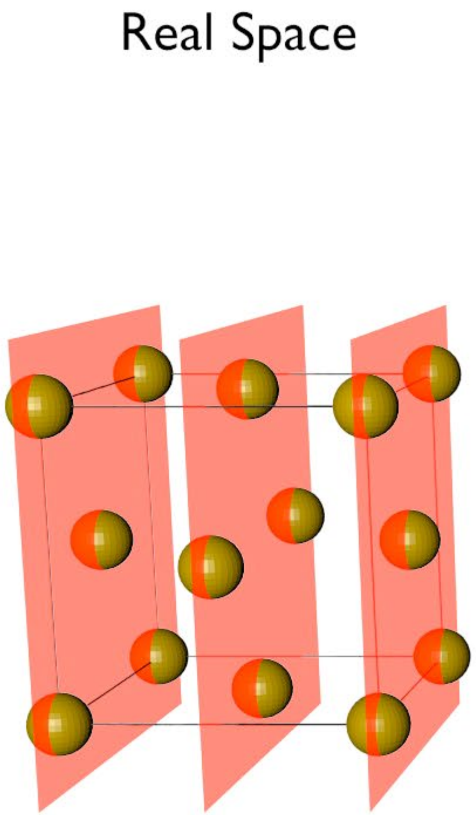
Real Space

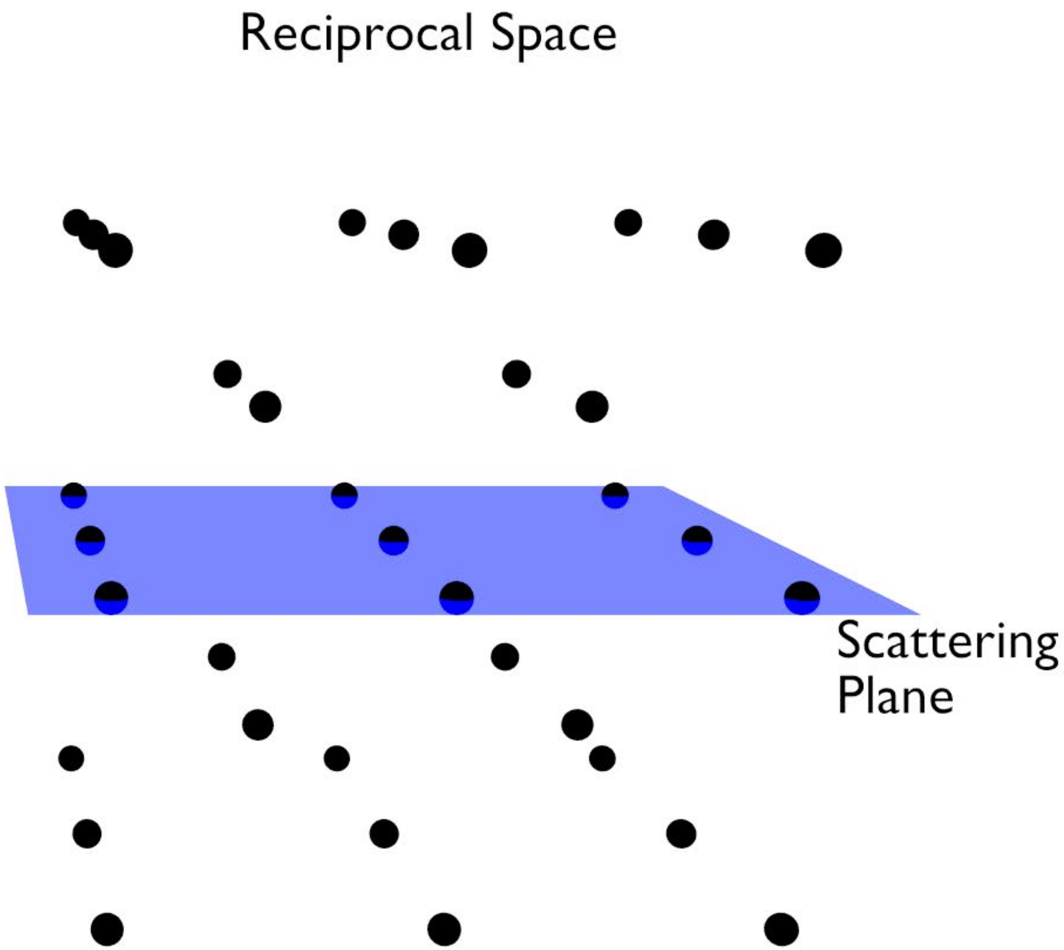


Reciprocal Space

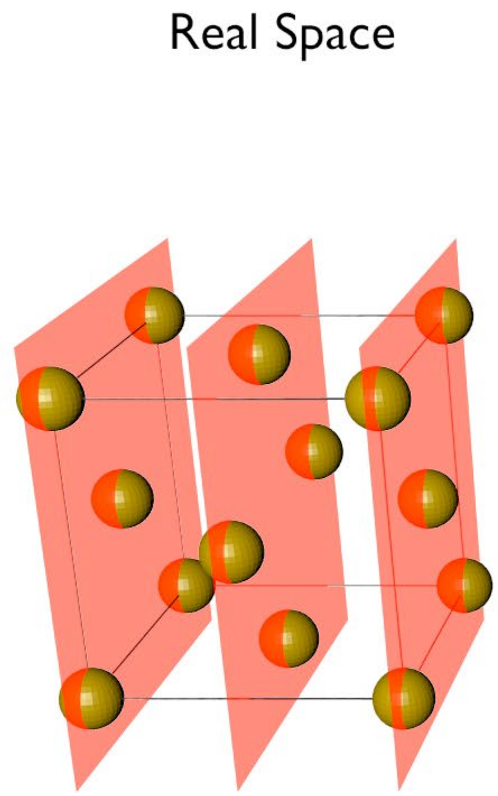


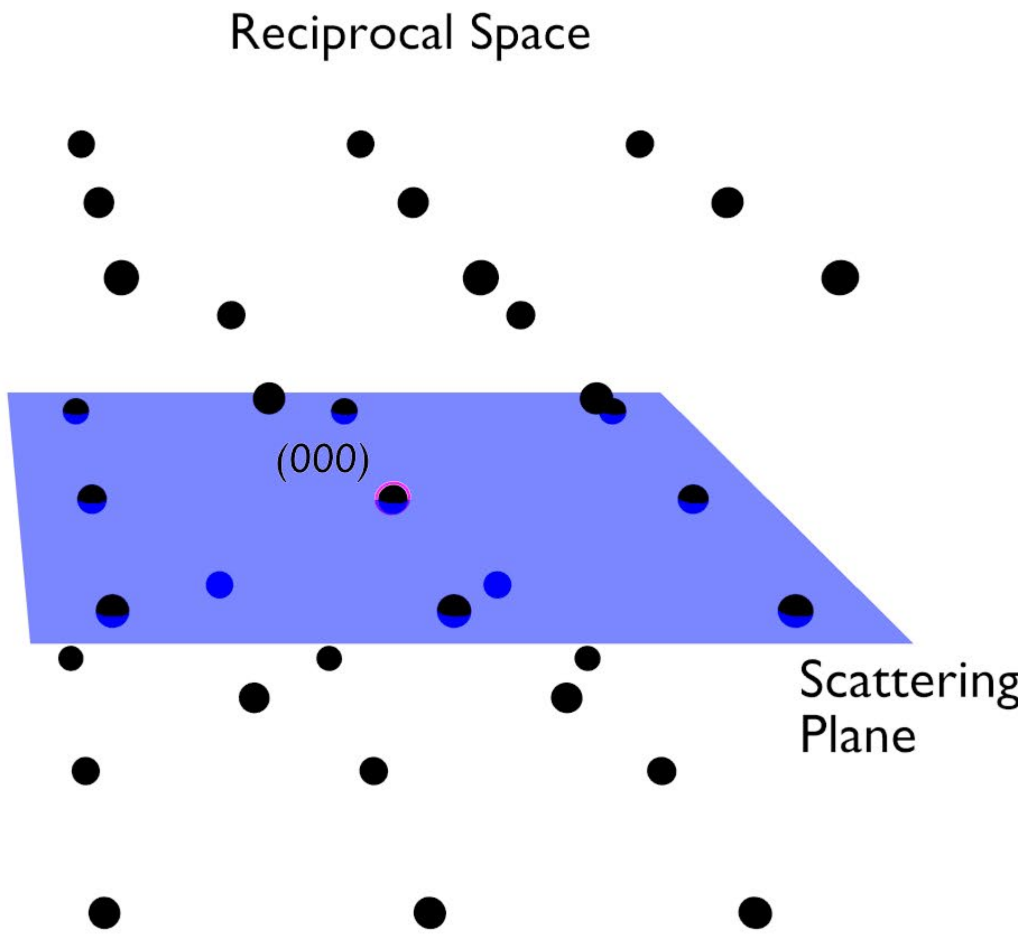
Bragg reflections from crystallographic planes





Centering operations lead to systematic absences

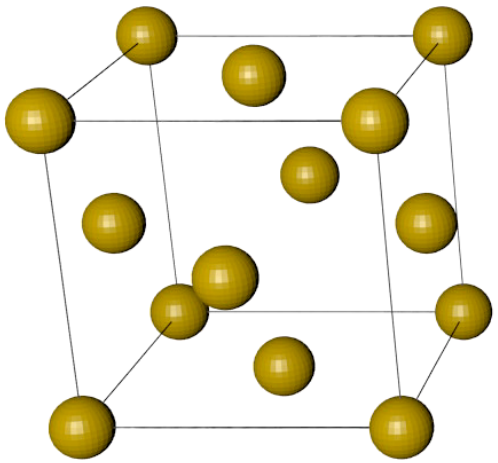




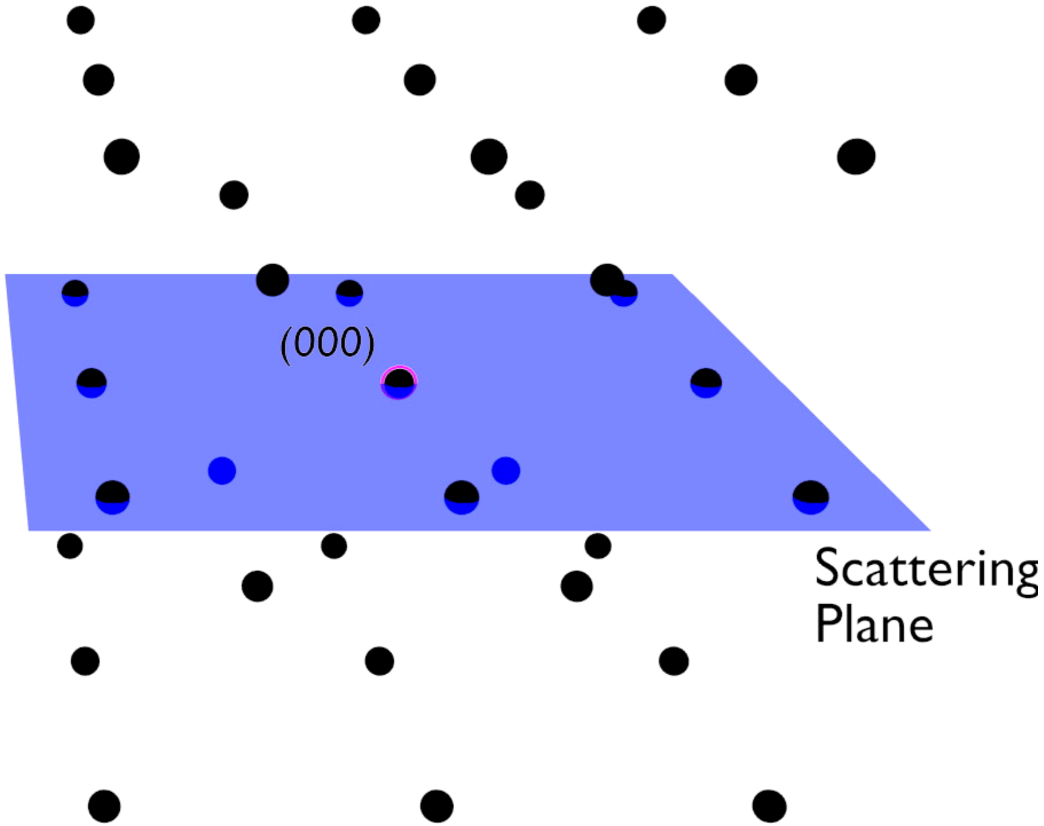
{001} family of planes are systematically absent

Other allowed reflections in fcc lattice

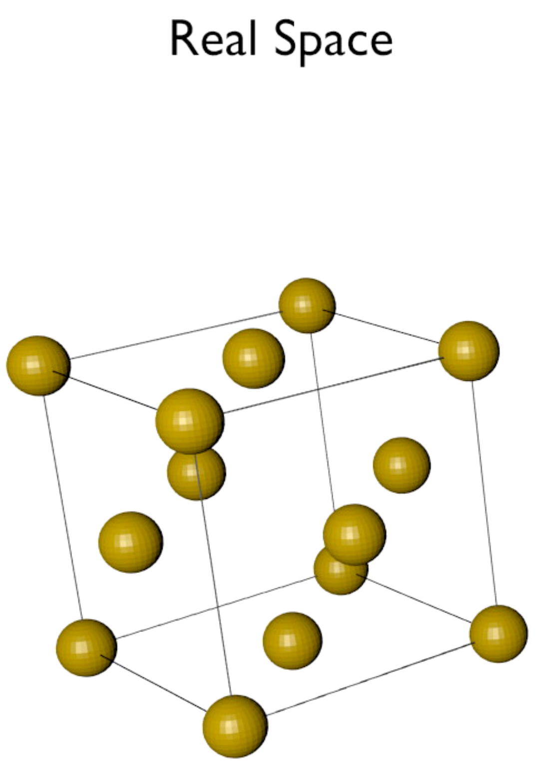
Real Space

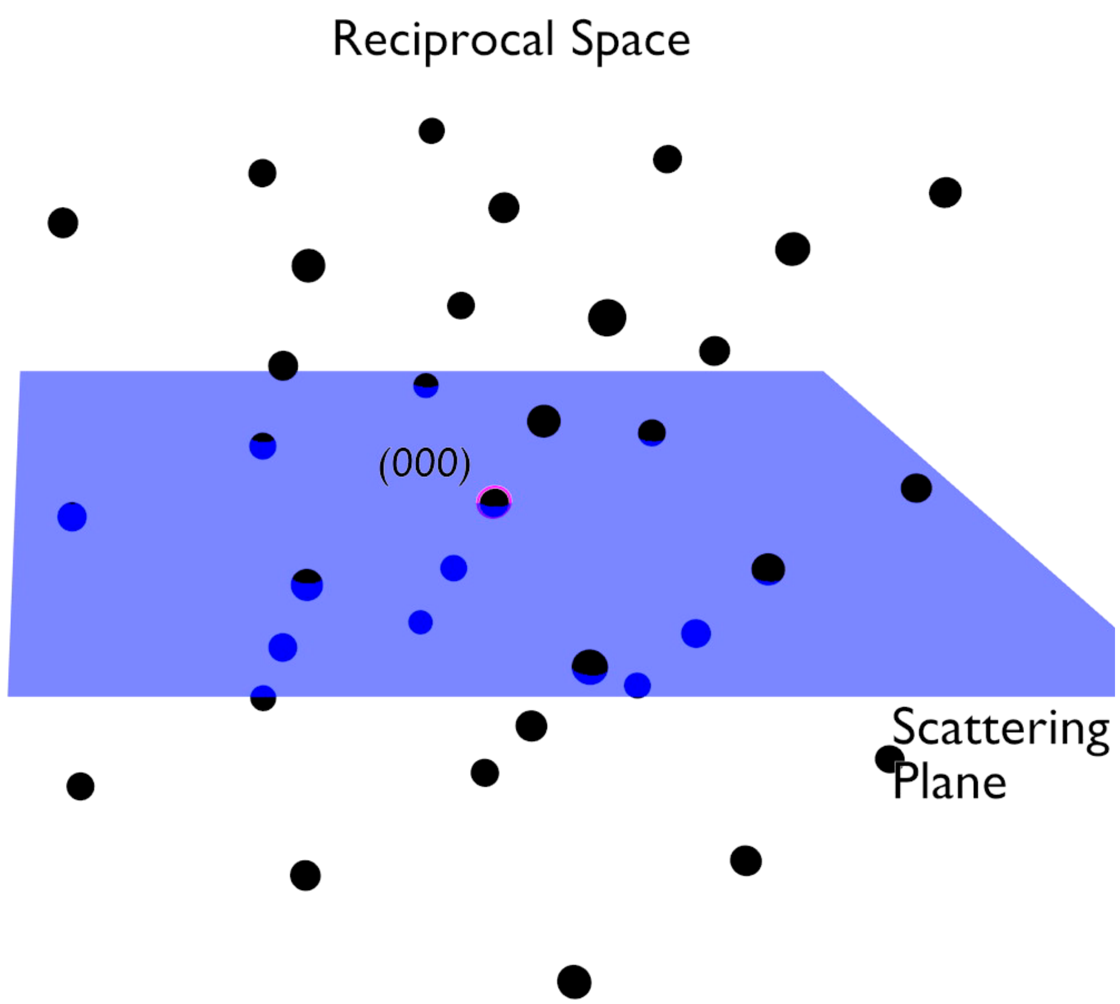


Reciprocal Space

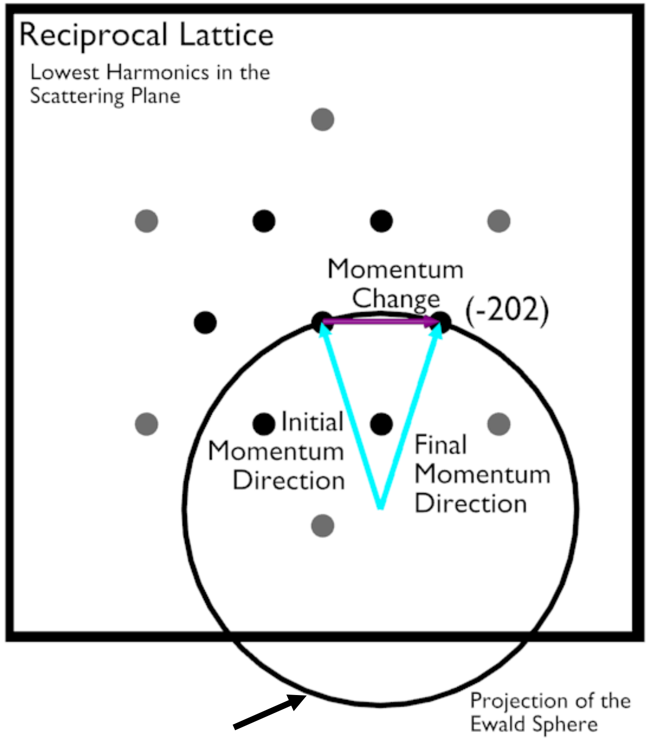


[111] view of the (220) reflection



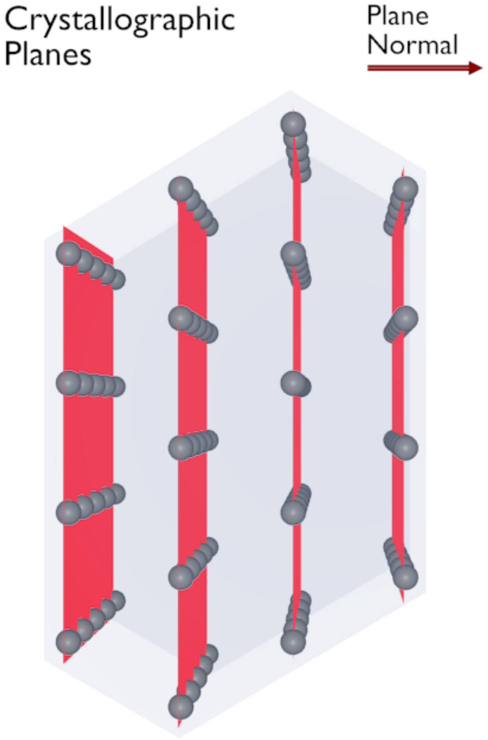


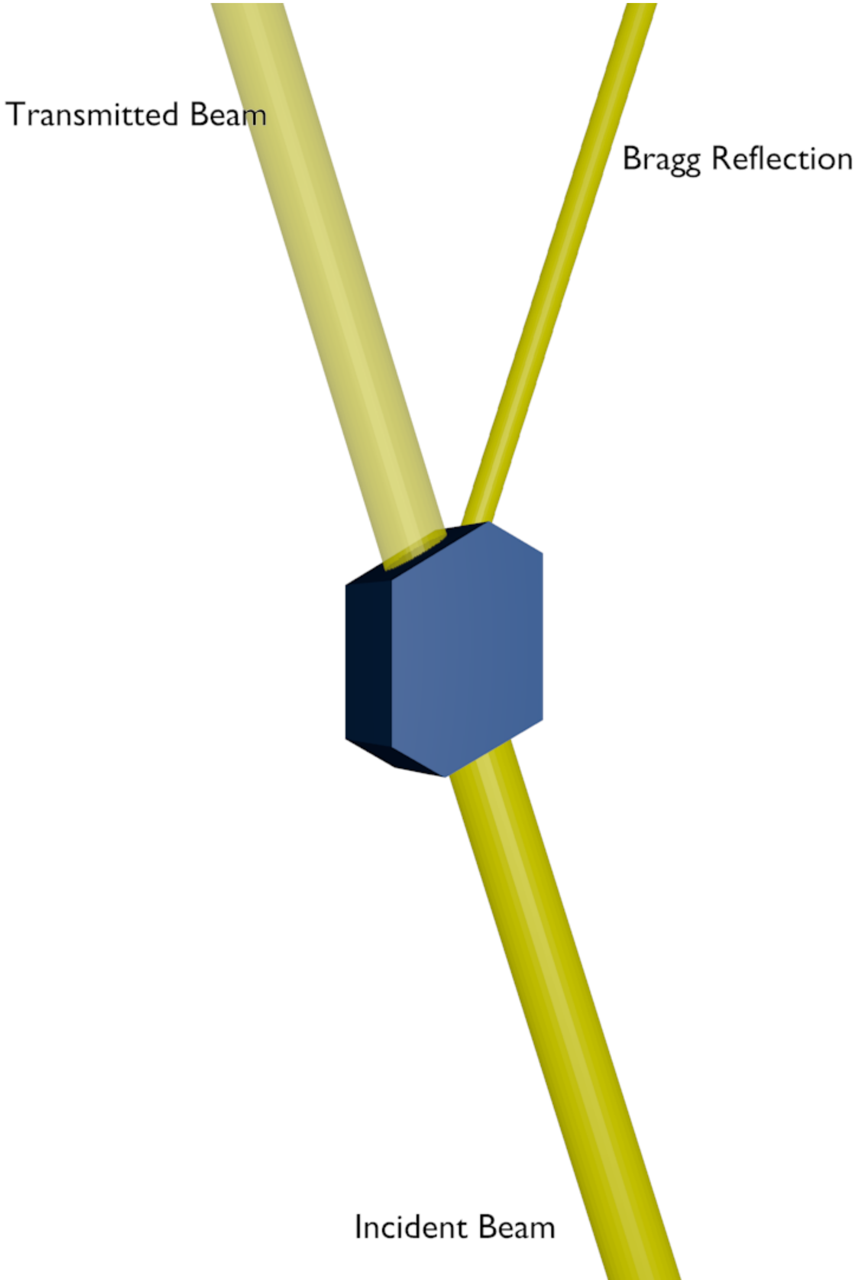
The Ewald sphere and scattering triangle

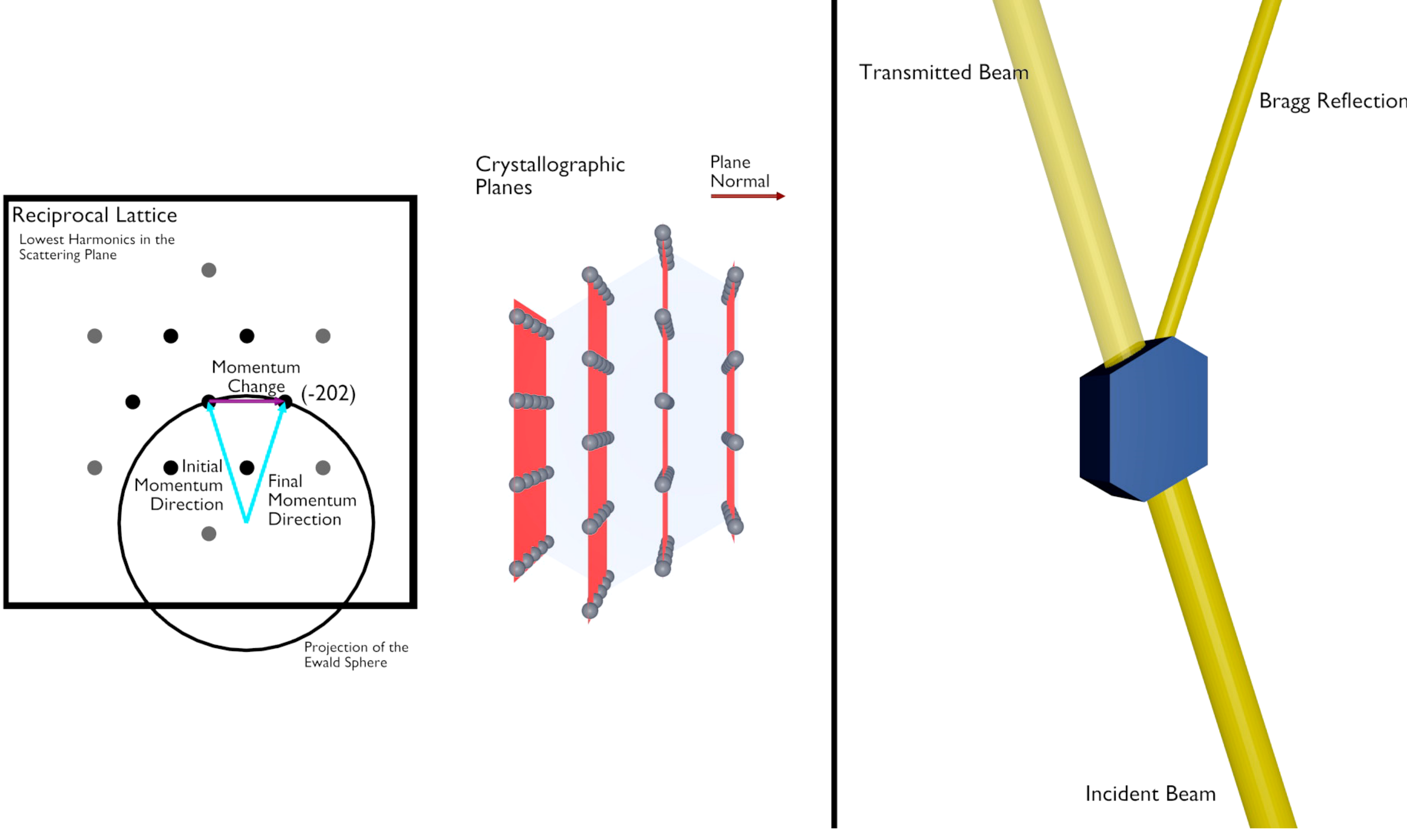


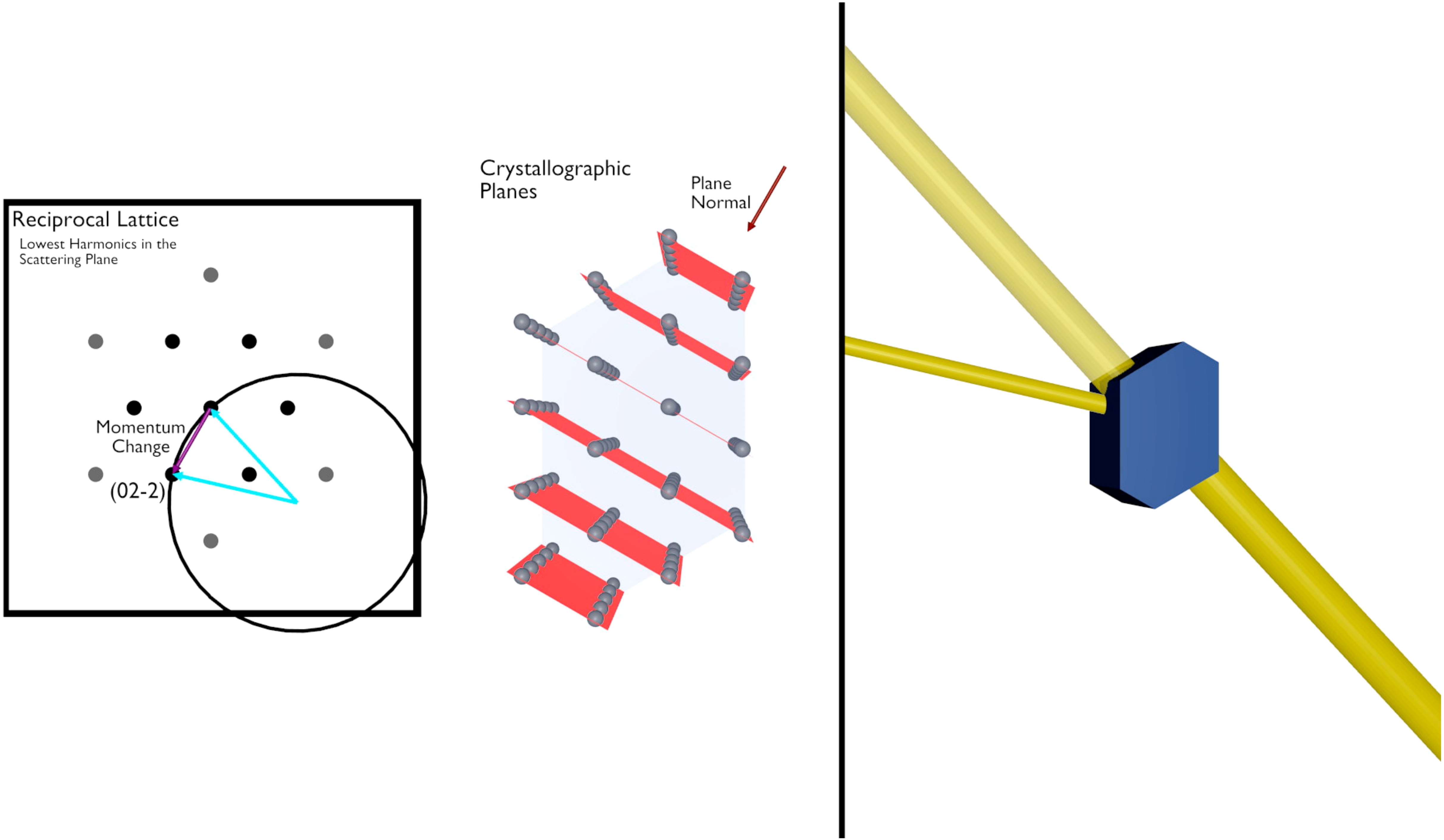
The Ewald Sphere

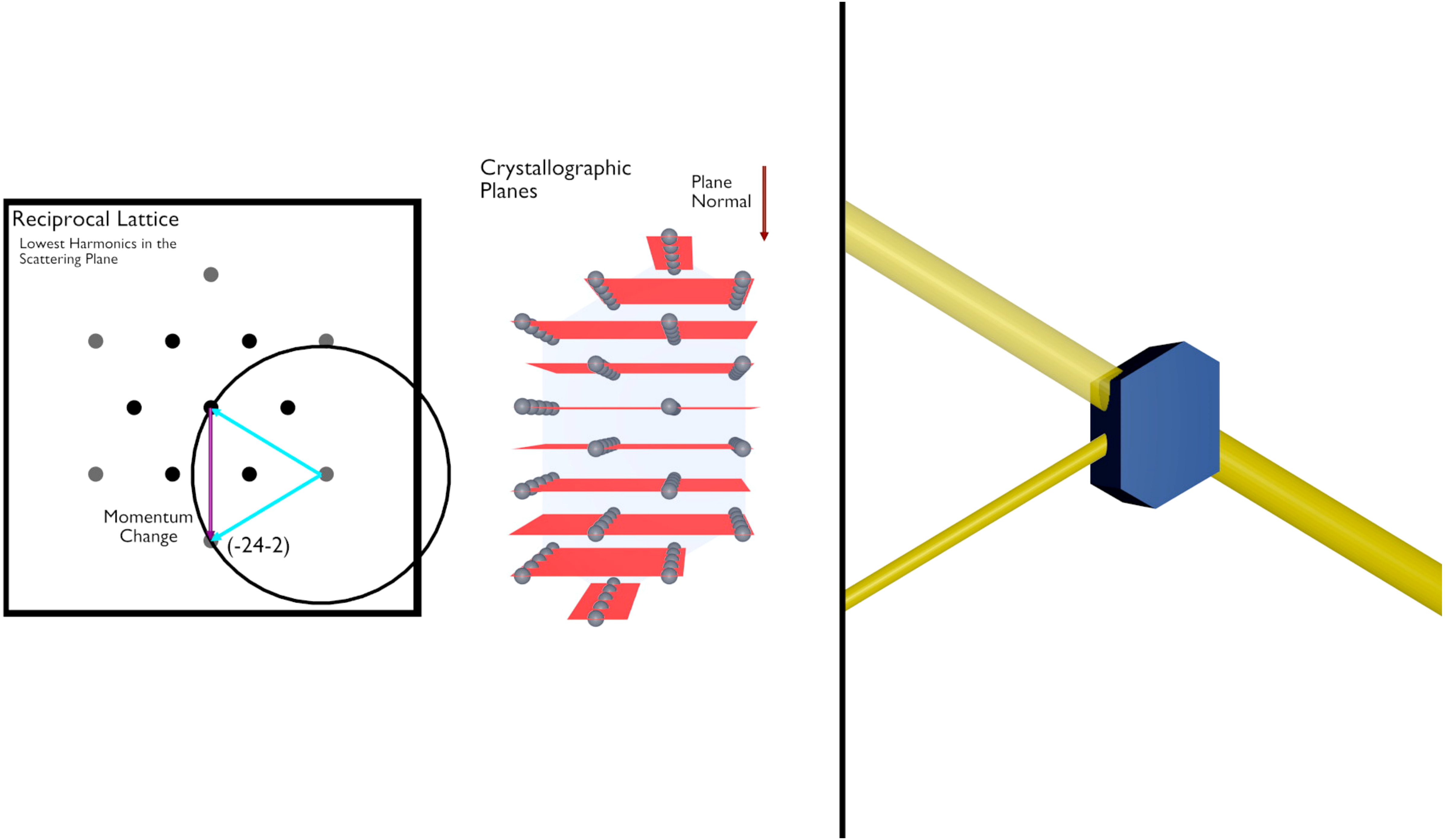
Radius is $2\pi/\lambda$

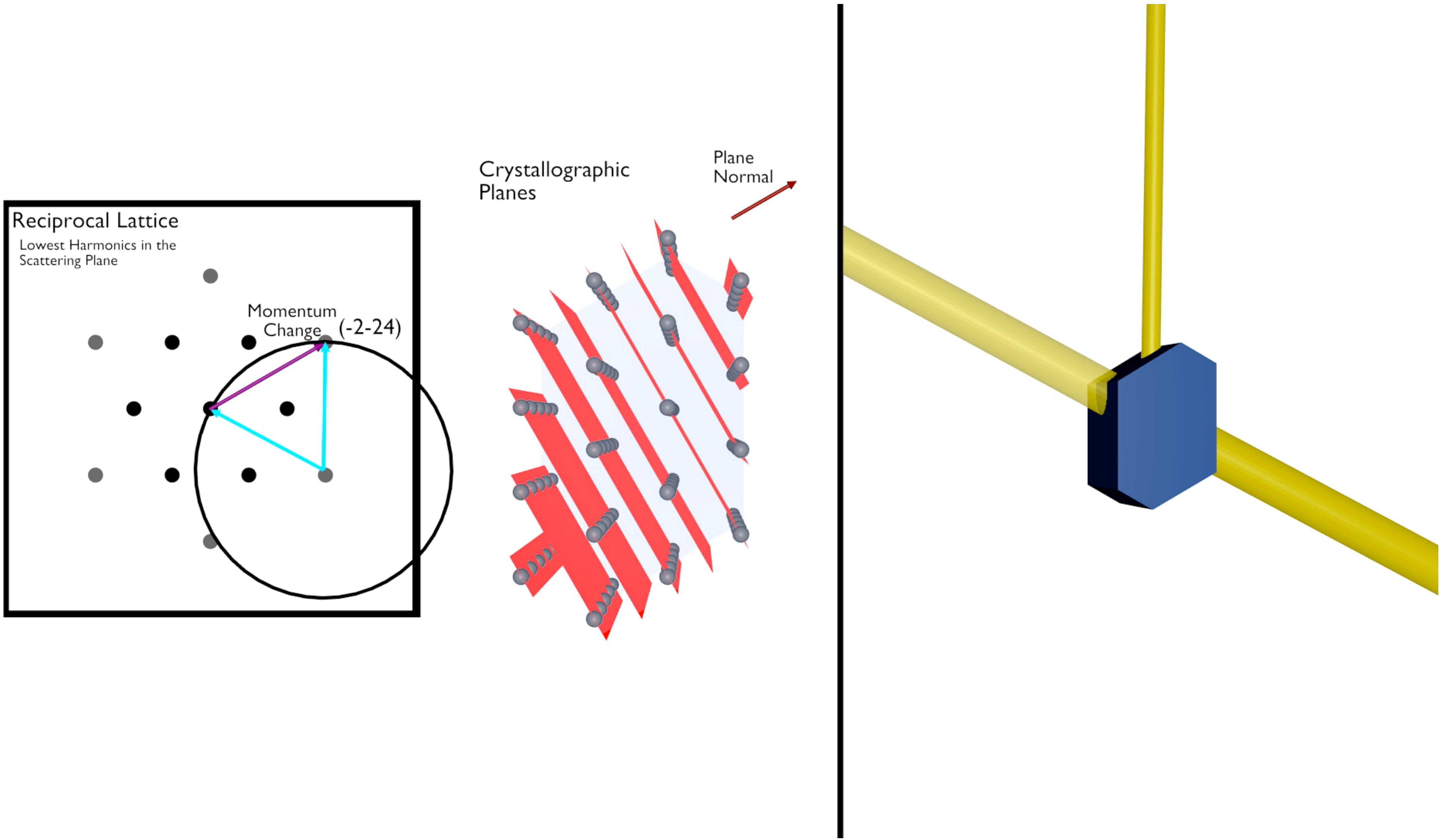


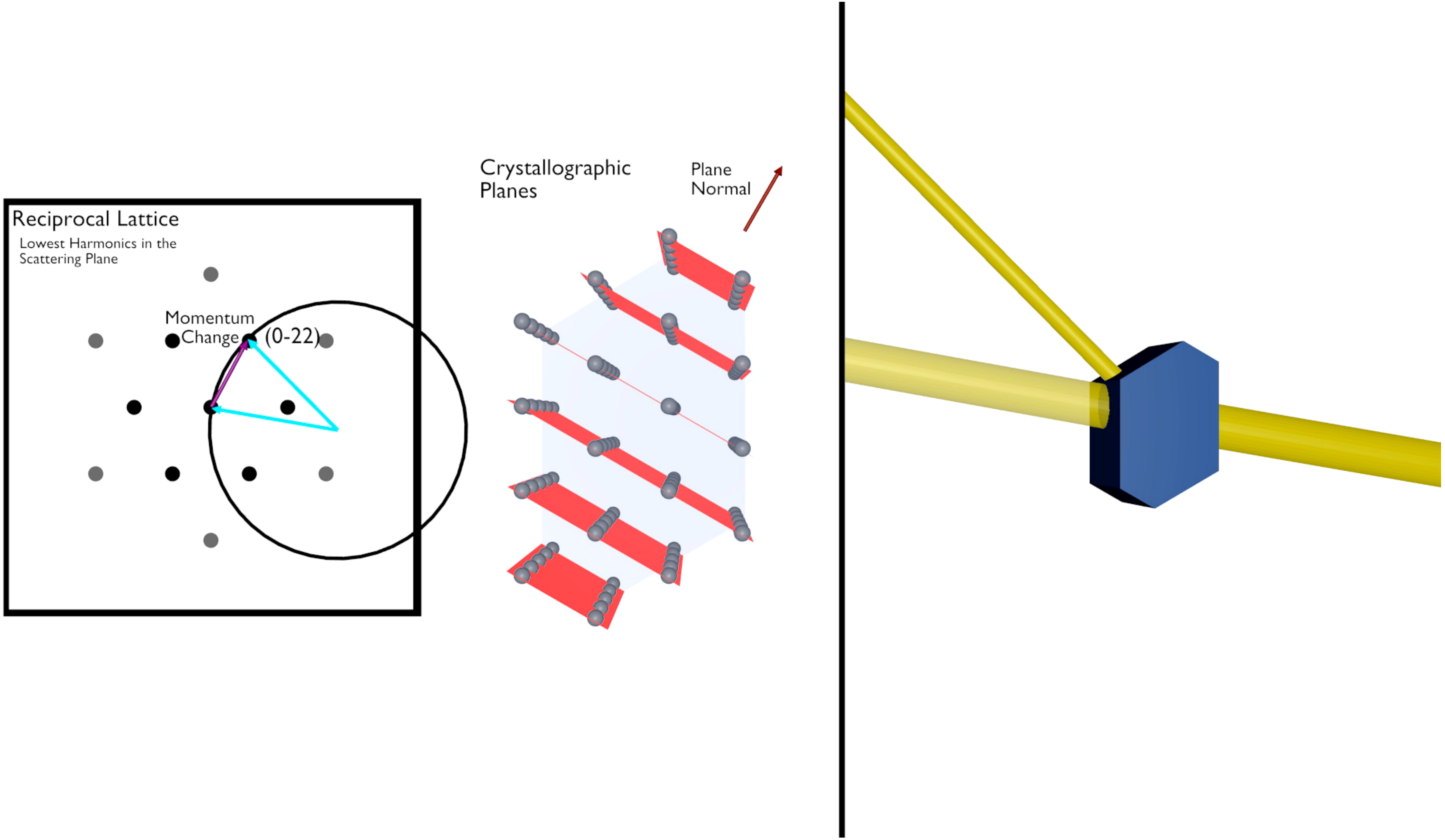



Reciprocal Lattice
Lowest Harmonics in the Scattering Plane
Momentum Change
(-202)
Initial Momentum Direction
Final Momentum Direction
Projection of the Ewald Sphere
Crystallographic Planes
Plane Normal
Transmitted Beam
Bragg Reflection
Incident Beam


Reciprocal Lattice
Lowest Harmonics in the Scattering Plane
Momentum Change
(02-2)
Crystallographic Planes
Plane Normal


Reciprocal Lattice
Lowest Harmonics in the Scattering Plane
Momentum Change
(-24-2)
Crystallographic Planes
Plane Normal


Reciprocal Lattice
Lowest Harmonics in the Scattering Plane
Momentum Change
(-2-24)
Crystallographic Planes
Plane Normal


Reciprocal Lattice
Lowest Harmonics in the
Scattering Plane
Momentum
Change
(0-22)
Crystallographic
Planes
Plane
Normal

Summary

For x-ray and neutron scattering, we are dealing with the scattering of plane waves by atoms and nuclei.

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-\mathrm{i}kx} \mathrm{d}x$$

neutrons

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{-\boldsymbol{Q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)}$$

x-rays

$$\frac{d\sigma}{d\Omega} = r_0^2 \sum_{i,j} |f(Q)|^2 e^{-\boldsymbol{Q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} P(2\theta)$$

$$|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

When $\mathbf{G_{hkl}}$ = ***Q*****,** Bragg's Law

$$n\lambda = 2dhkl \sin\theta$$

Questions?