The Structure Factor: Elastic, Inelastic, and Magnetic

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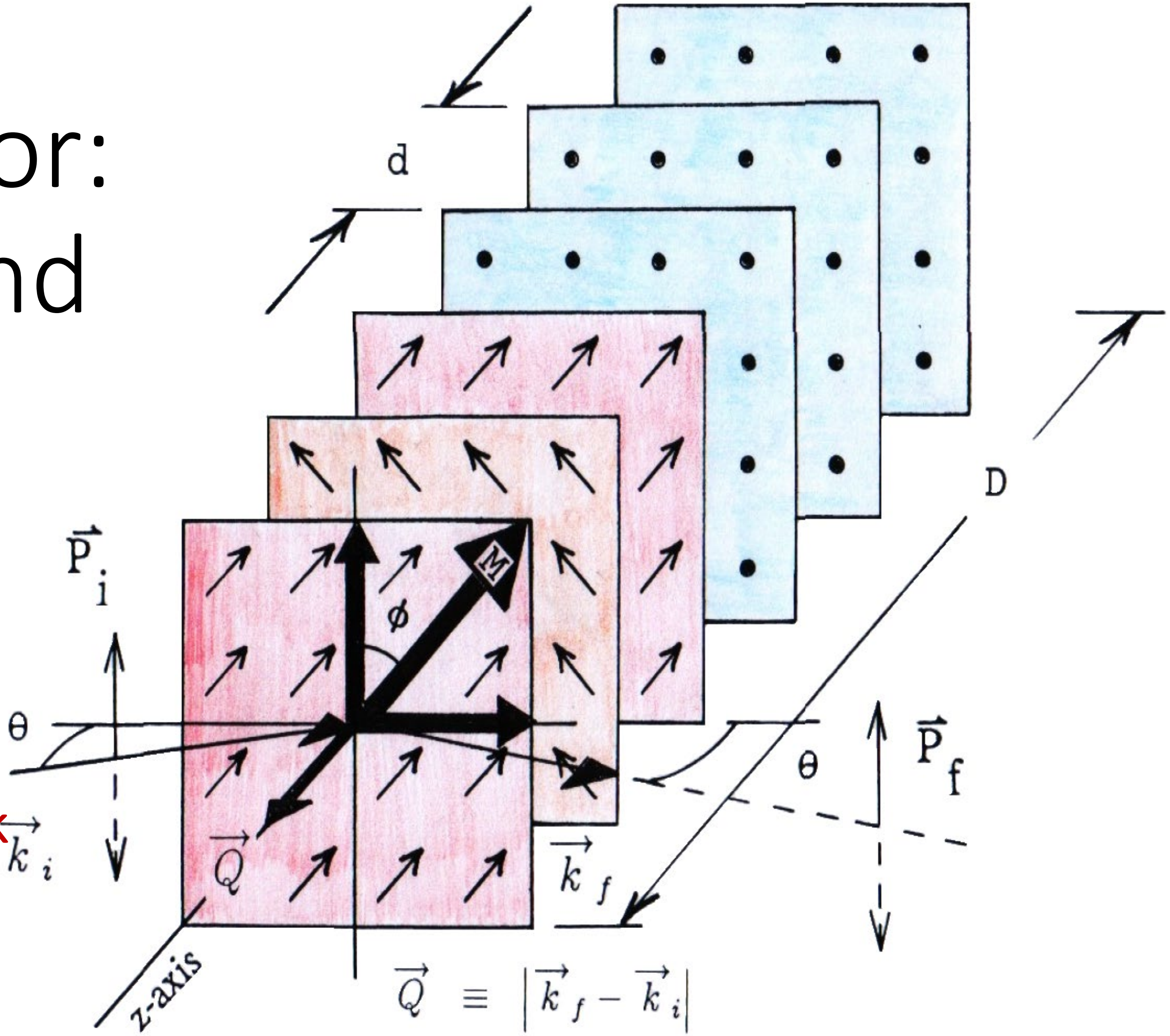
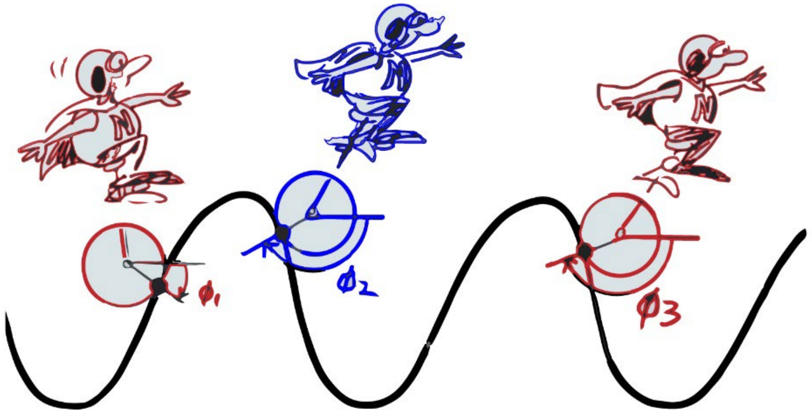


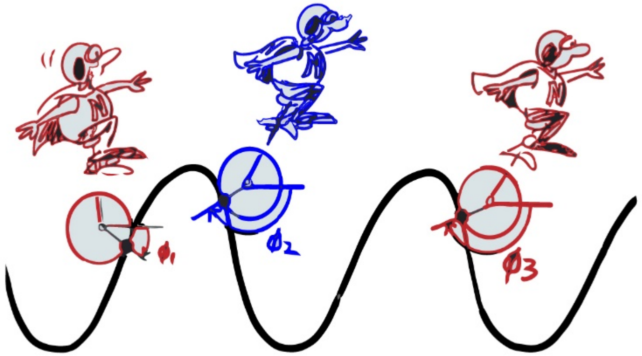
Outline

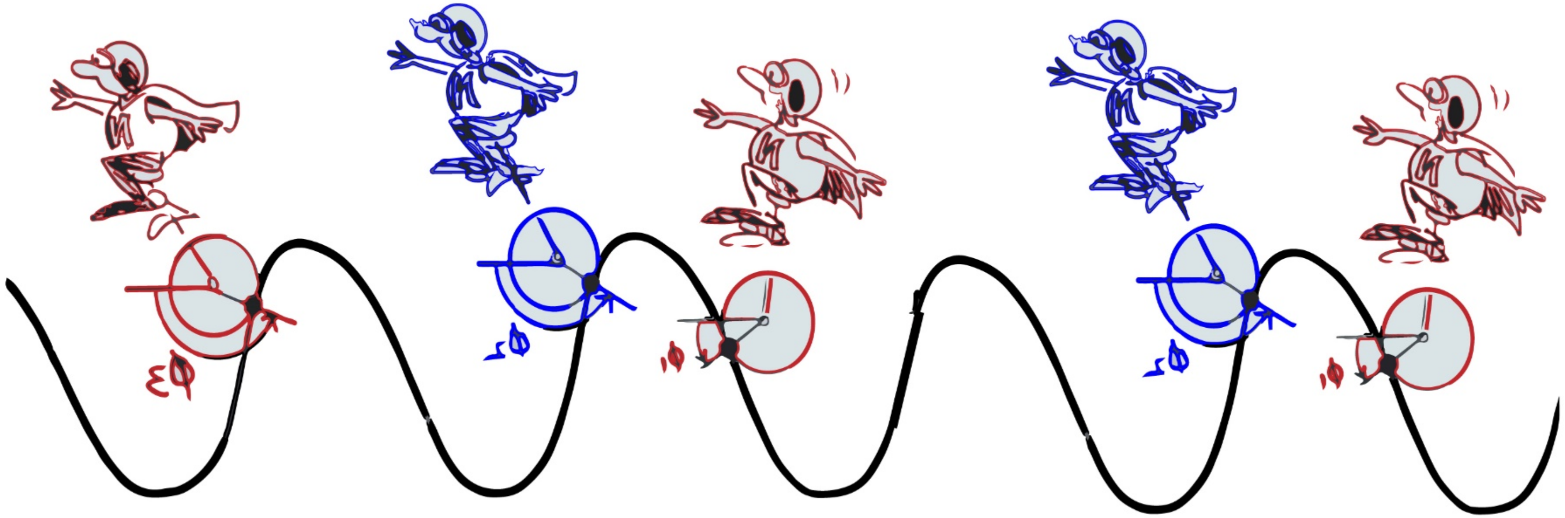
1. The elastic structure factor $S(Q)$ for neutrons and x-rays



2. Dynamics for the structure factor or $S(Q,\omega)$

3. Magnetic scattering from neutrons



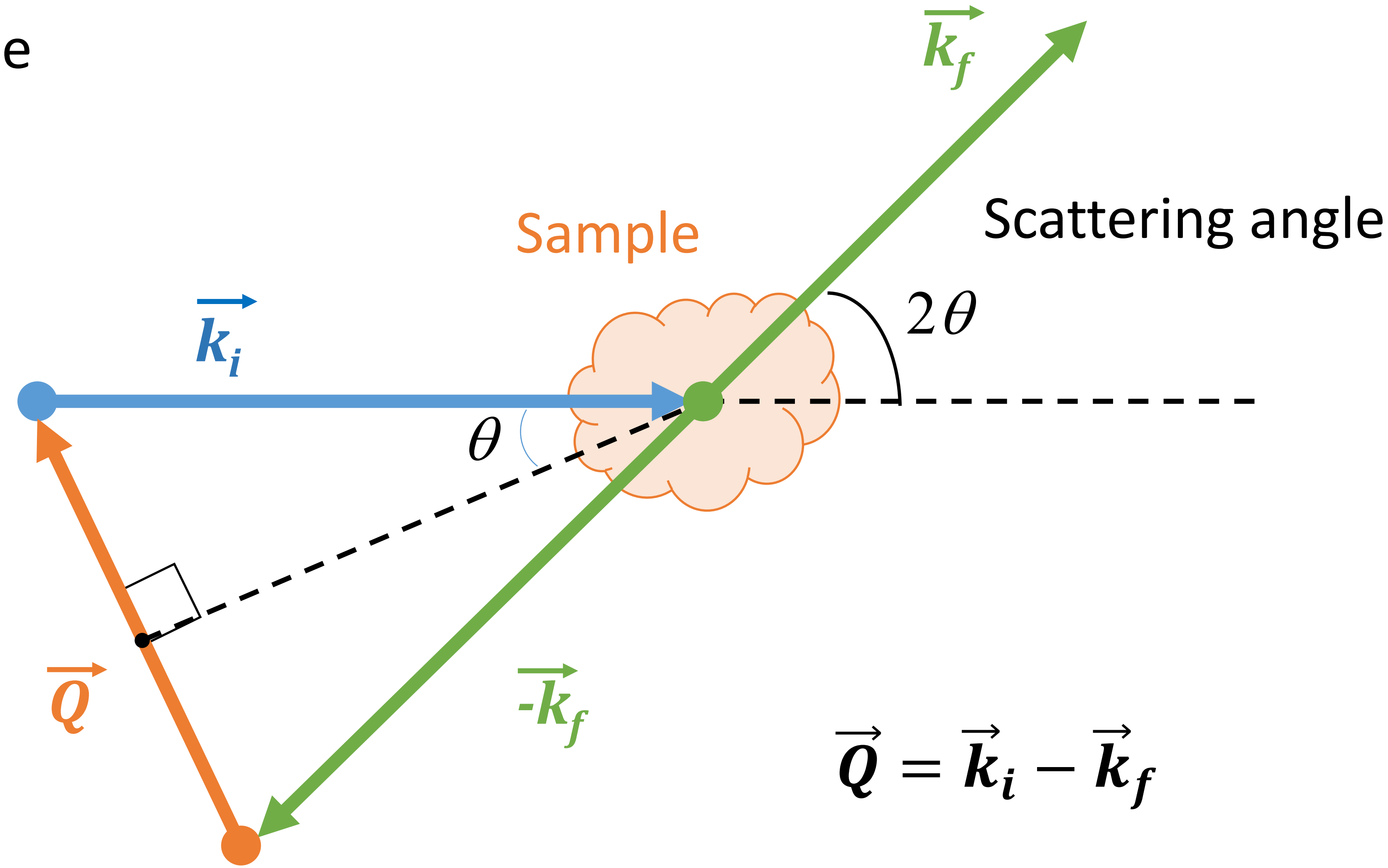


The Structure Factor $S(Q)$

Elastic scattering

The scattering triangle

- $\boldsymbol{k_i}$ is the incident wavevector and $\boldsymbol{k_f}$ is the scattered wavevector
- Sometimes those are also written as $\boldsymbol{k_0}$ or $\boldsymbol{k'}$
- We define $\boldsymbol{Q}$ as our **momentum transfer**



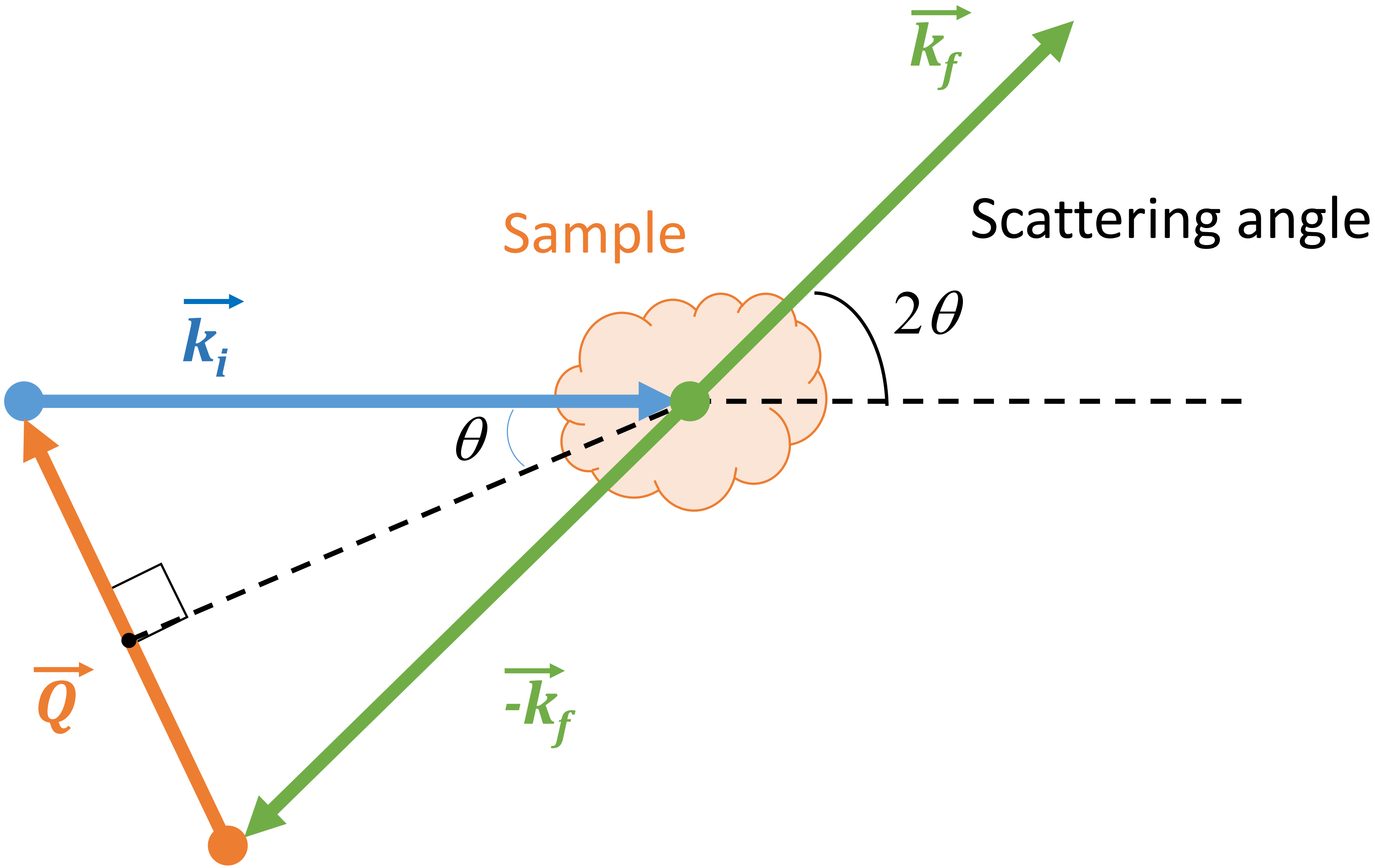
$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

Momentum transfer, or Q-space

For elastic scattering,
no energy transfer

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

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



And the differential cross section for elastic scattering

neutrons

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

- b_i is the neutron scattering length of atom i at position R_i
- Q is the momentum transfer

x-rays

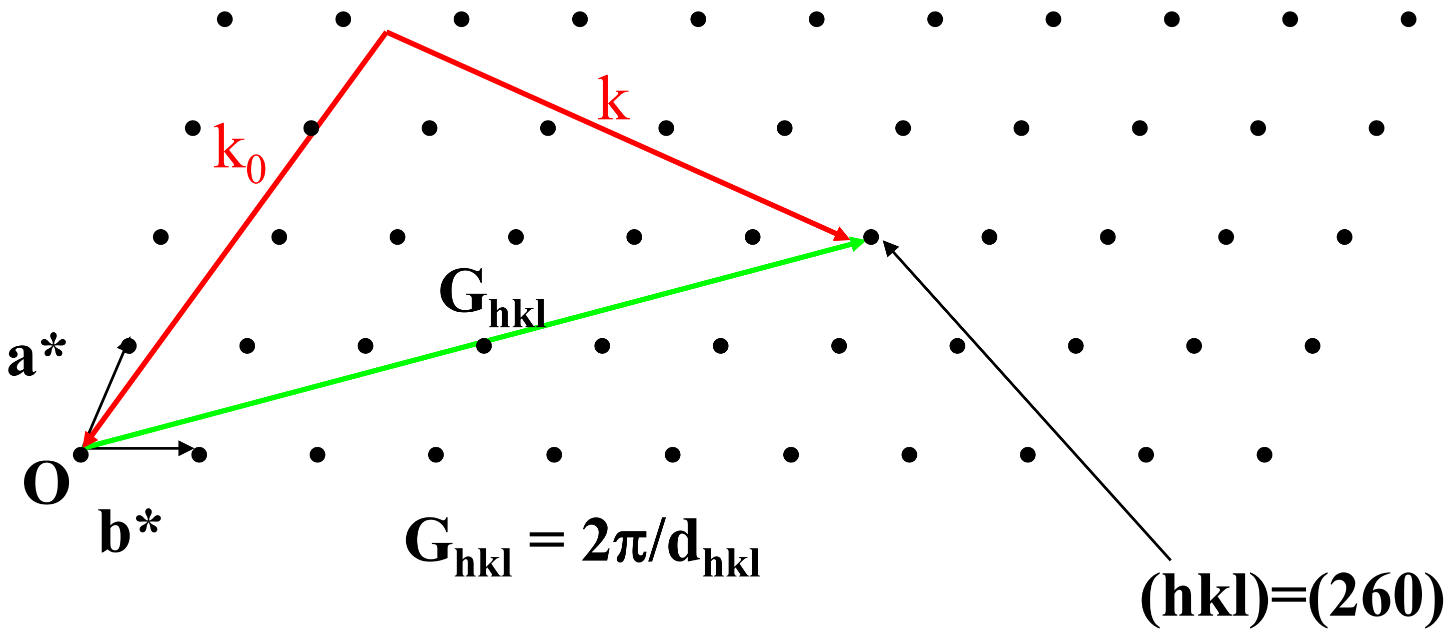
$$\frac{d\sigma}{d\Omega} = r_0^2 \sum_{i,j} |f(Q)|^2 e^{-\mathbf{Q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} P(2\theta)$$

- r_0 is the Thomson x-ray scattering length
- $f(Q)$ is the atomic form factor
- $P(2\theta)$ is the polarization factor

Diffraction and Bragg's law

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

h, k and l are called Miller indices



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

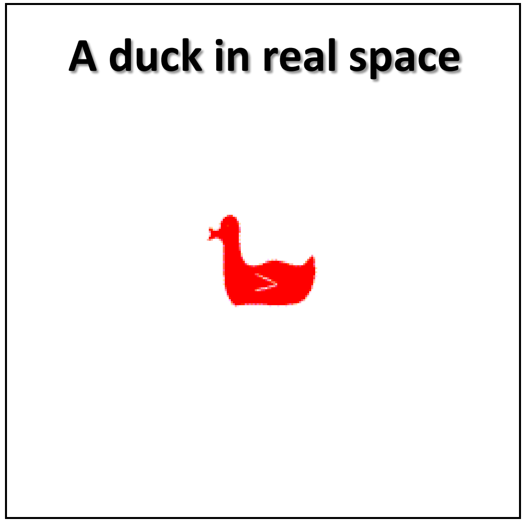
$$\frac{2\pi n}{d_{hkl}} = \frac{4\pi \sin\theta}{\lambda}$$

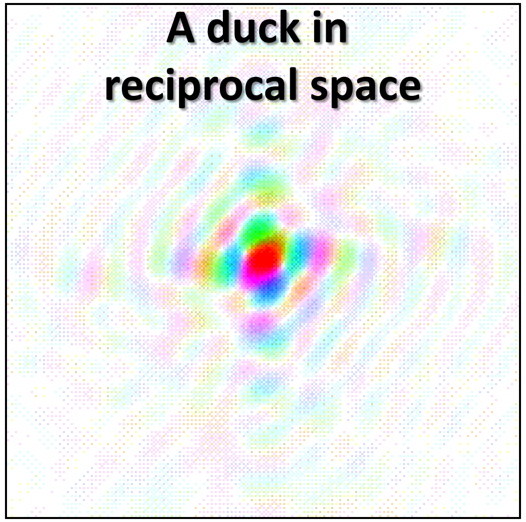
$$n\lambda = 2d_{hkl}\sin\theta$$

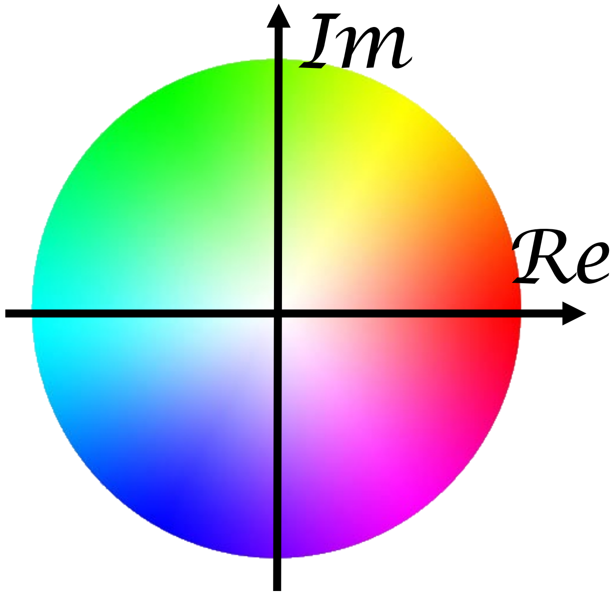
Previously we learned of the Fourier transform

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

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







Argand diagram for real and imaginary components

Credit: David Cowtan, University of York

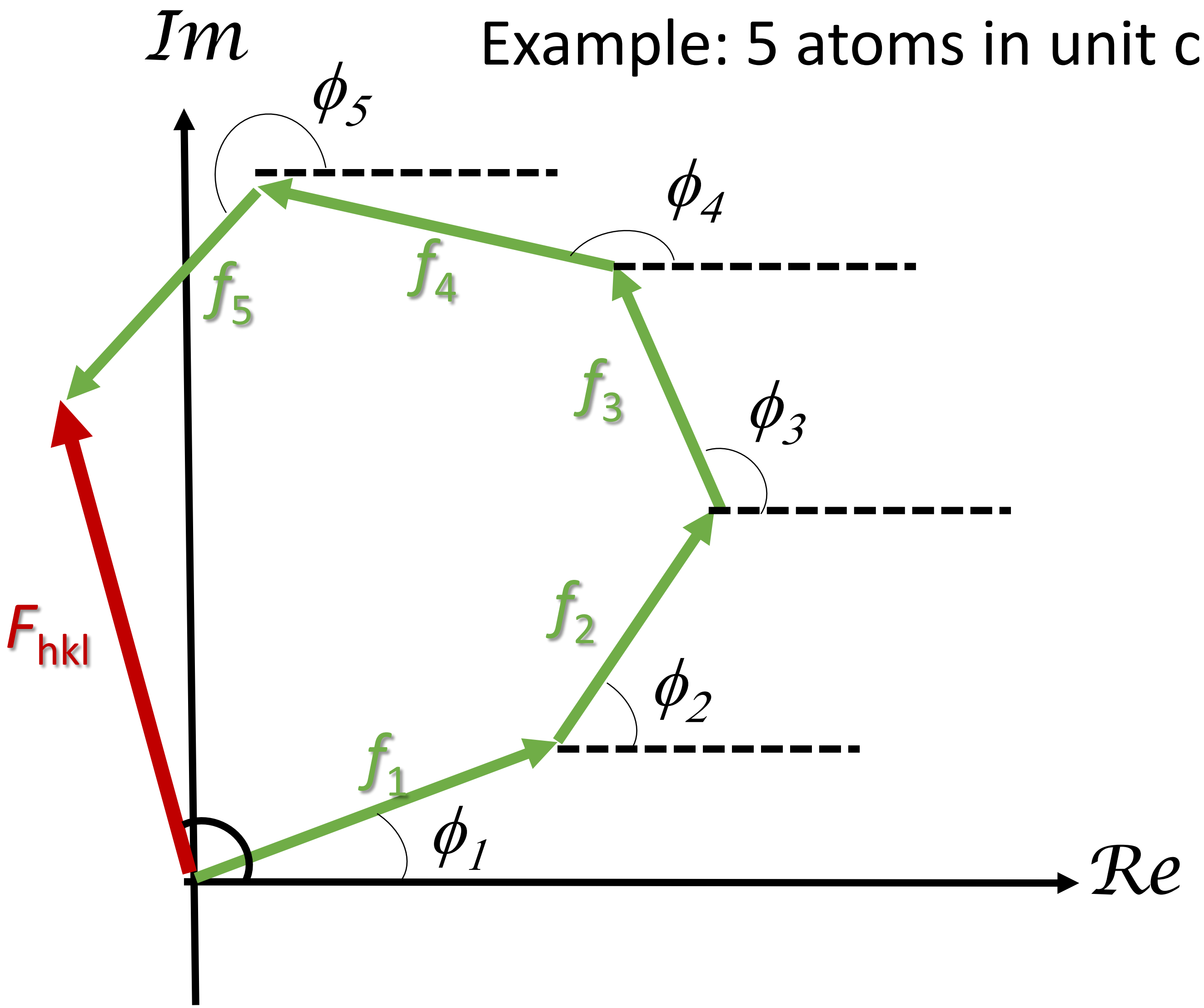
Let's explore the structure factor F_{hkl} for crystals

For N atoms in the unit cell

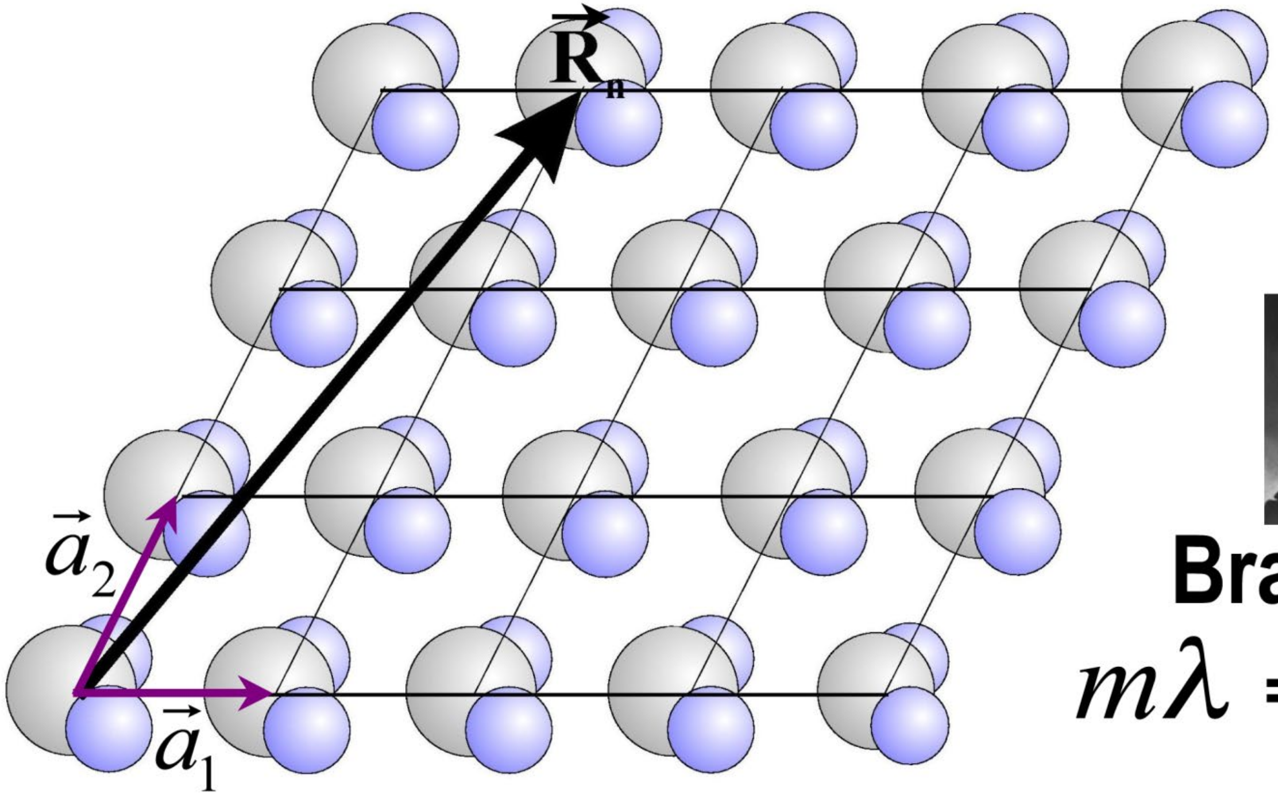
$$F_{hkl} = \sum_{j=1}^{N} f_j e^{i\vec{Q}\cdot\vec{r_j}}$$

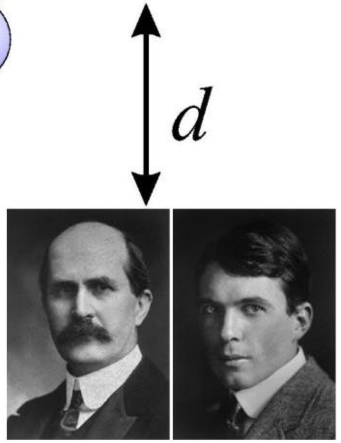
When $\mathbf{G}_{hkl}$ = $\boldsymbol{Q}$, Bragg's Law

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



The structure factor for non-Bravais Crystals





Bragg's Law:

$$m\lambda = 2d\sin\theta$$

$$F_{\text{crystal}}(\vec{Q}) = \left(\sum_{j=1}^{N} f_j(\vec{Q})\, e^{i\vec{Q}\,\vec{r}_j}\right)\cdot\left(\sum_{n=1}^{M} e^{i\vec{Q}\,\vec{R}_n}\right)$$

Unit Cell Structure Factor $F_{uc}(\vec{q}\,)$

Lattice Sum

Structure factors for neutrons and x-rays

$$\left(\frac{d\sigma}{d\Omega}\right)_{Neutron} = N\frac{(2\pi)^3}{V_0}\sum_{hkl}\delta(\vec{Q}-\vec{G}_{hkl})\left|F_{hkl}(\vec{Q})\right|^2$$

Neutrons add up the scattering lengths multiplied by the phase factor

Delta function is for Bragg condition (***Q*** = ***G***$_{hkl}$)

$$F_{hkl}(\vec{Q}) = \sum_d \bar{b}_d e^{i\vec{Q}.\vec{d}} e^{-W_d}$$

Debye-Waller factor for thermal motion of atoms

$$\left(\frac{d\sigma}{d\Omega}\right)_{x-ray} = r_0^2\left[\frac{1+\cos^2 2\theta}{2}\right]N\frac{(2\pi)^3}{V_0}\sum_{hkl}\delta(\vec{Q}-\vec{G}_{hkl})\left|F_{hkl}(\vec{Q})\right|^2$$

$$F_{hkl}(\vec{Q}) = \sum_d f_d(\vec{Q},\omega) e^{i\vec{Q}.\vec{d}} e^{-W_d}$$

x-rays add up the form factors multiplied by the phase factor

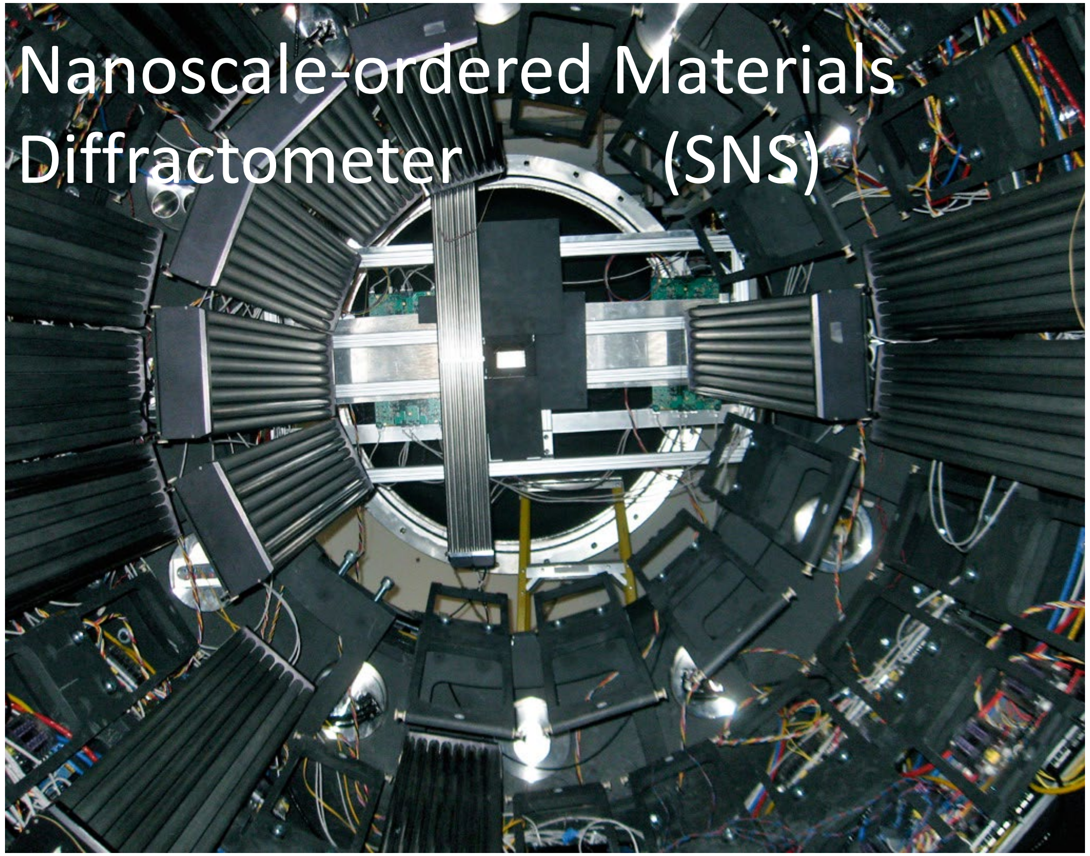
The Structure Factor S(Q) beyond crystalline matter

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 N.S(\vec{Q})$$ for an assembly of similar atoms where $$S(\vec{Q}) = \frac{1}{N}\left\langle \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} \right\rangle_{\text{ensemble}}$$

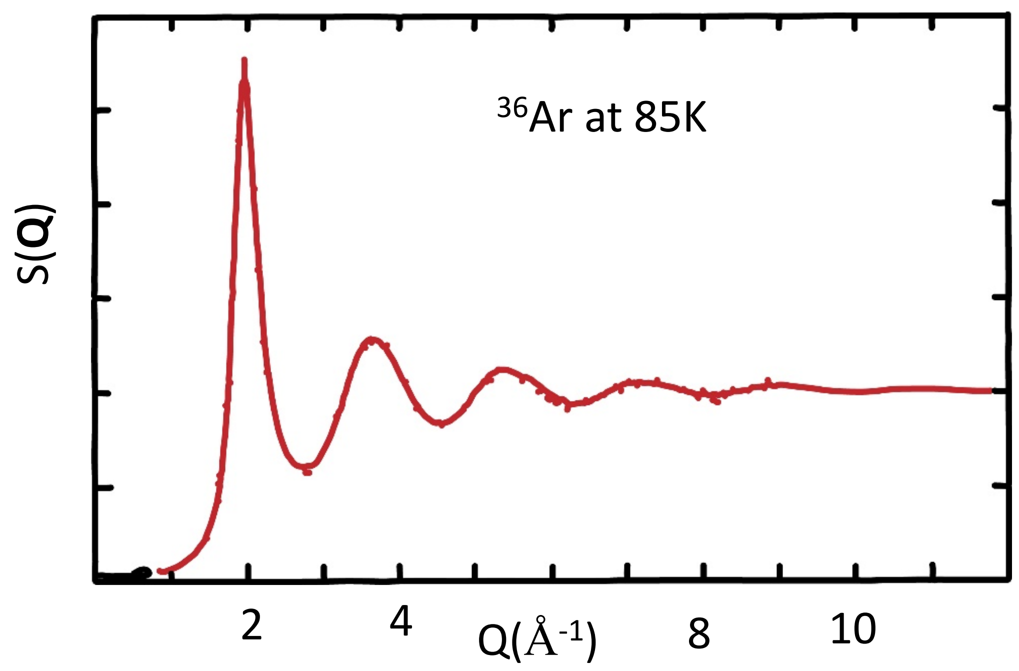
If $\rho_N(\mathbf{r})$ is the nuclear density function

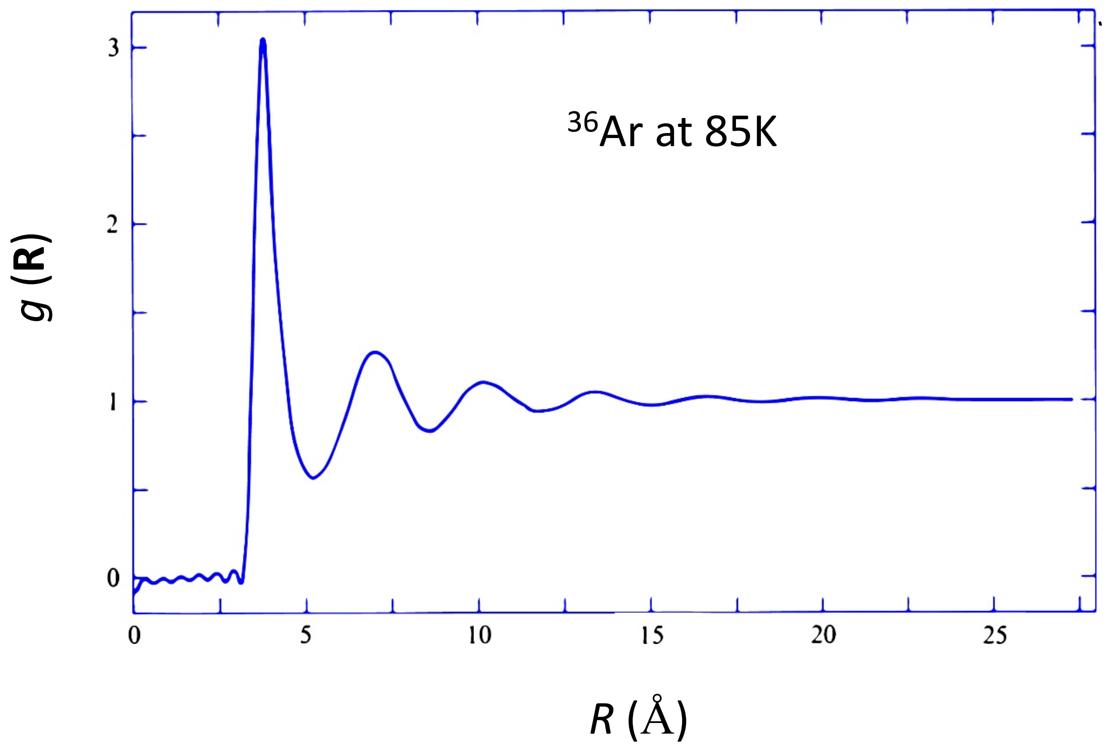
so $$S(\vec{Q}) = \frac{1}{N}\left\langle \left| \int d\vec{r}.e^{-i\vec{Q}.\vec{r}} \rho_N(\vec{r}) \right|^2 \right\rangle$$

$S(\mathbf{Q})$ is in square of the Fourier transform of this function



S(Q) as the Fourier transform of pair distribution function g(r)





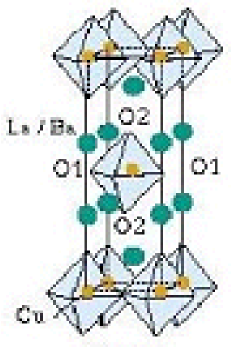
$$S(\vec{Q}) = 1 + \int d\vec{R}.\{g(\vec{R}) - \overline{\rho}\}.e^{-i\vec{Q}.\vec{R}}$$

where $g(\vec{R}) = \sum_{i \neq 0} \left\langle \delta(\vec{R} - \vec{R}_i + \vec{R}_0) \right\rangle$ is a function of $\vec{R}$ only.

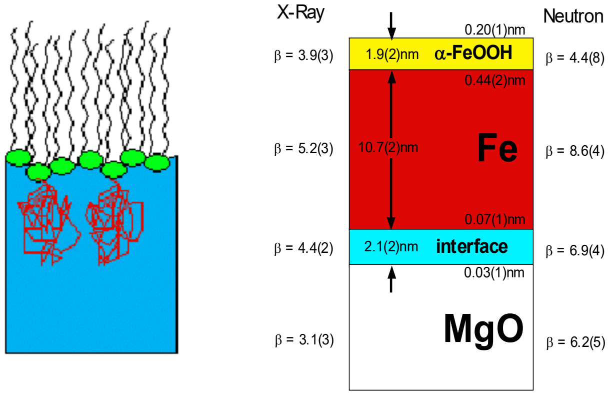
Dynamics and $S(\boldsymbol{Q},\omega)$

Energy transfer

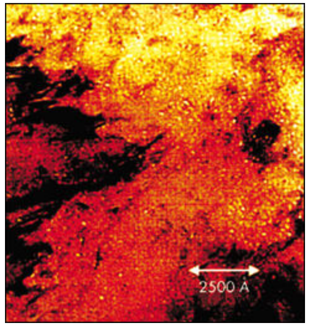
X-ray & Neutron Scattering Determine a Variety of Structures



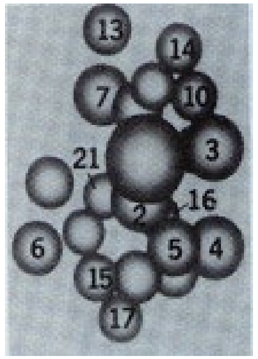
crystals



surfaces & interfaces

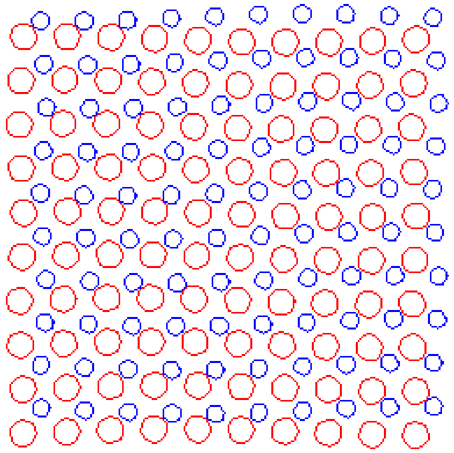


disordered/fractals



biomachines

but what happens when the atoms are moving?



- Can we determine the directions and
- time-dependence of atomic motions?
- Can well tell whether motions are periodic?
- These are the types of questions answered by inelastic neutron & x-ray scattering

Now we are after $S(Q,\omega)$

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

$$\hbar\omega = E_i - E_f$$ Energy transfer

$$E = \frac{\hbar^2 k^2}{2m_n}$$ Energy of a neutron for certain wavelength

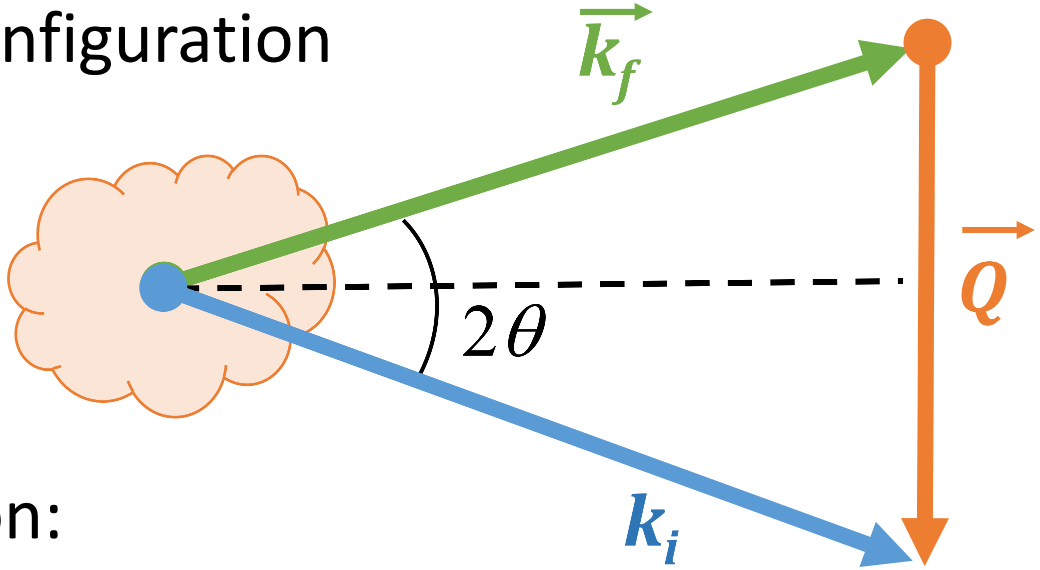
$$\hbar\omega = \frac{\hbar^2}{2m_n}(k_i^2 - k_f^2)$$

For neutrons, energy resolution is not as small as it is for x-rays

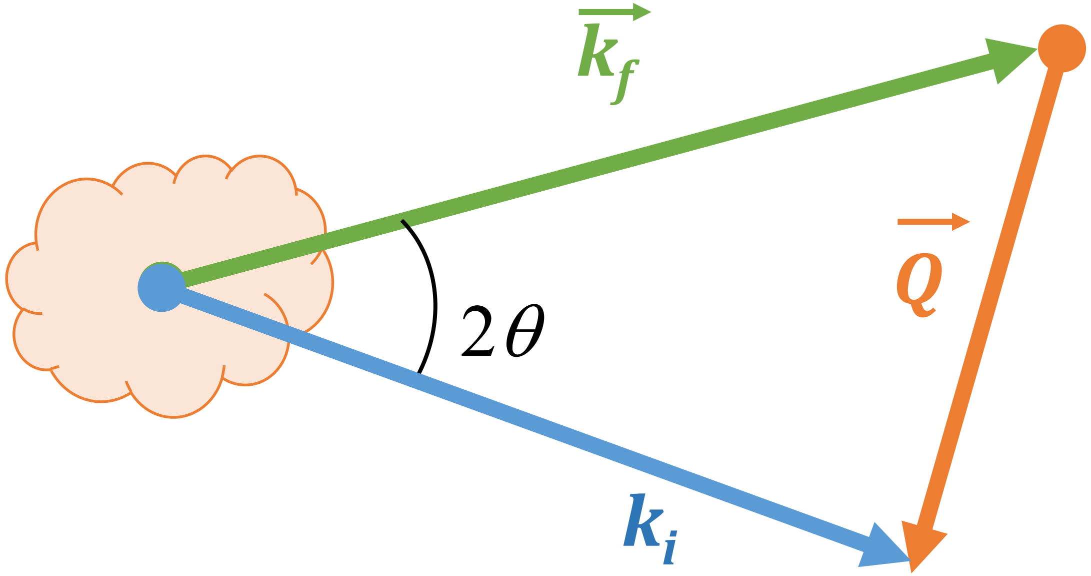
neutrons	x-rays
$\frac{\Delta E}{E} \sim 10\ \%$	$\frac{\Delta E}{E} \sim 10^{-7}$

Scattering triangle for inelastic processes

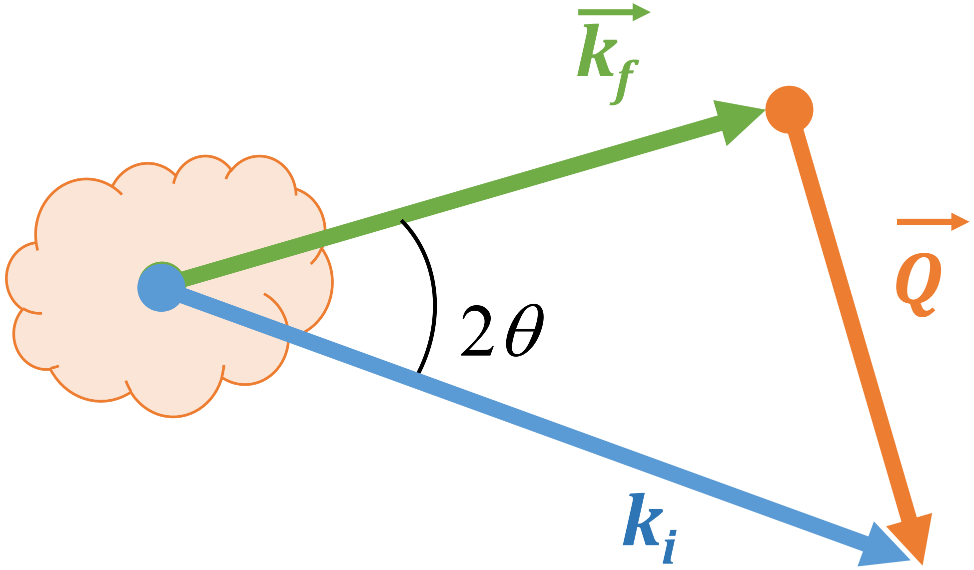
Elastic scattering configuration



Inelastic configuration:
neutron energy gain



Inelastic configuration:
neutron energy loss



How to think about the various energy scales

Quantity	Relationship	Value at $E = 10\,\mathrm{meV}$
Energy	$[\mathrm{meV}] = 2.072k^2[\text{Å}^{-1}]$	10 meV
Wavelength	$\lambda[\text{Å}] = 9.044/\sqrt{E[\mathrm{meV}]}$	2.86 Å
Wave vector	$k[\text{Å}^{-1}] = 2\pi/\lambda[\text{Å}]$	2.20 Å^{-1}
Frequency	$\nu[\mathrm{THz}] = 0.2418E[\mathrm{meV}]$	2.418 THz
Wavenumber	$\nu[\mathrm{cm}^{-1}] = \nu[\mathrm{Hz}]/(2.998 \times 10^{10}\,\mathrm{cm/s})$	80.65 cm^{-1}
Velocity	$v[\mathrm{km/s}] = 0.6302k[\text{Å}^{-1}]$	1.38 km/s
Temperature	$T[\mathrm{K}] = 11.605E[\mathrm{meV}]$	116.05 K

From Tranquada, Shirane, and Shapiro, “Neutron Scattering from a Triple Axis Spectrometers: Basic Techniques”

Fermi's Golden Rule and the double differential cross section

- Neutrons interact very weakly with matter
- The scattering process will cause a change from a one quantum state to another
- BUT, it will not modify the nature of the states themselves

$$\left.\frac{d^2\sigma}{d\Omega_f dE_f}\right|_{\lambda_i \to \lambda_f} = \frac{k_f}{k_i}\left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left[\langle \boldsymbol{k}_f \lambda_f | V | \boldsymbol{k}_i \lambda_i \rangle\right]^2 \delta(\hbar\omega + E_i - E_f)$$

The two quantum states, initial and final

The interaction operator of neutron with the sample

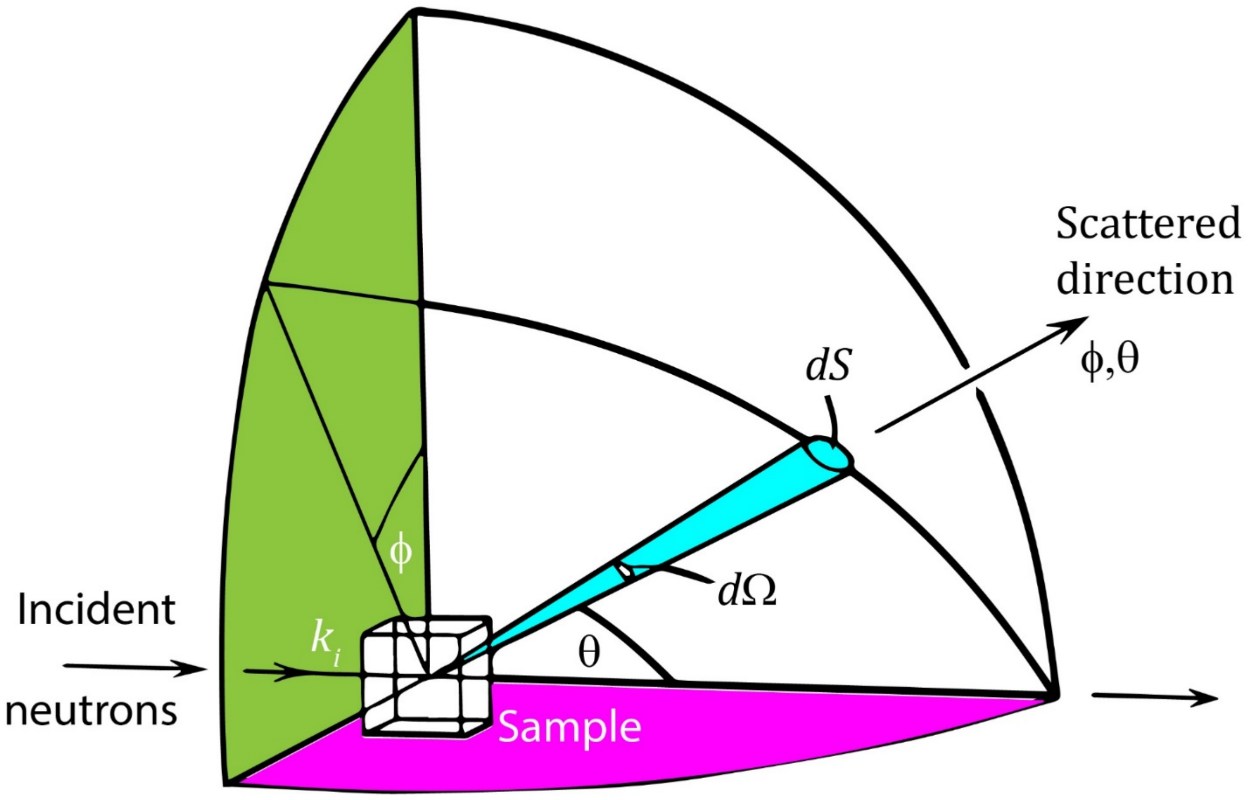
Delta function, observation for energy transfer at certain hw

$S(Q,\omega)$ and the double differential cross section

$$\frac{d^2\sigma}{d\Omega dE} = N\frac{k_f}{k_i}b^2 S(\vec{Q},\omega)$$

N = number of nuclei

t = time



$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar N}\sum_{ll'}\int_{-\infty}^{\infty} dt\ \left\langle e^{-i\mathbf{Q}\cdot\mathbf{r}_{l'}(0)} e^{i\mathbf{Q}\cdot\mathbf{r}_l(t)}\right\rangle e^{-i\omega t}$$

Inelastic neutron scattering measures atomic motions

$$\left(\frac{d^2\sigma}{d\Omega . dE}\right)_{coh} = b_{coh}^2 \frac{k'}{k} N S(\vec{Q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega . dE}\right)_{inc} = b_{inc}^2 \frac{k'}{k} N S_s(\vec{Q},\omega)$$

where

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\iint G(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt \quad \text{and} \quad S_s(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\iint G_s(\vec{r},t)e^{i(\vec{Q}.\vec{r}-\omega t)}d\vec{r}dt$$

- Inelastic coherent scattering measures *correlated* motions of different atoms
- Inelastic incoherent scattering measures *self-correlations* e.g. diffusion
- These days it is possible to do inelastic scattering using x-rays also.

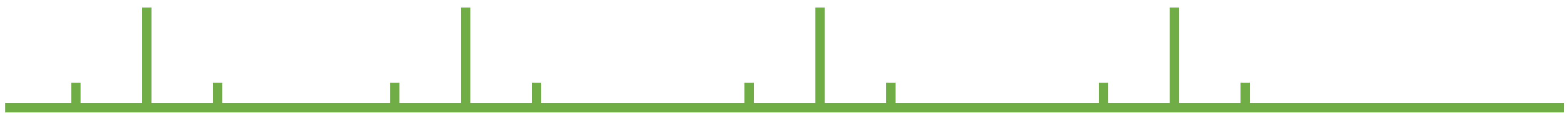
The pair correlation functions

1. **Elastic, coherent** neutron scattering is proportional to the spatial Fourier Transform of the Pair Correlation Function, **G(r)** i.e. the probability of finding a particle at position r if there is simultaneously a particle at r=0

2. **Inelastic coherent** neutron scattering is proportional to the space *and time* Fourier Transforms of the *time-dependent* pair correlation function function, **G(r,t)** = probability of finding a particle at position r *at time t* when there is a particle at r=0 and *t=0*.

3. **Inelastic *incoherent*** scattering, the intensity is proportional to the **space and time Fourier Transforms** of the ***self-correlation*** function, $G_s(r,t)$ i.e. the probability of finding a particle at position r at time t when *the same* particle was at *r*=0 at *t*=0

Step 1: construct a frozen wave of atomic density



What happens if we put a "frozen" wave in the chain of atoms so that the atomic positions are $x_p = pa + u\cos kpa$ where p is an integer and u is small?

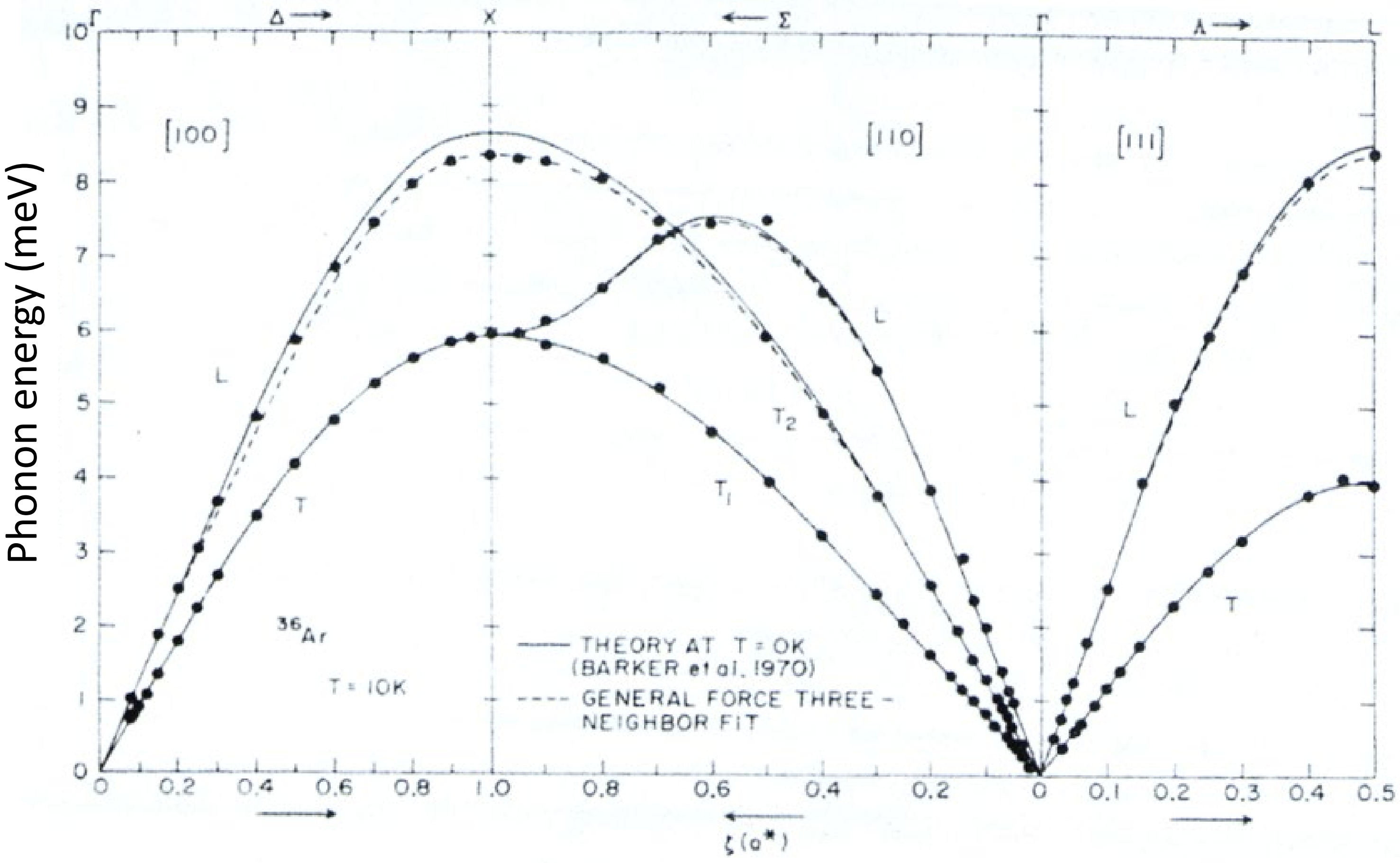
$$S(Q) = \left|\sum_p e^{iQpa} e^{iQu\cos kpa}\right|^2 \approx \left|\sum_p e^{iQpa}(1 + iQu[e^{ikpa} + e^{-ikpa}])\right|^2$$

$$\approx \left|\sum_p e^{iQpa} + iQu[e^{i(Q+k)pa} + e^{i(Q-k)pa}]\right|^2$$

so that in addition to the Bragg peaks we get weak satellites at $Q = G \pm k$

Step 2: What happens if the wave moves?

- If the wave moves through the chain, the scattering still occurs at wavevectors G + k and G – k but now the scattering is inelastic
- In a crystal, the vibration frequency at a given value of $\vec{q}$ (called the phonon wavevector) is determined by interatomic forces. These frequencies map out the so-called phonon dispersion curves.



phonon dispersion curves for a crystal of ^{36}Ar

From Roger Pynn

A phonon is a quantized lattice vibration

$$F_n = \alpha_0 u_n + \alpha_1 (u_{n-1} + u_{n+1}) + \alpha_2 (u_{n-2} + u_{n+2}) + \ldots$$

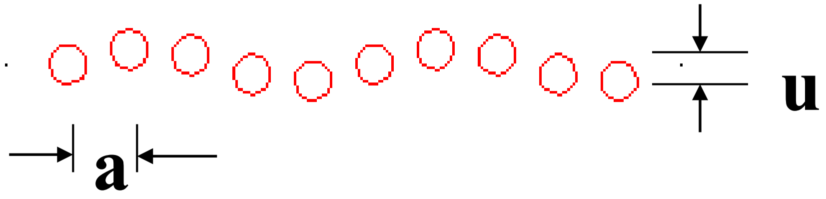
First neighbor force constant

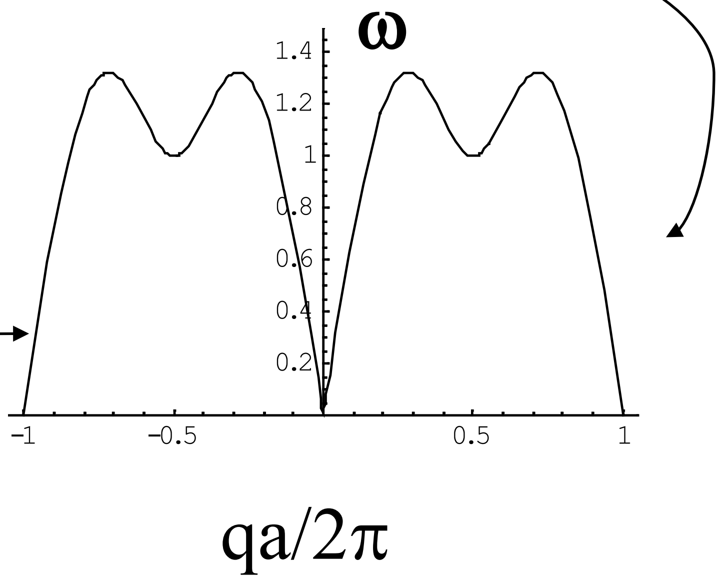
displacements

$$F_n = M\ddot{u}_n$$

$$u_n(t) = A_q e^{i(qna - \omega t)} \quad \text{with } \omega_q^2 = \frac{4}{M}\sum_\nu \alpha_\nu \sin^2(\frac{1}{2}\nu q a)$$

$$q = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots\ldots \pm\frac{N}{2}\frac{2\pi}{L}$$

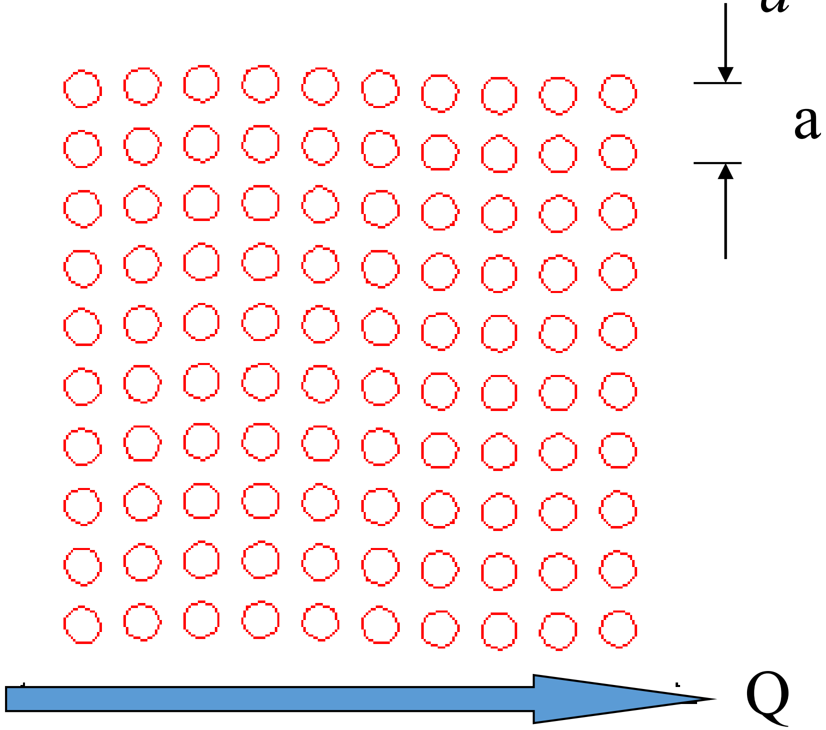




Phonon Dispersion Relation:
Measurable by inelastic neutron scattering

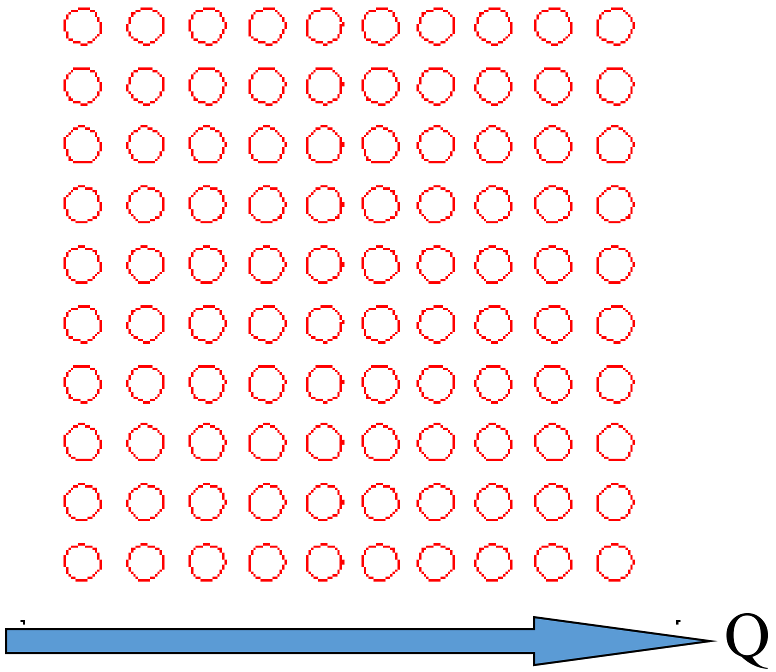
Atomic motions for longitudinal & transverse phonons

$$\vec{Q} = \frac{2\pi}{a}(0.1,0,0)$$



Transverse phonon

$$\vec{e}_T = (0,0.1,0)a$$

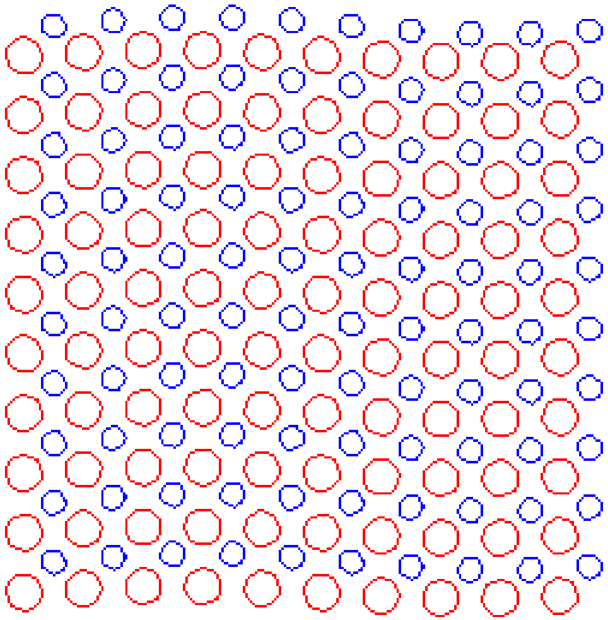


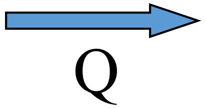
Longitudinal phonon

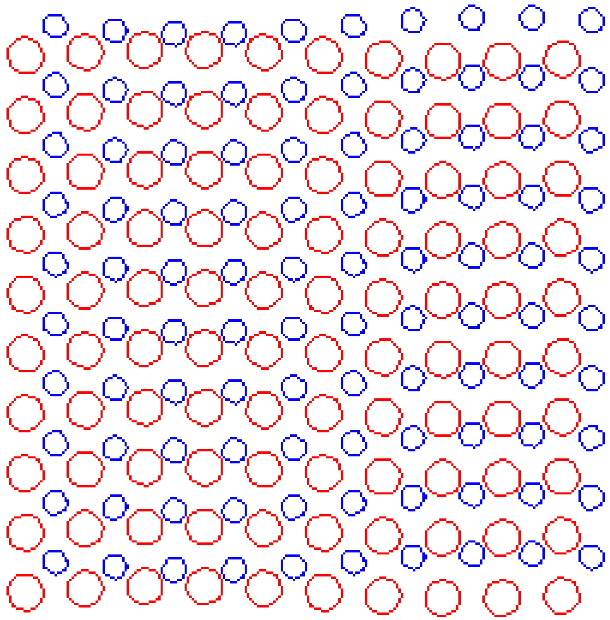
$$\vec{e}_L = (0.1,0,0)a$$

$$\vec{R}_l = \vec{R}_{l0} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)}$$

Transverse optic and acoustic phonons







Acoustic

$\vec{e}_{red} = (0,0.1,0)a$

$\vec{e}_{blue} = (0,0.14,0)a$

Optic

$\vec{e}_{red} = (0,0.1,0)a$

$\vec{e}_{blue} = (0,-0.14,0)a$

$$\vec{R}_{lk} = \vec{R}_{lk}^{0} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)}$$

Inelastic magnetic scattering of neutrons

- In the simplest case, atomic spins in a ferromagnet precess about the direction of mean magnetization

$$H = \sum_{l,l'} J(\vec{l} - \vec{l}')\vec{S}_l.\vec{S}_{l'} = H_0 + \sum_q \hbar\omega_q b_q^+ b_q$$

exchange coupling

ground state energy

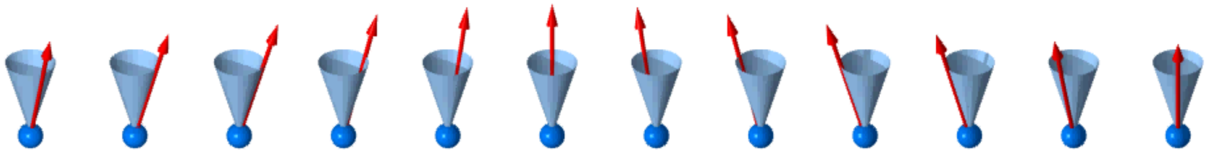
spin waves (magnons)

with

$$\hbar\omega_q = 2S(J_0 - J_q) \qquad \text{where} \quad J_q = \sum_l J(\vec{l})e^{i\vec{q}.\vec{l}}$$

$\hbar\omega_q = Dq^2$ is the dispersion relation for a ferromagnet

Fluctuating spin is perpendicular to mean spin direction



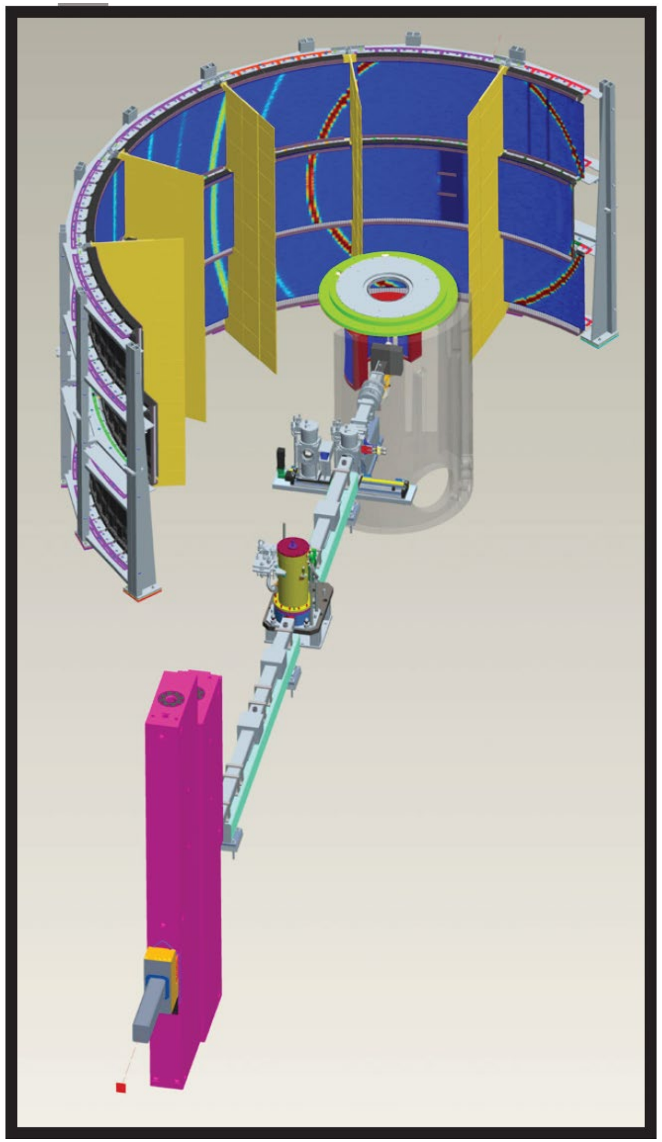
Spin wave animation courtesy of A. Zheludev (ORNL)

Two (of several) ways to do inelastic scattering

Triple-axis spectrometer

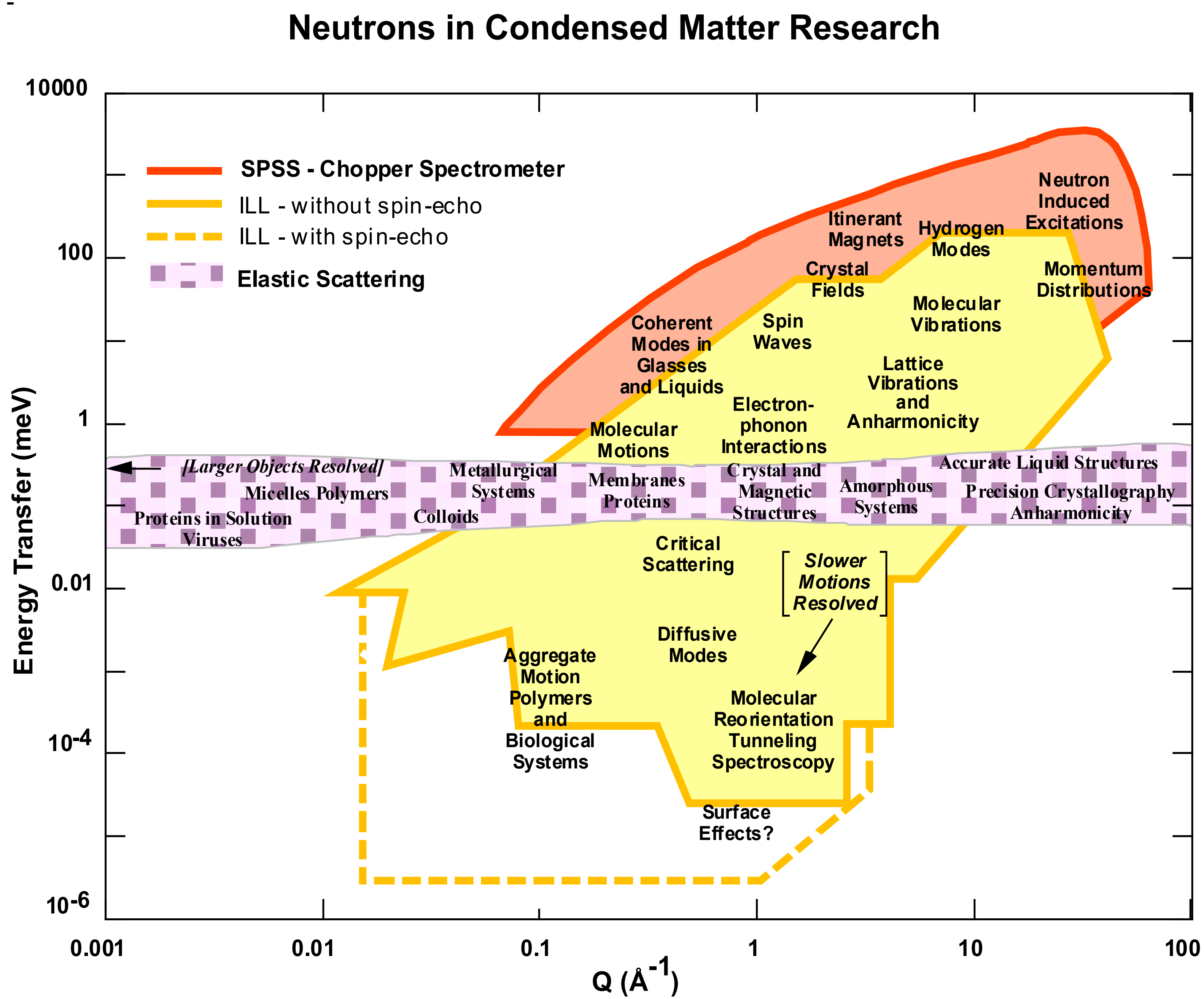
CG-4C cold TAS (HFIR)

Time-of-flight spectrometer



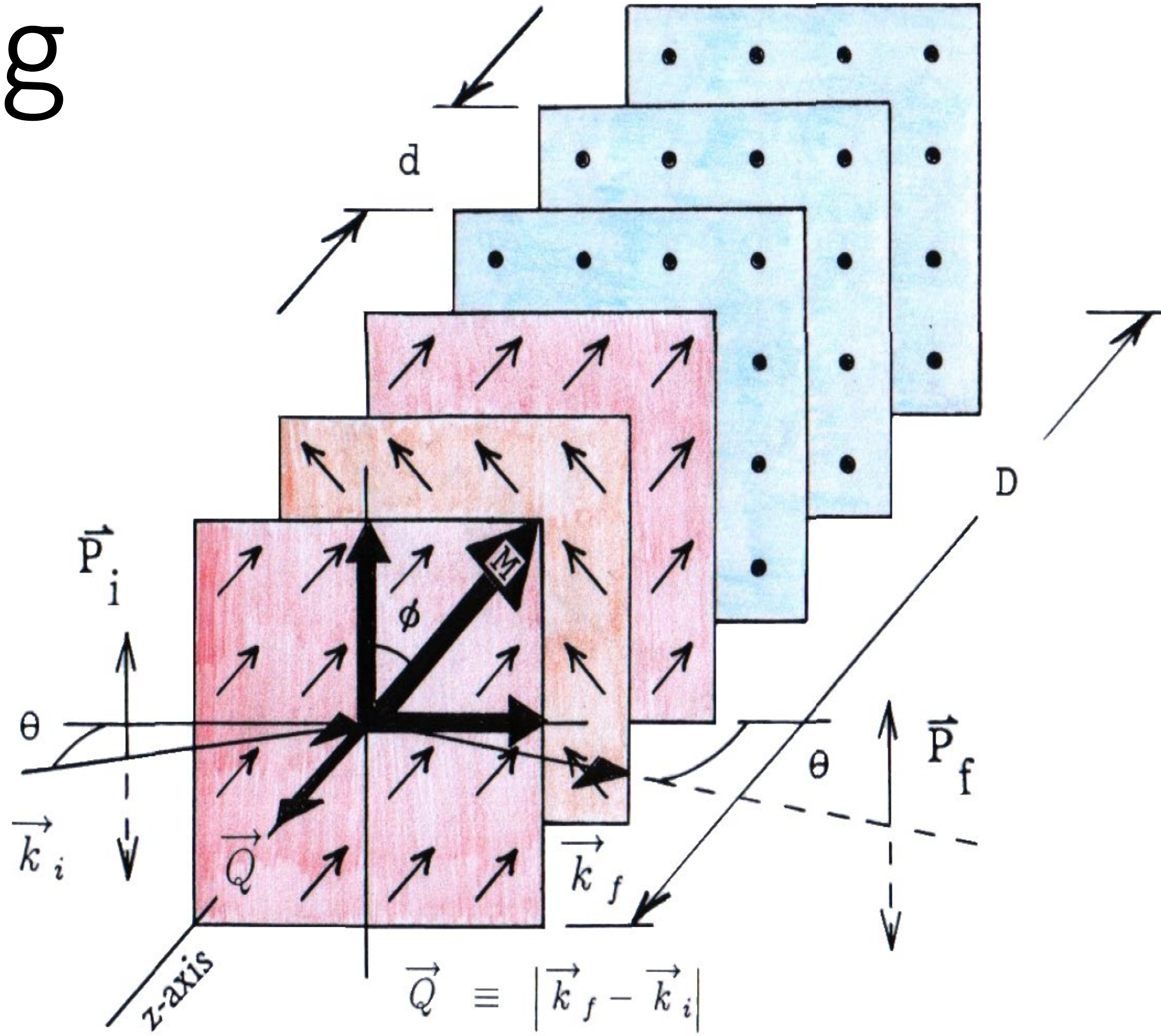
ARCS (SNS)

Energy and wavevector transfers accessible to neutron scattering



Magnetic scattering

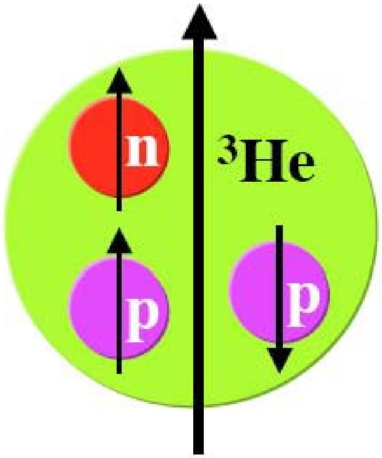
$S(\boldsymbol{Q},\omega)$ from $M_{\perp}$



The neutron and its moment

Neutron spin

$$-\gamma\mu_N\sigma$$



γ = gyromagnetic ratio
μ_N = nuclear magneton
σ = spin operator

Spin amplitude of atom in crystal is pM

$$p = \left(\frac{\gamma r_0}{2}\right) g f(\mathbf{Q})$$

g = 2 for spin only
$f(\mathbf{Q})$ magnetic form factor

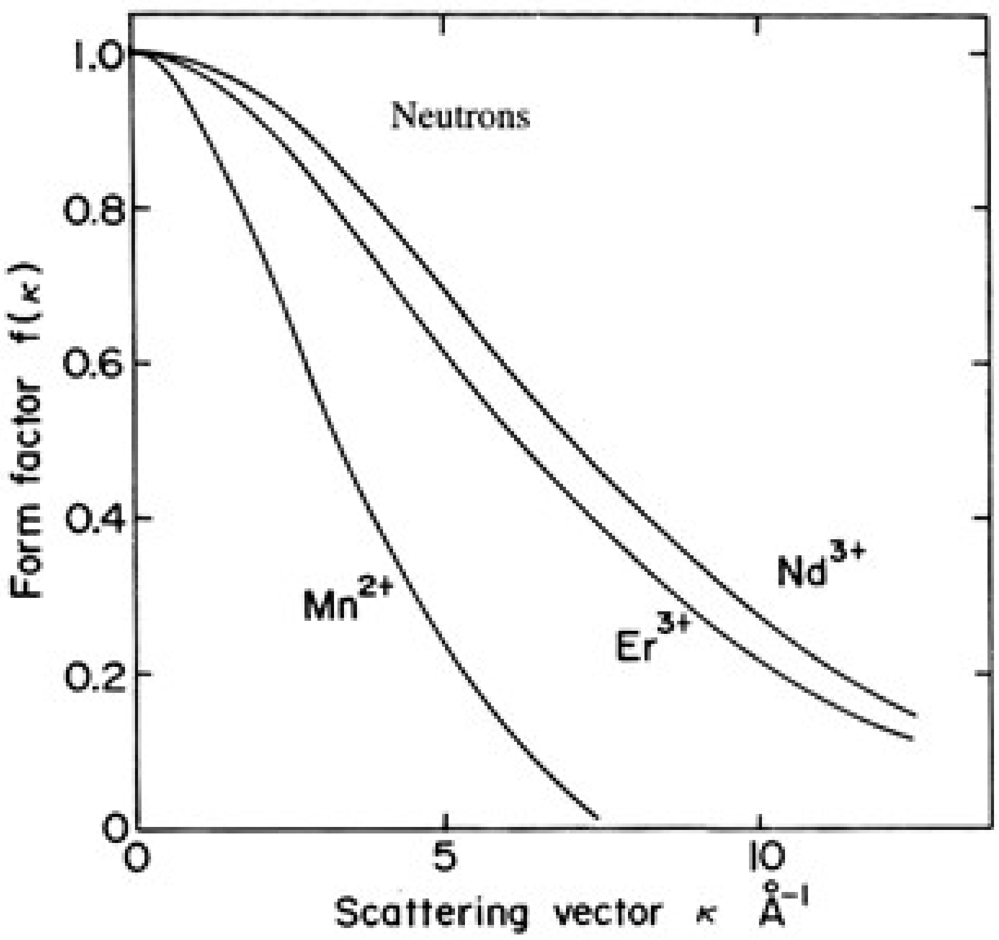
The magnetic form factor and structure factor

$$f(\mathbf{Q}) = \int p_s(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r}$$

$$f(0) \equiv 1$$

$$\mathbf{F}_{\mathrm{M}}(\mathbf{G}_{\mathrm{M}}) = \sum_j f(\mathbf{Q}) \mathbf{M}_{\perp} e^{i\mathbf{G}_{\mathrm{M}}\cdot\mathbf{d}_{\mathrm{j}}}$$

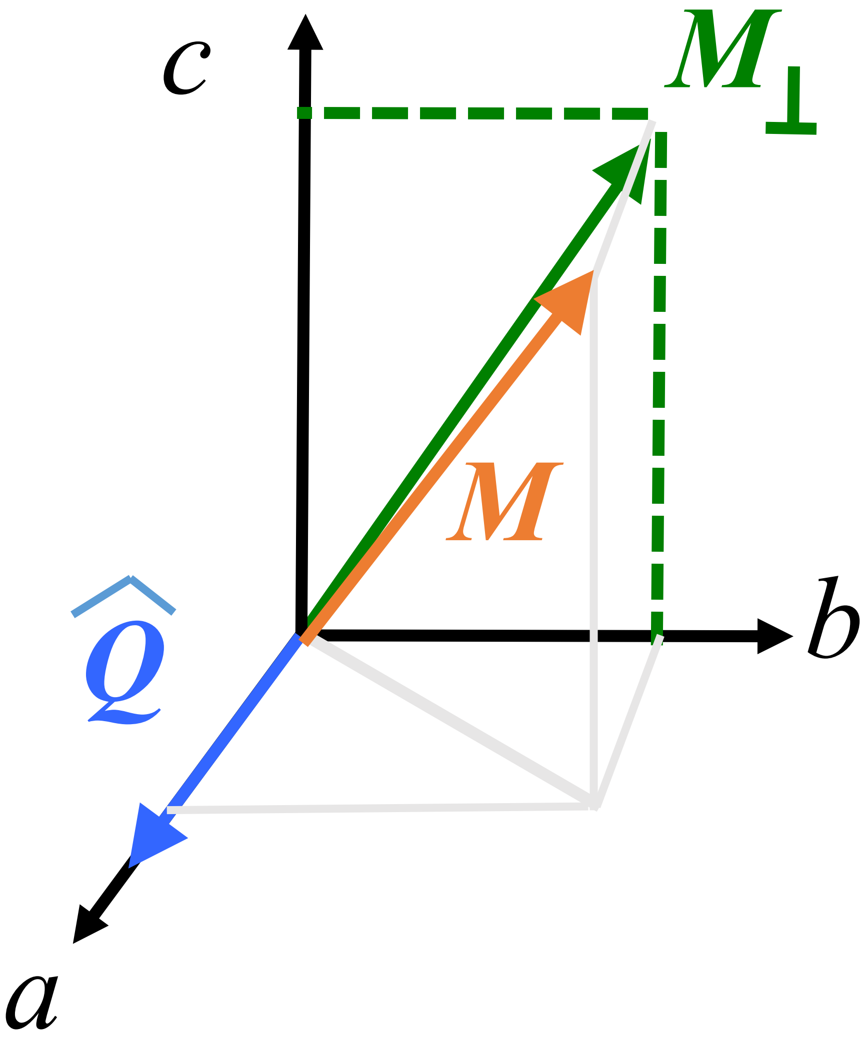
Taken from D. H. Ryan, McGill University



The magnetic interaction vector

$$\mathbf{M}_\perp = \widehat{\mathbf{Q}} \times (\mathbf{M} \times \widehat{\mathbf{Q}})$$

$$\mathbf{M}_\perp = \mathbf{M} - \widehat{\mathbf{Q}}(\widehat{\mathbf{Q}} \cdot \mathbf{M})$$



Neutron can have also initial polarization and final polarization

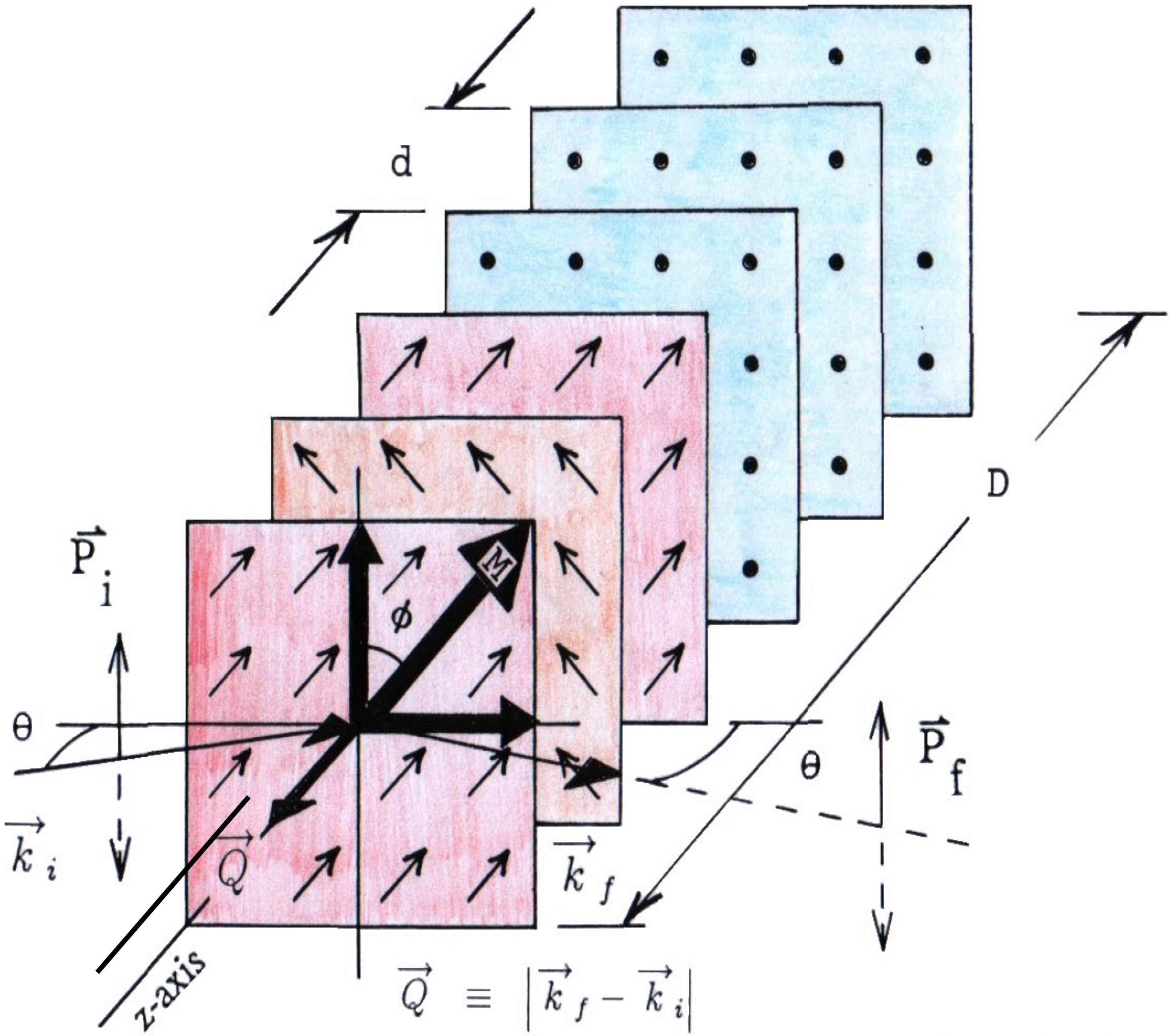
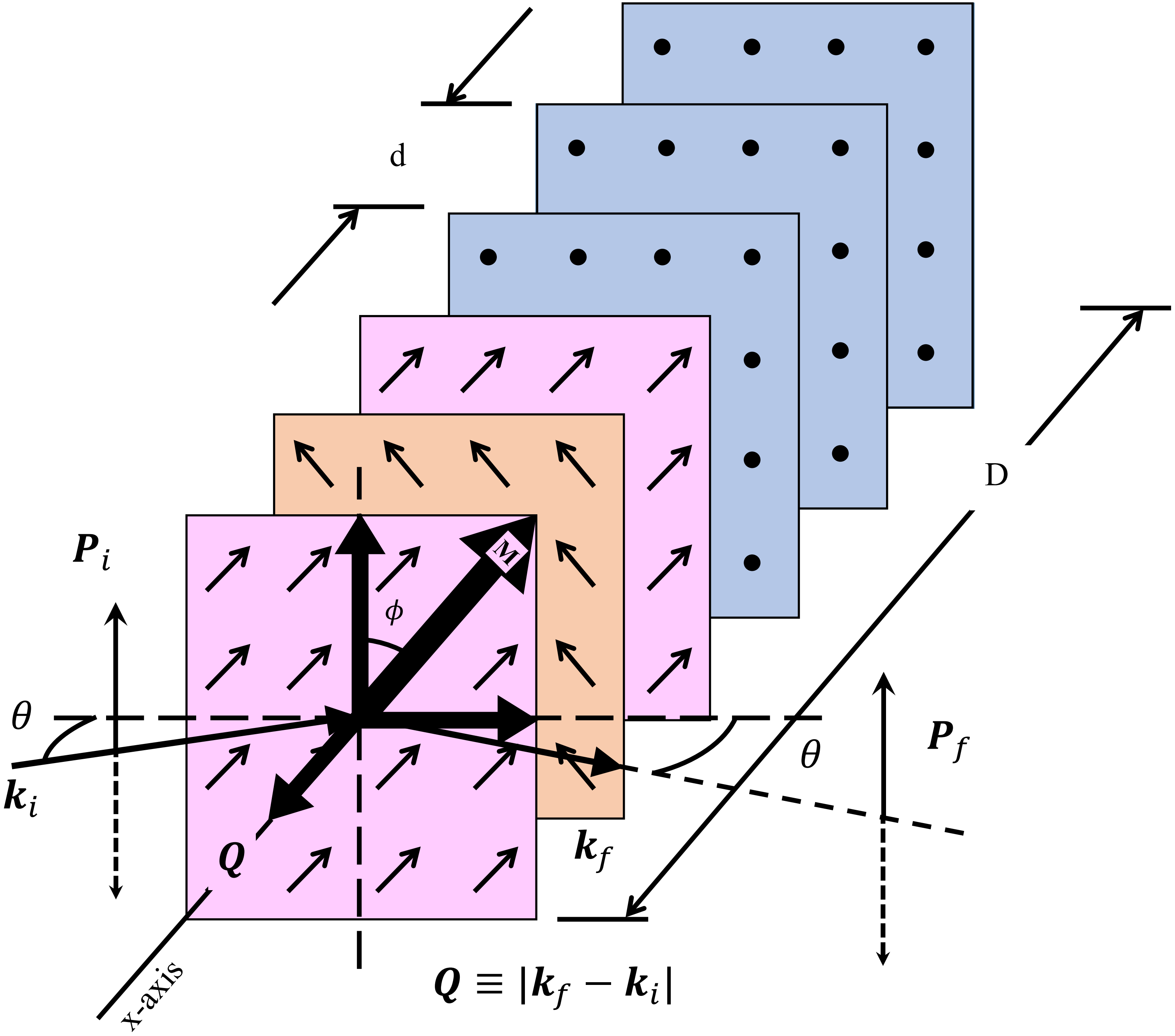
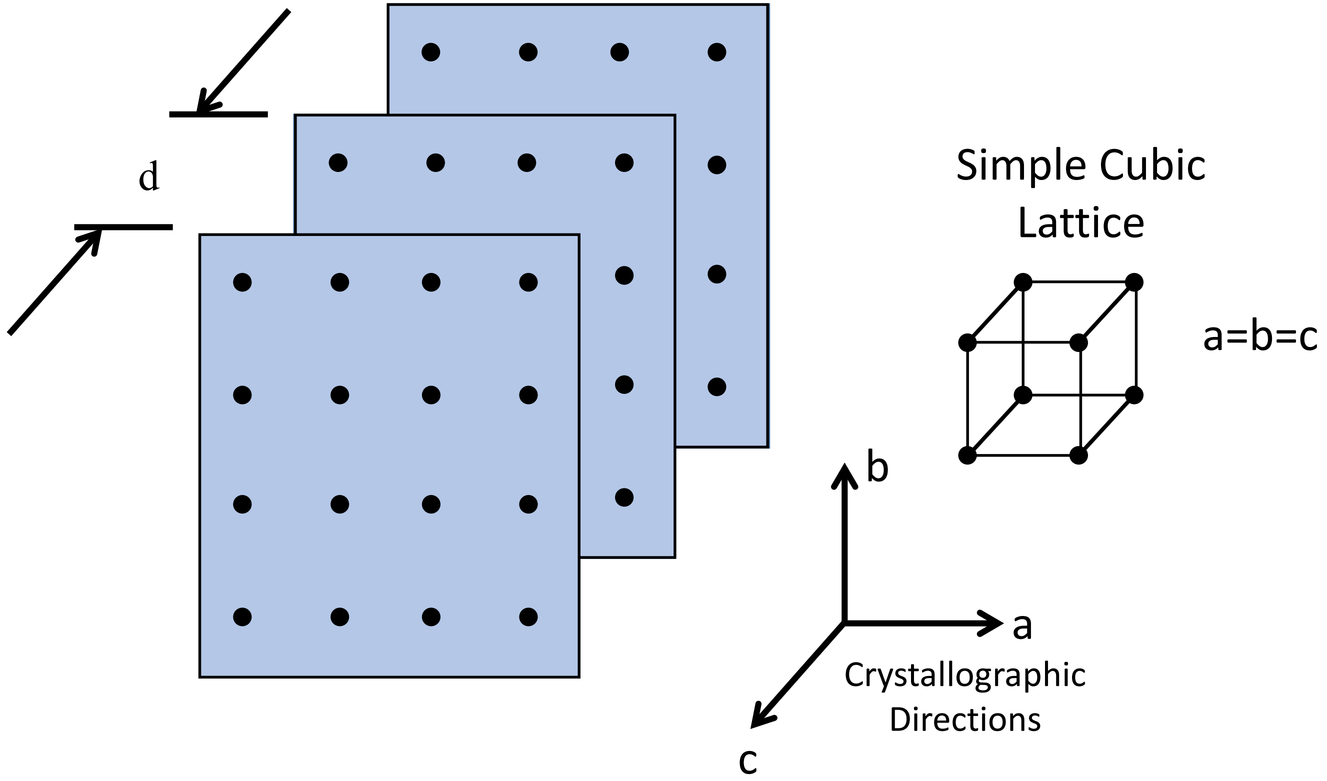


Illustration by Chuck Majkrzak

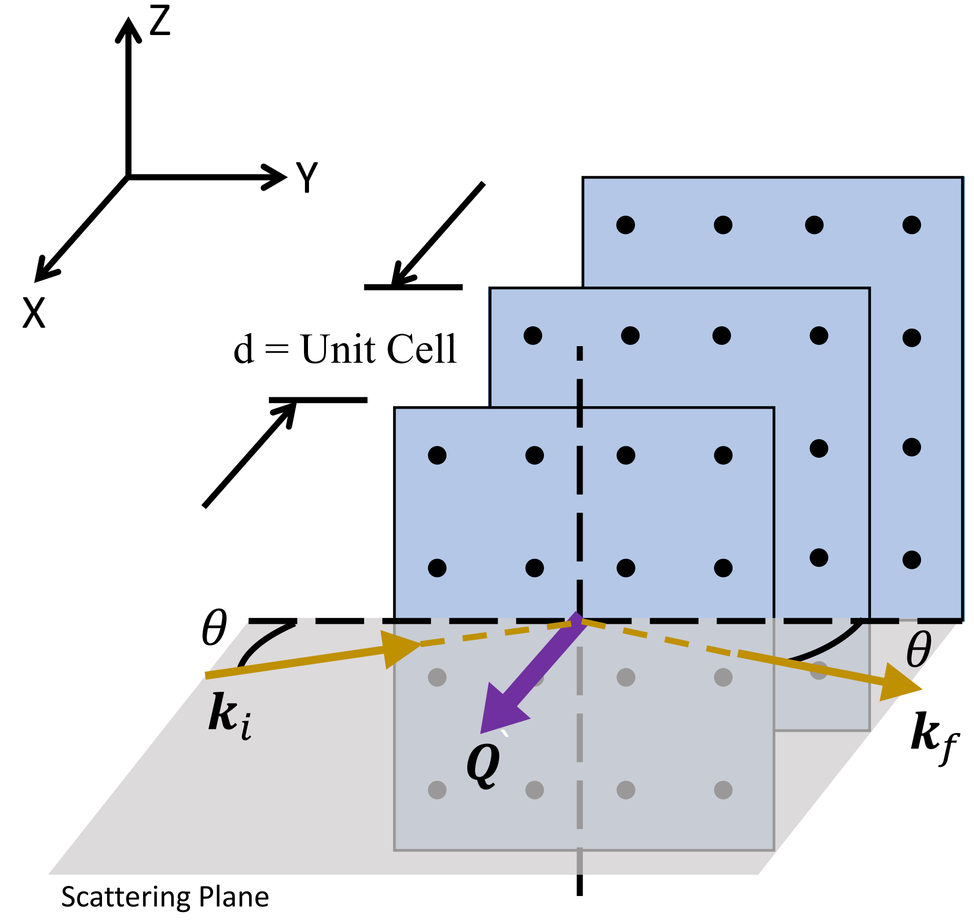


d
D
P_i
P_f
θ
θ
ϕ
M
k_i
k_f
Q
x-axis
$Q \equiv |k_f - k_i|$

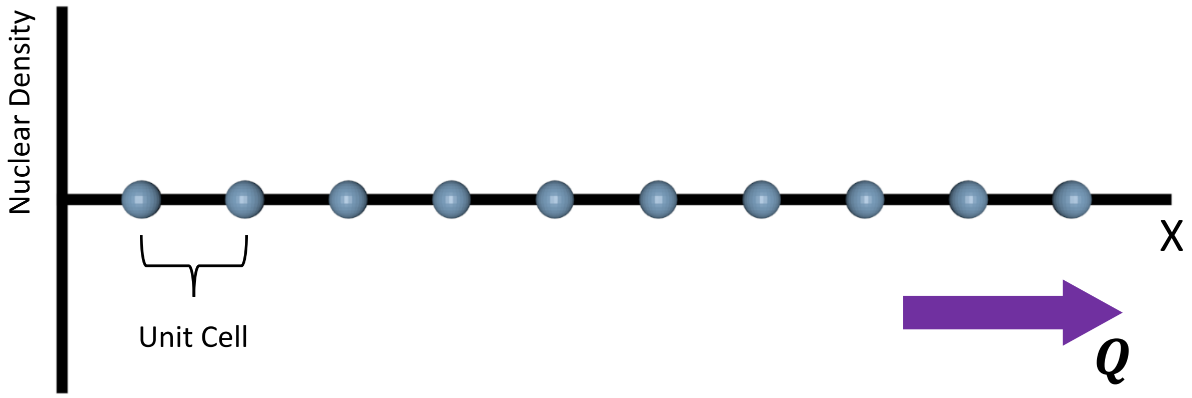
First, let's look at nuclear scattering once again

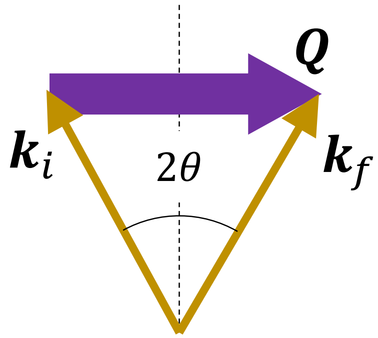


More on the Q for nuclear scattering



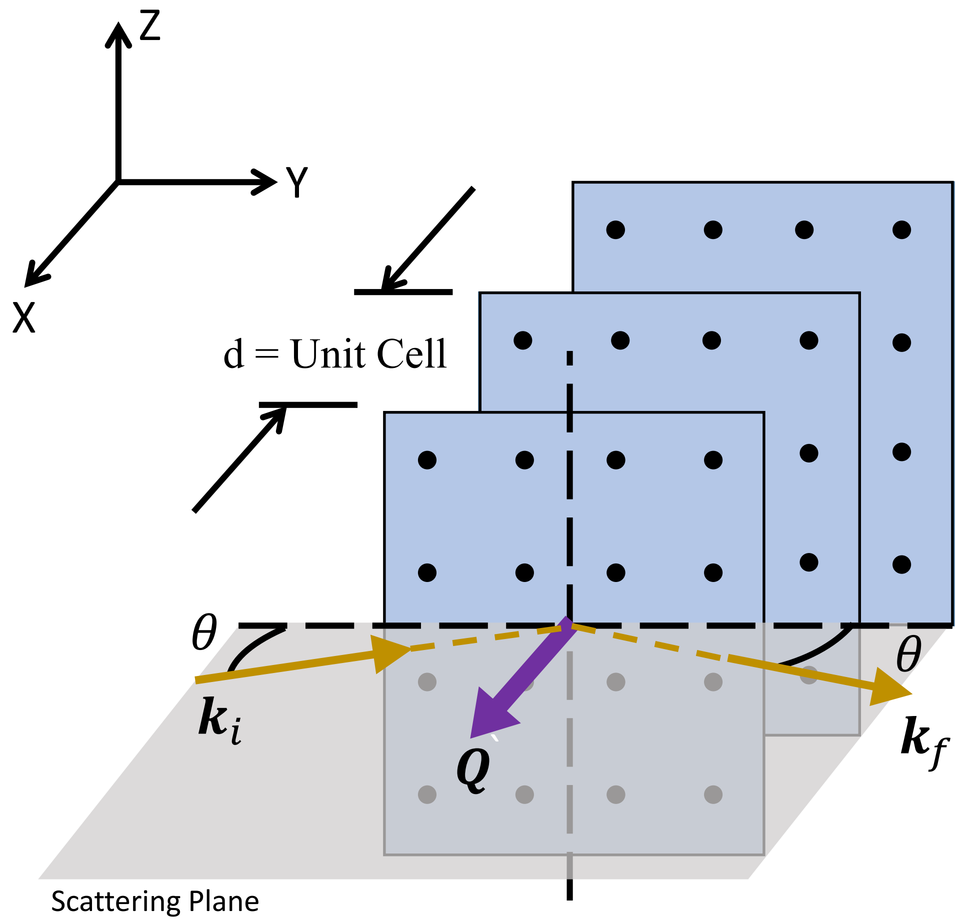
X is parallel with $\boldsymbol{Q}$





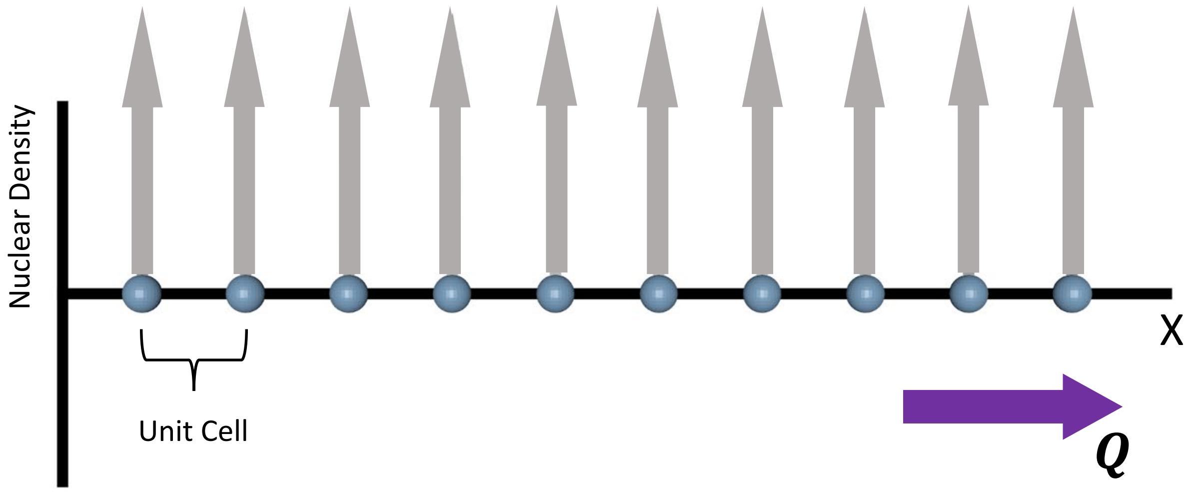
Accessing the [0 0 L] Reflections

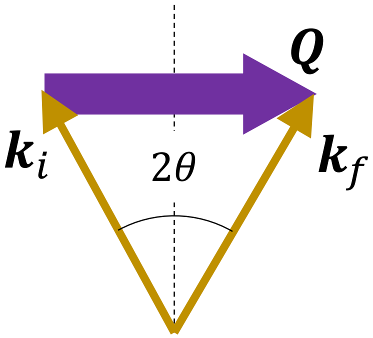
More on the Q for nuclear scattering



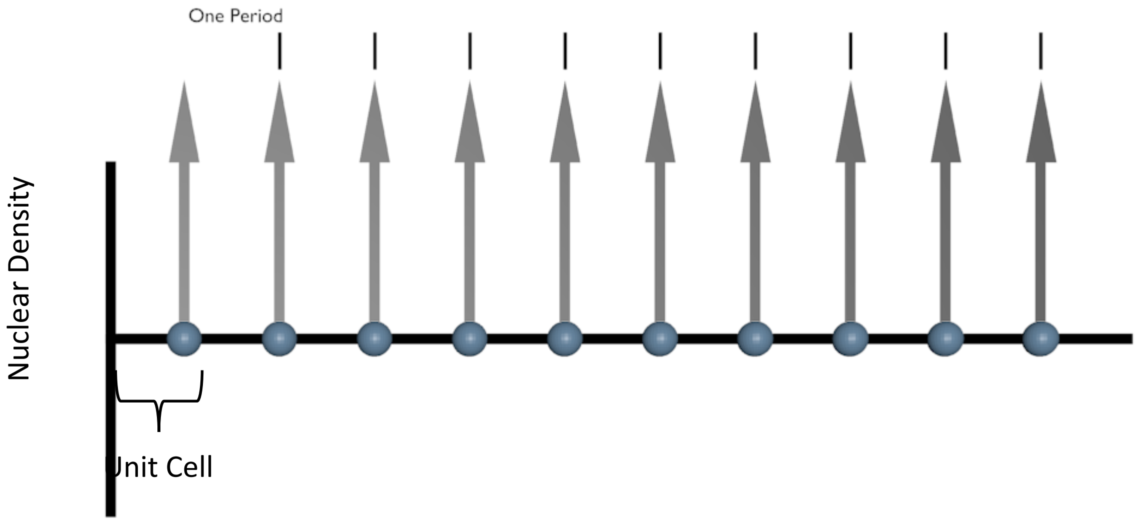
Accessing the [0 0 L] Reflections

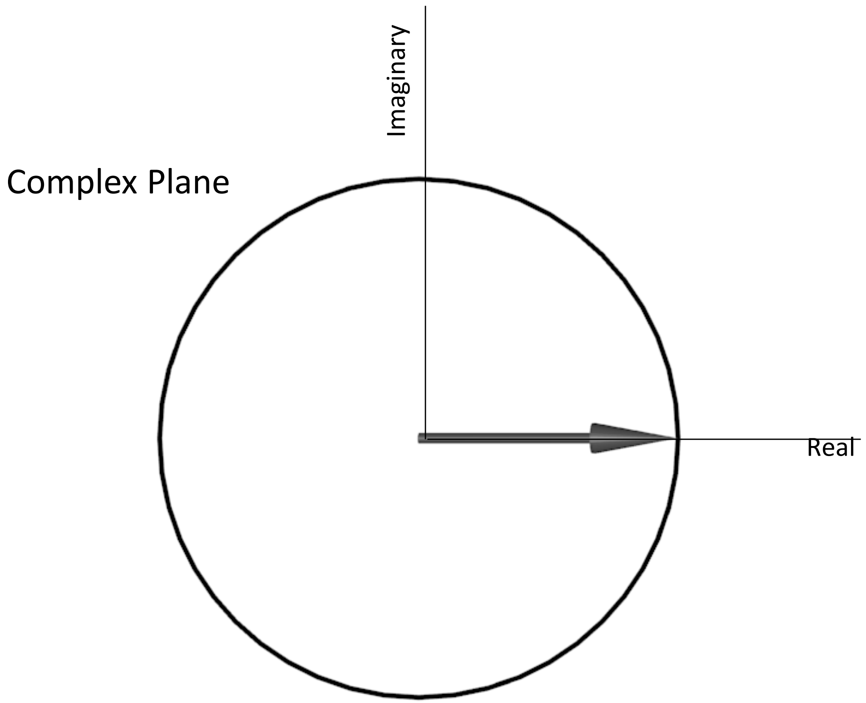
Arrows used to represent Delta Function Nuclear Density





More on the structure factor for nuclear scattering

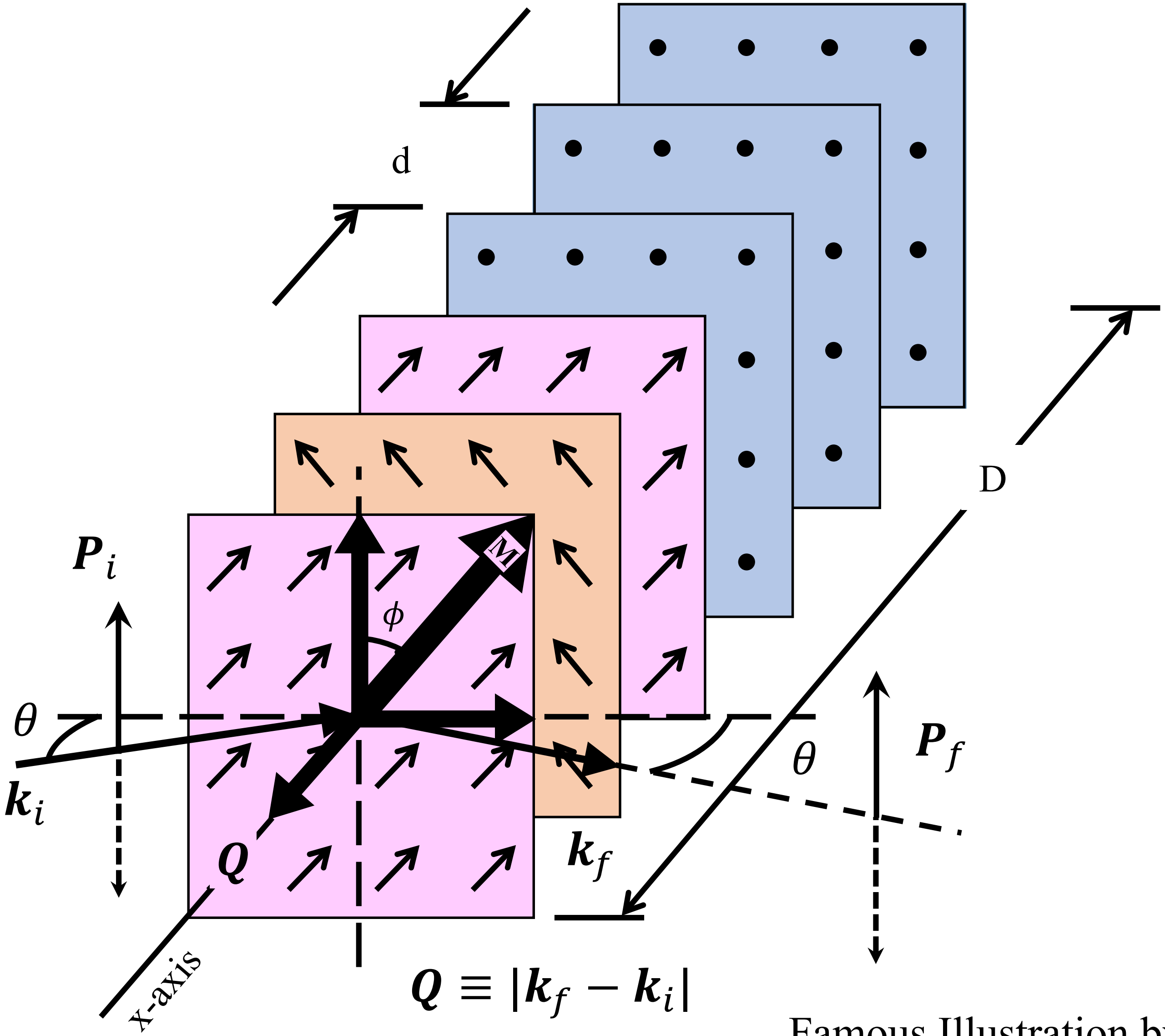




[0 0 1] Reflection

Lowest Harmonic

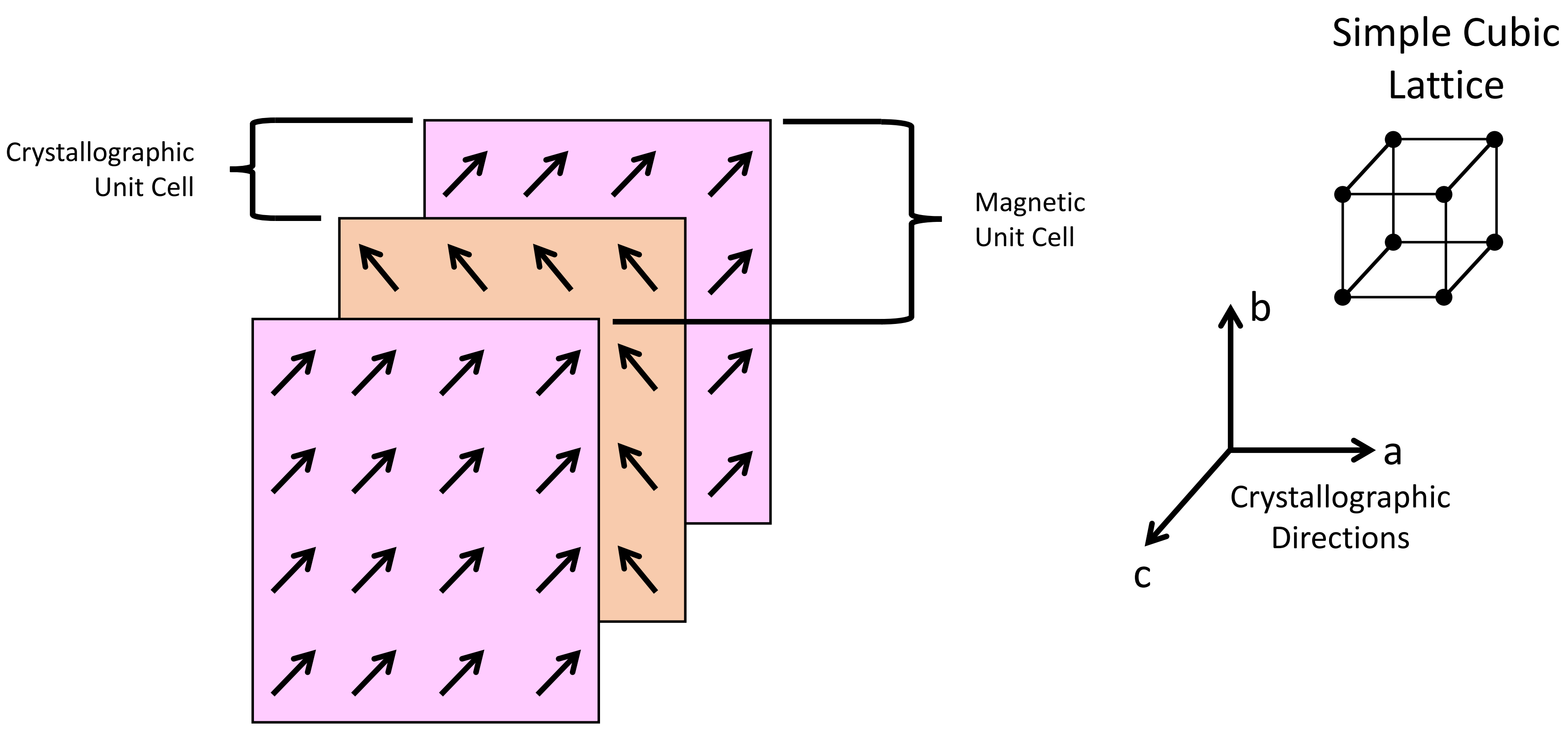
Magnetic Scattering



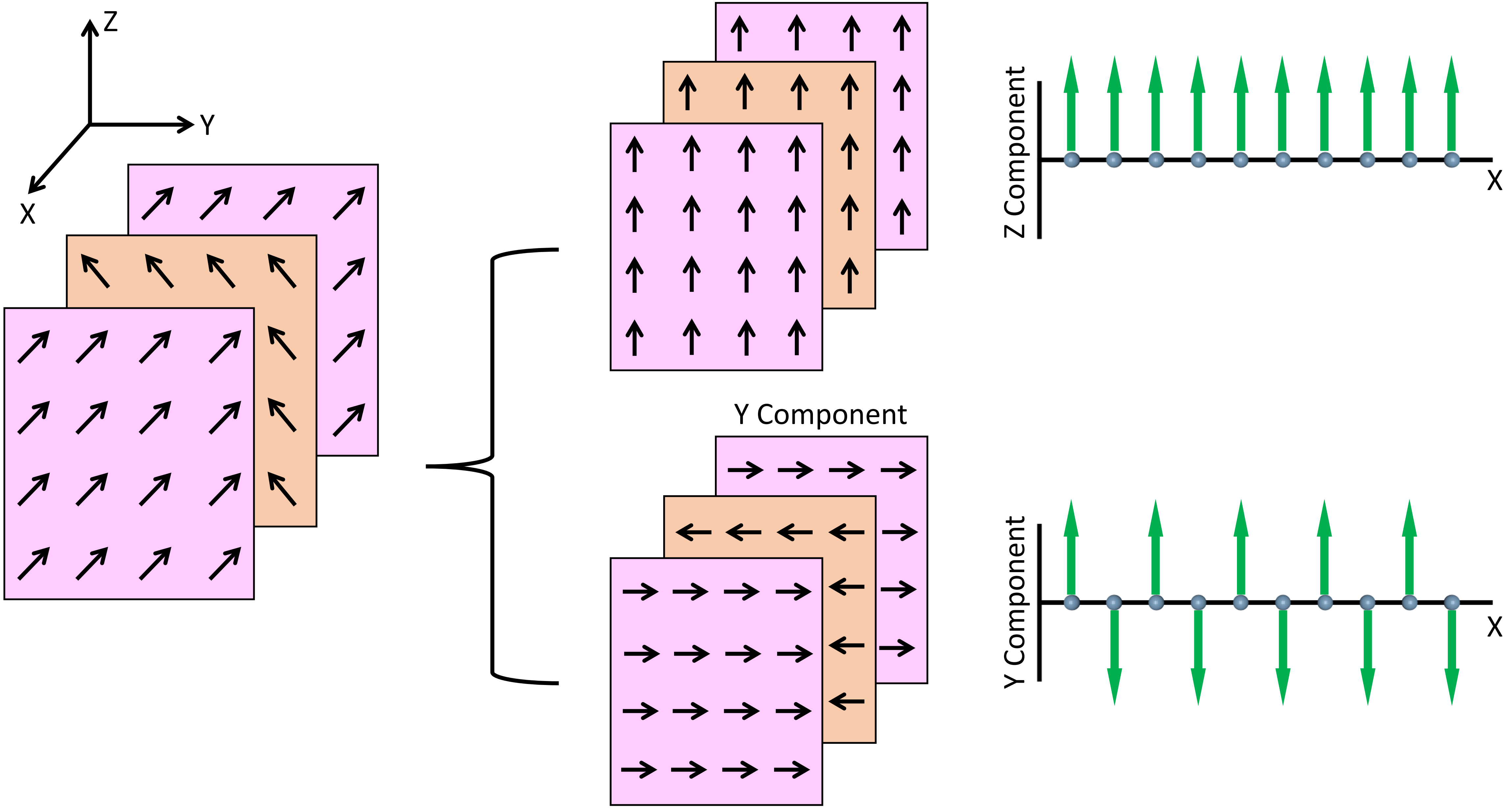
Famous Illustration by
Chuck Majkrzak, c.XXXX

Magnetic Scattering

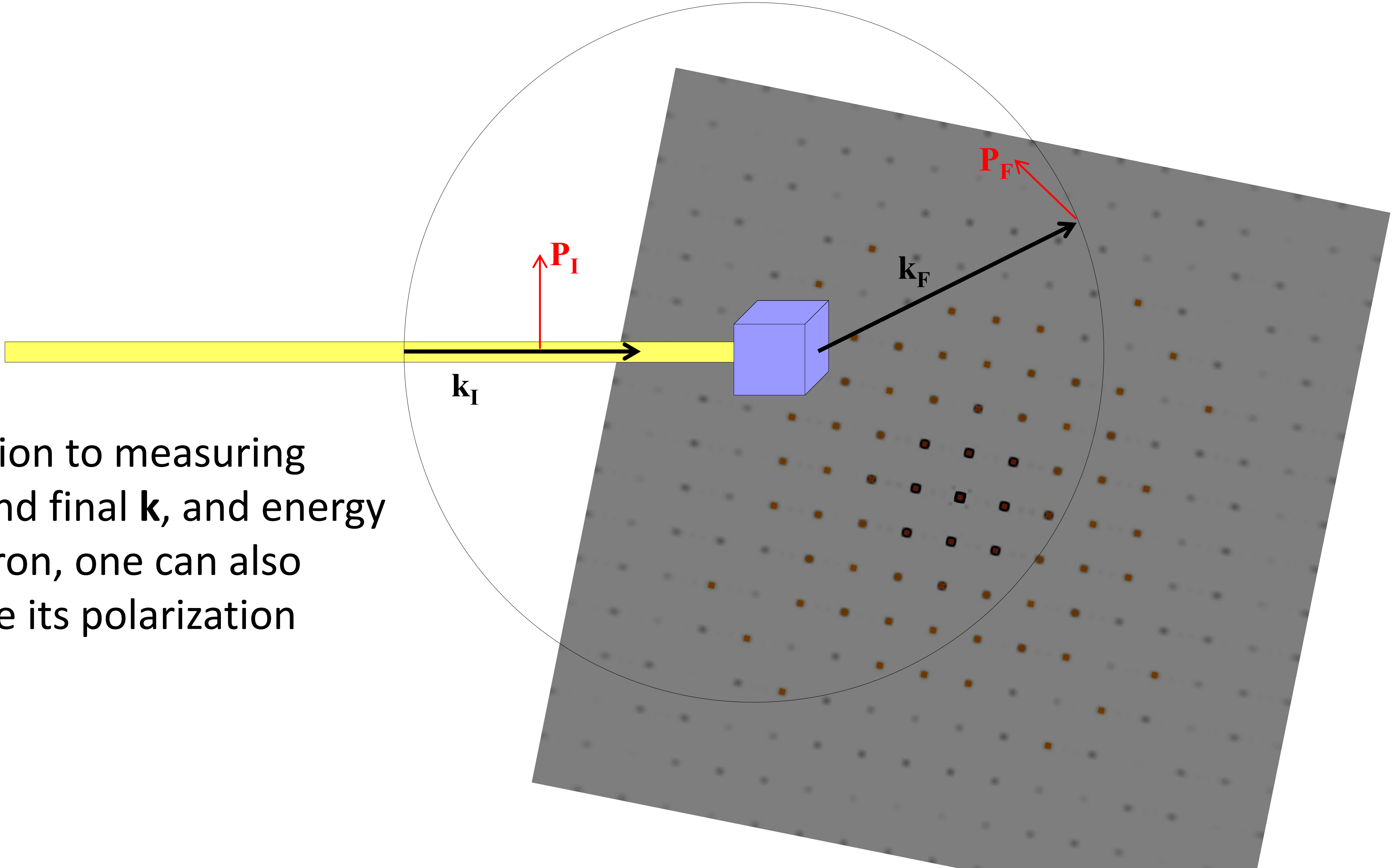
Crystallographic Unit Cell ≠ Magnetic Unit Cell



Magnetic Scattering



Neutrons can be polarized

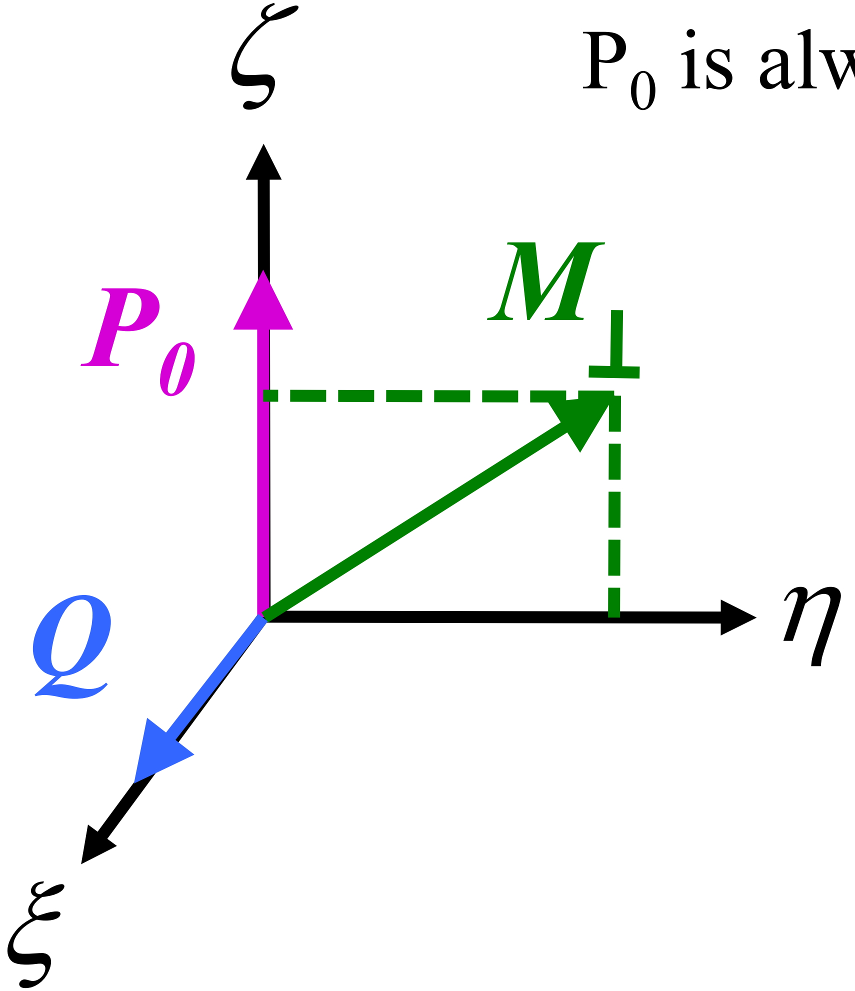


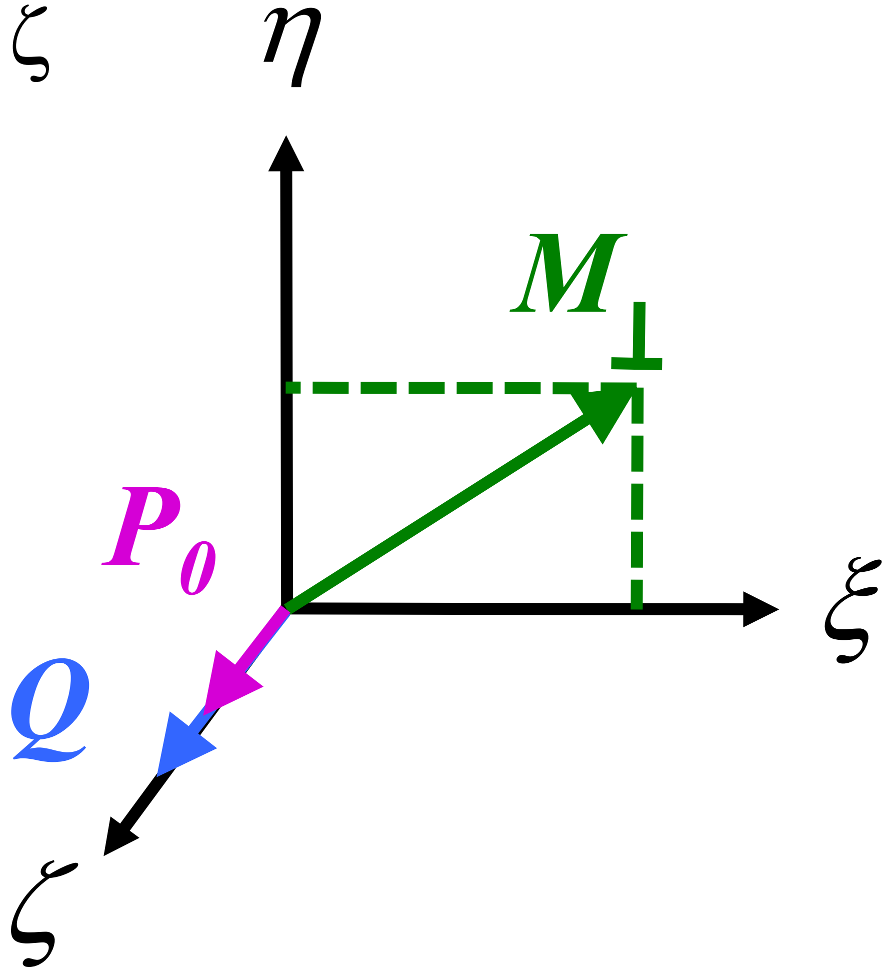
In addition to measuring initial and final **k**, and energy of neutron, one can also measure its polarization

Two traditional ways to polarize neutrons

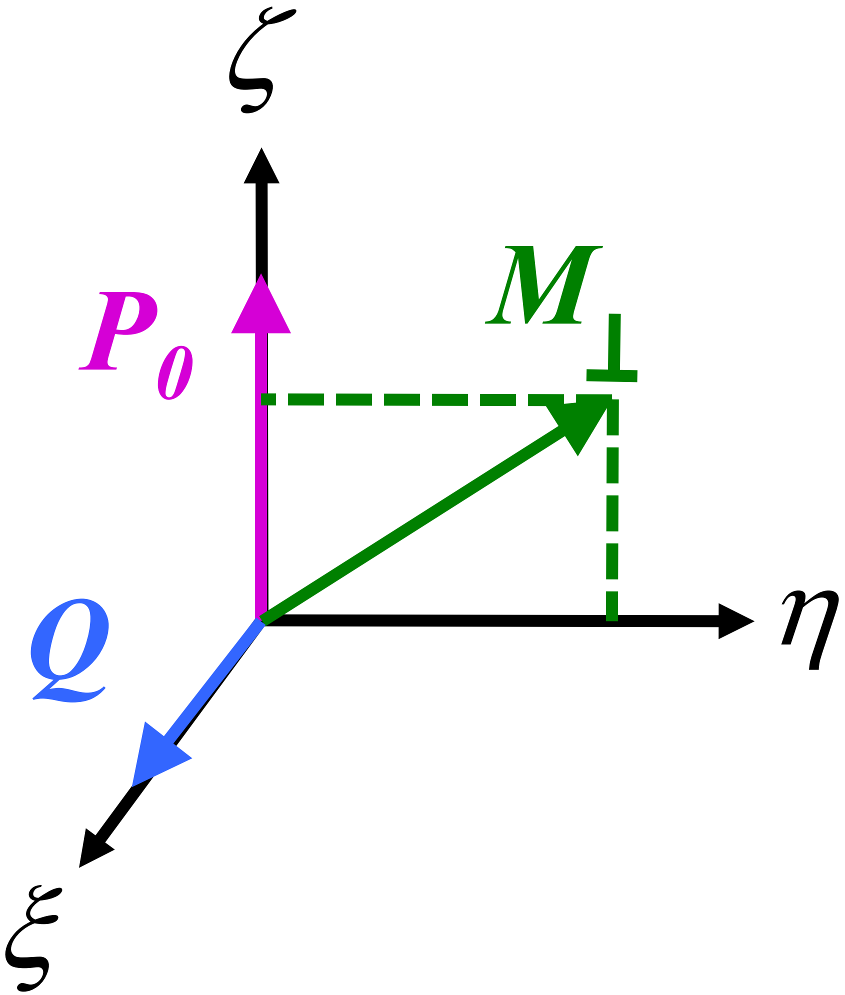
ζ, η, ξ is our reference frame

P_0 is always along ζ





Vertical polarization



The non-spin flip channels

$$U^{++} = b - pM_{\perp\zeta}$$

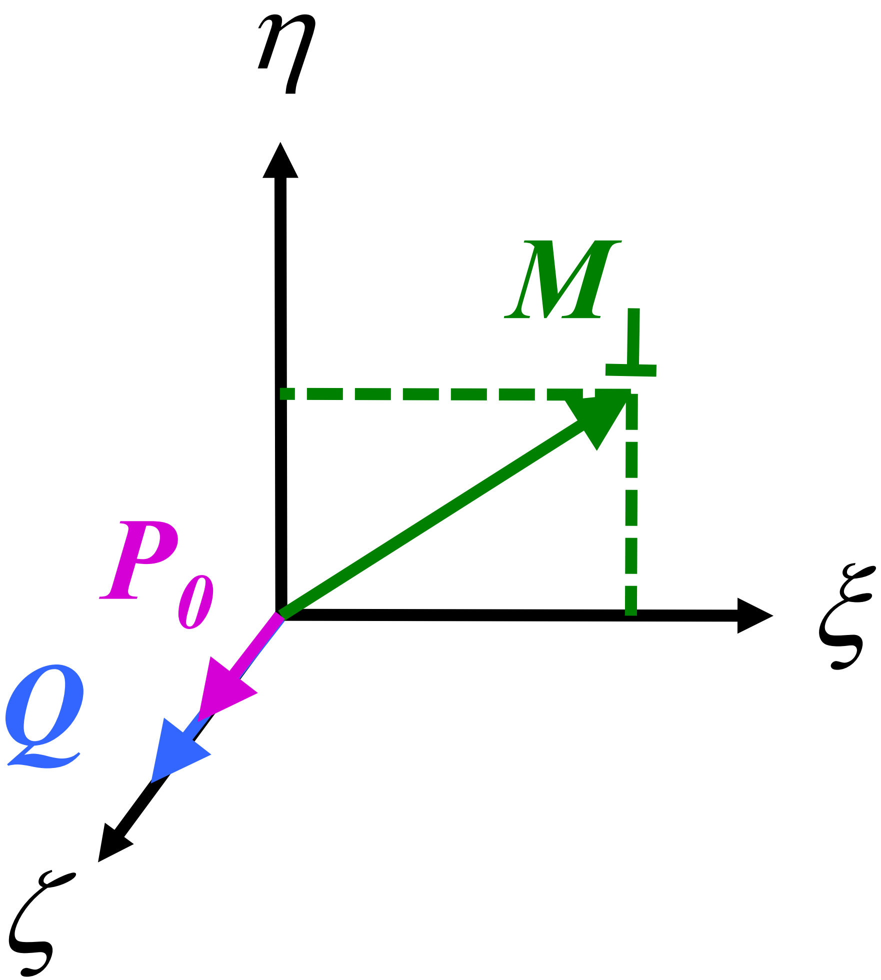
$$U^{--} = b + pM_{\perp\zeta}$$

The spin flip channels

$$U^{+-} = -(M_{\perp\zeta} + iM_{\perp\eta})$$

$$U^{-+} = -(M_{\perp\zeta} - iM_{\perp\eta})$$

Uniaxial polarization along Q



<u>The non-spin flip channels</u>

$$U^{++} = b - pM_{\perp}$$

$$U^{--} = b + pM_{\perp}$$

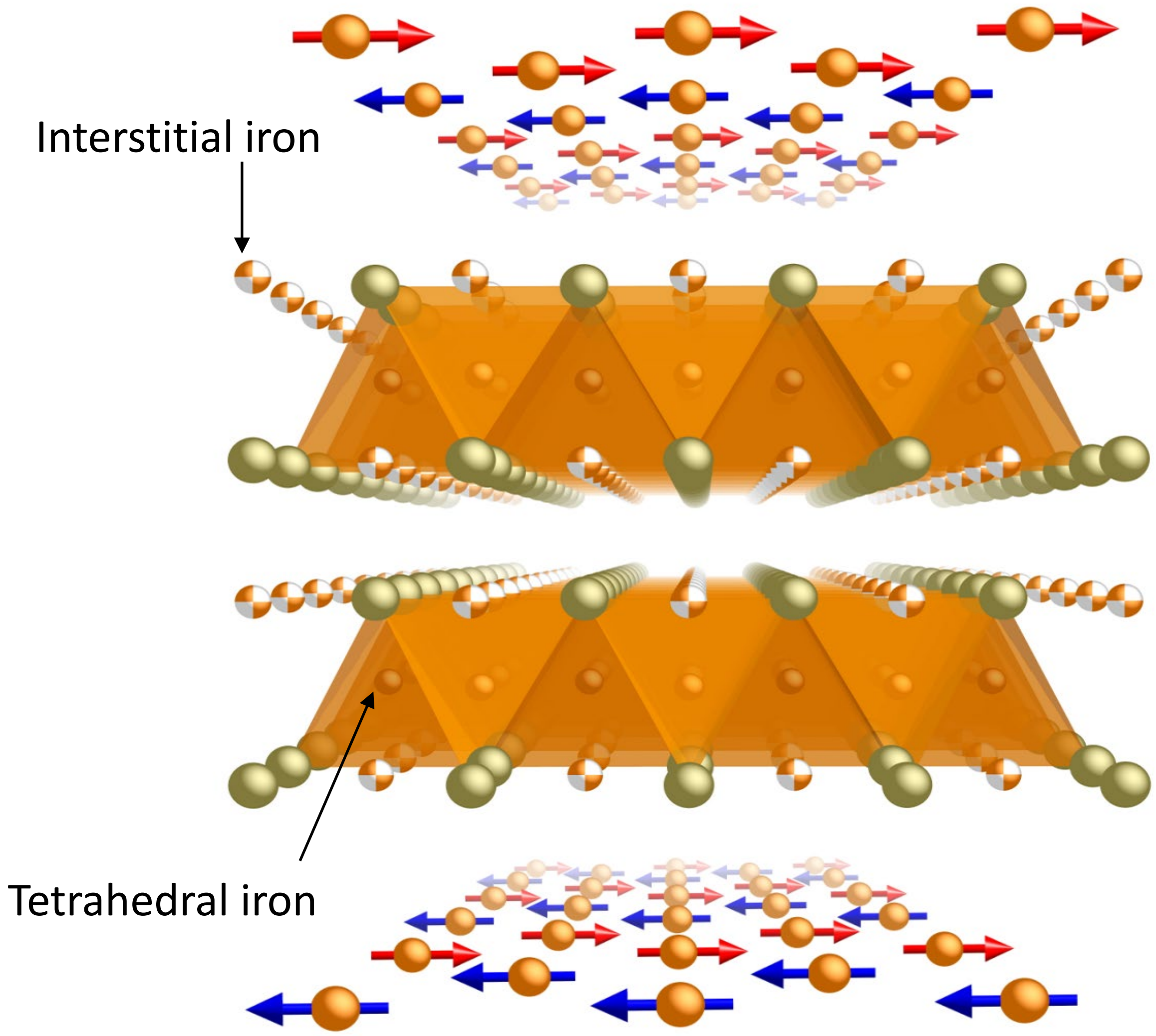
<u>The spin flip channels</u>

$$U^{+-} = -(M_{\perp\xi} + iM_{\perp\eta})$$

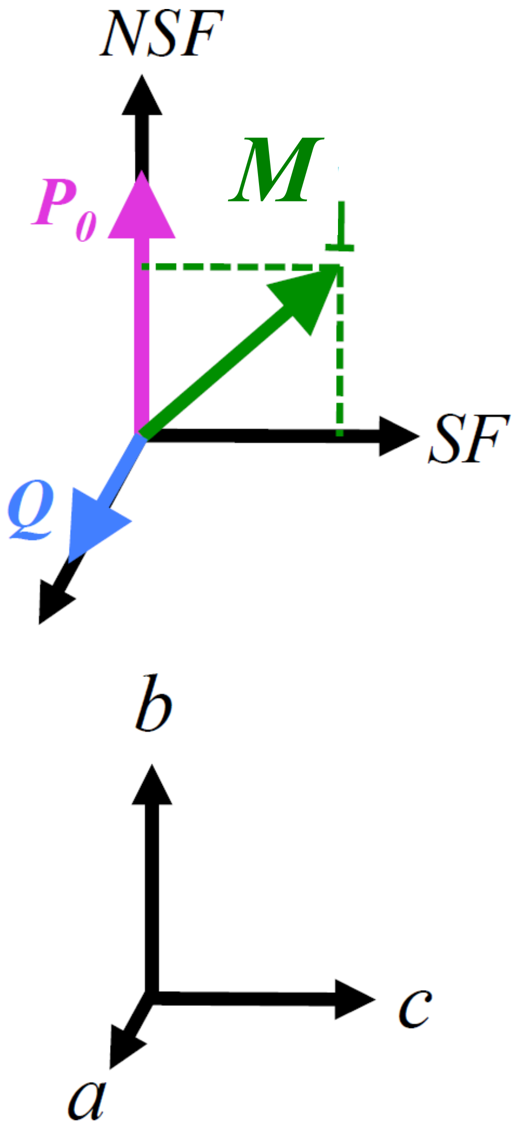
$$U^{-+} = -(M_{\perp\xi} - iM_{\perp\eta})$$

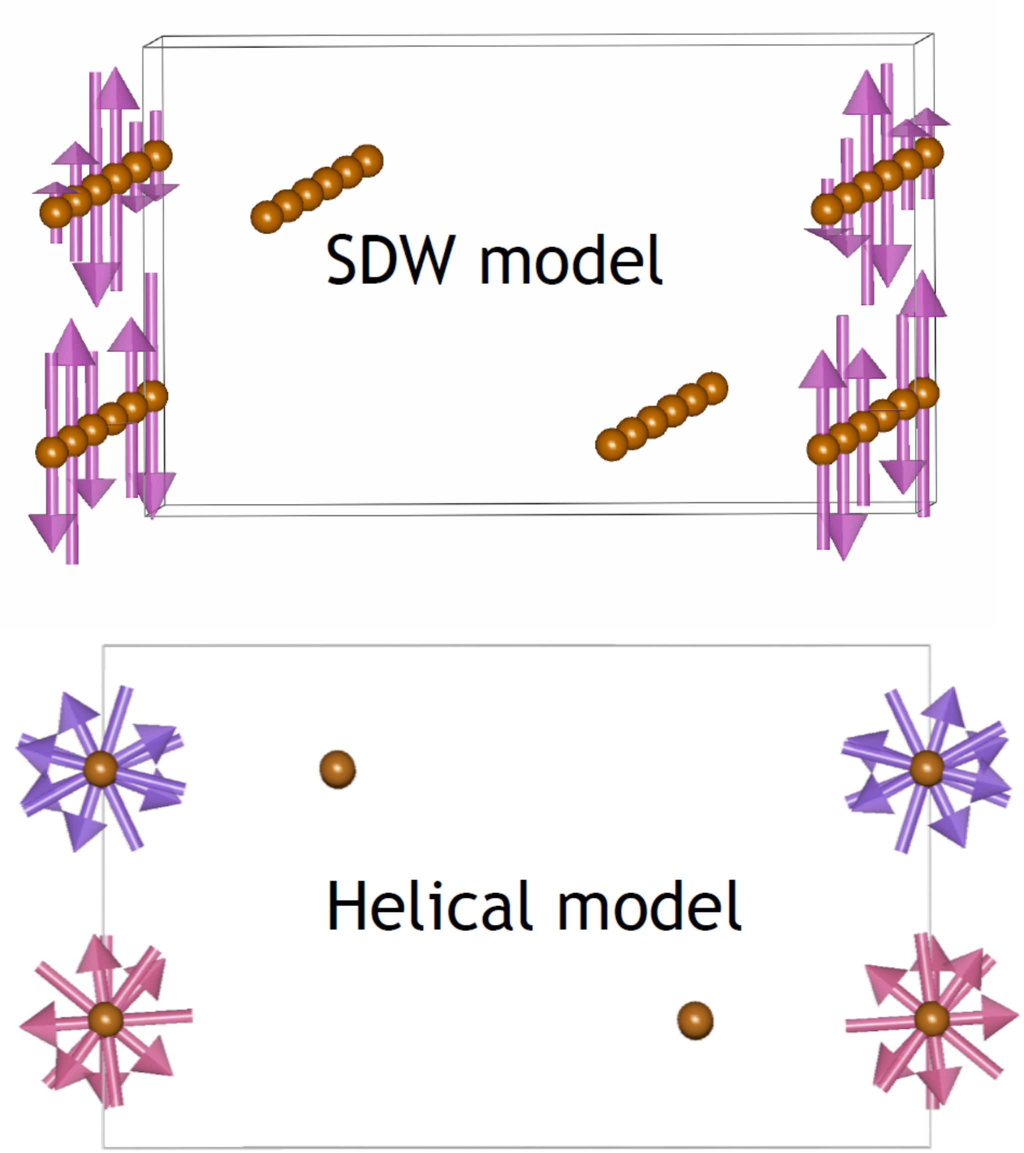
Example: Parent superconductor $Fe_{1+x}Te$

- $Fe_{1+x}Te$ is an antiferromagnetic semiconductor or semimetal depending on value of x.
- *x* is the amount of interstitial iron between the FeTe sheets
- Structurally similar to the FeAs-based superconductors
- Magnetic properties and magnetic structure also dependent on *x*.
- Becomes superconducting with anion substitution, e.g. $FeTe_{1-y}Se_y$ and $FeTe_{1-y}S_y$



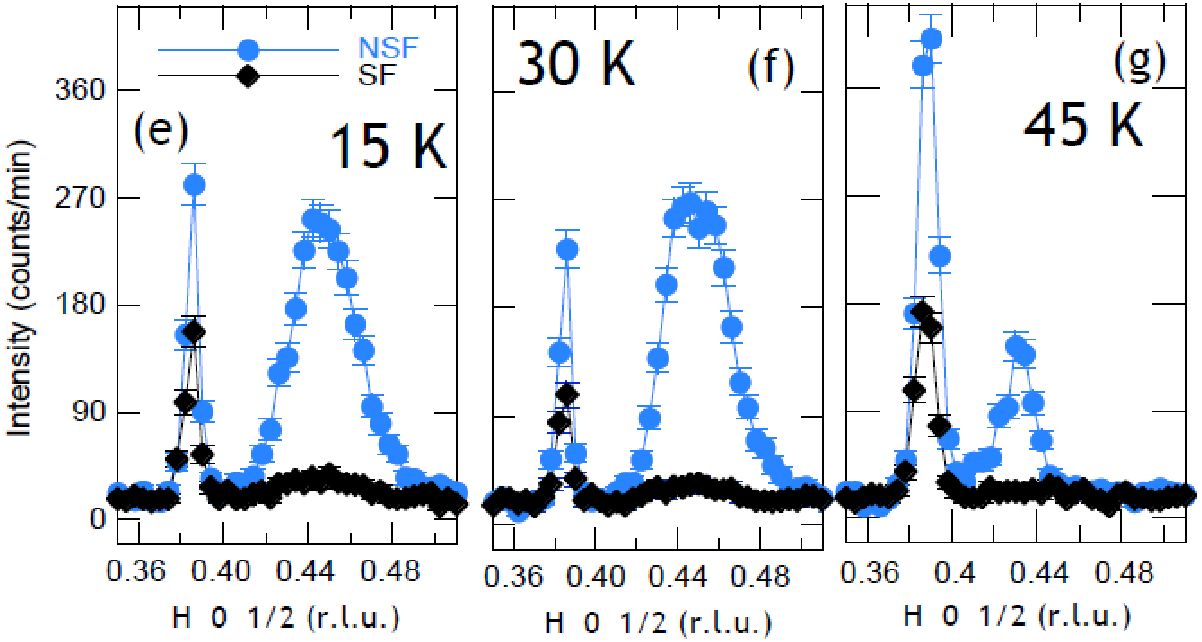
Vertically polarized neutron diffraction on crystals

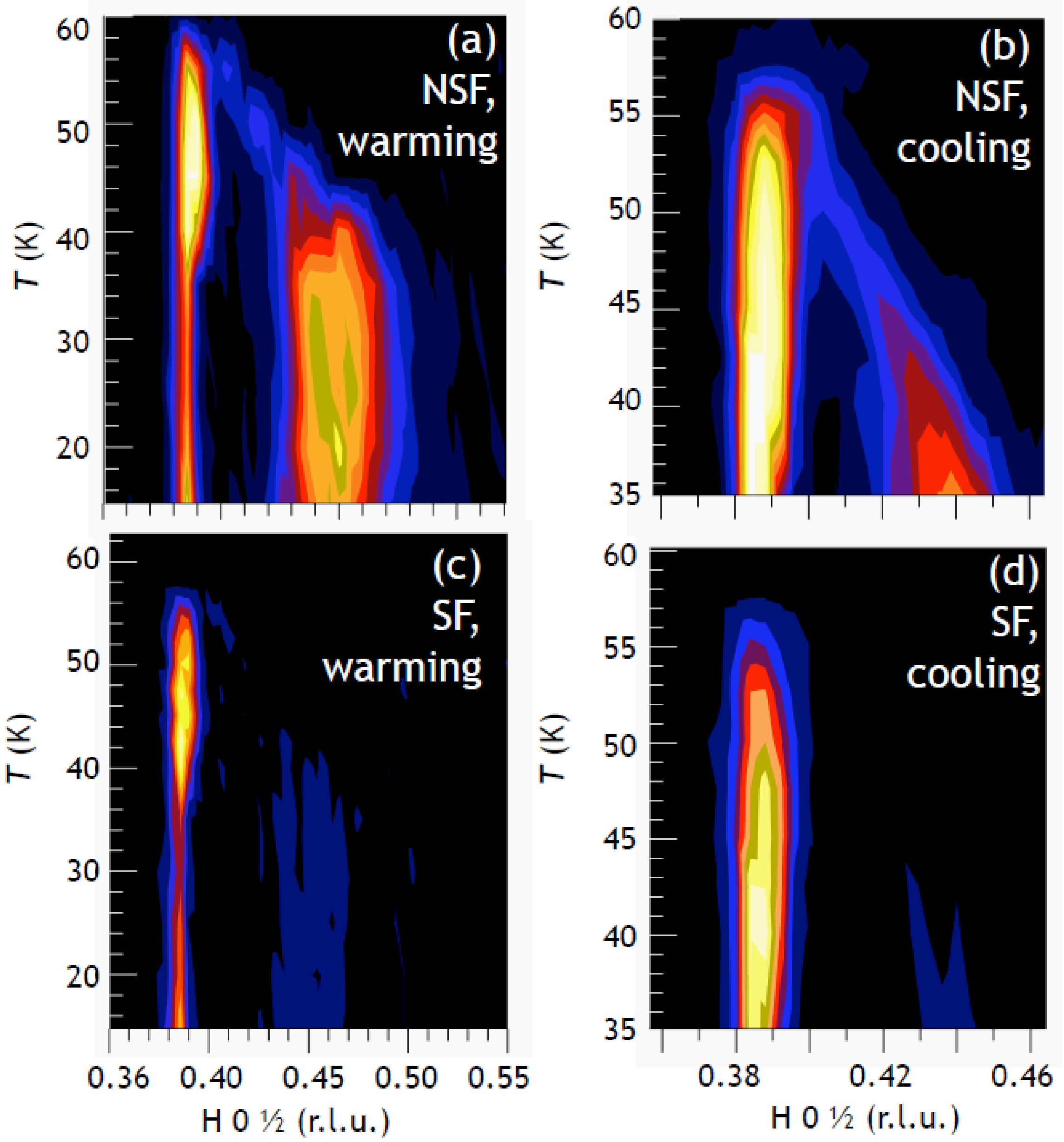




Polarized results for $Fe_{1+x}Te$ crystal, x = 12 %

- Two magnetic structures related
- One is a spiral, resolution-limited
- Other is a spin density wave, with broad peak width
- Spectral weight is shifted as transition temperature is approached





Questions?