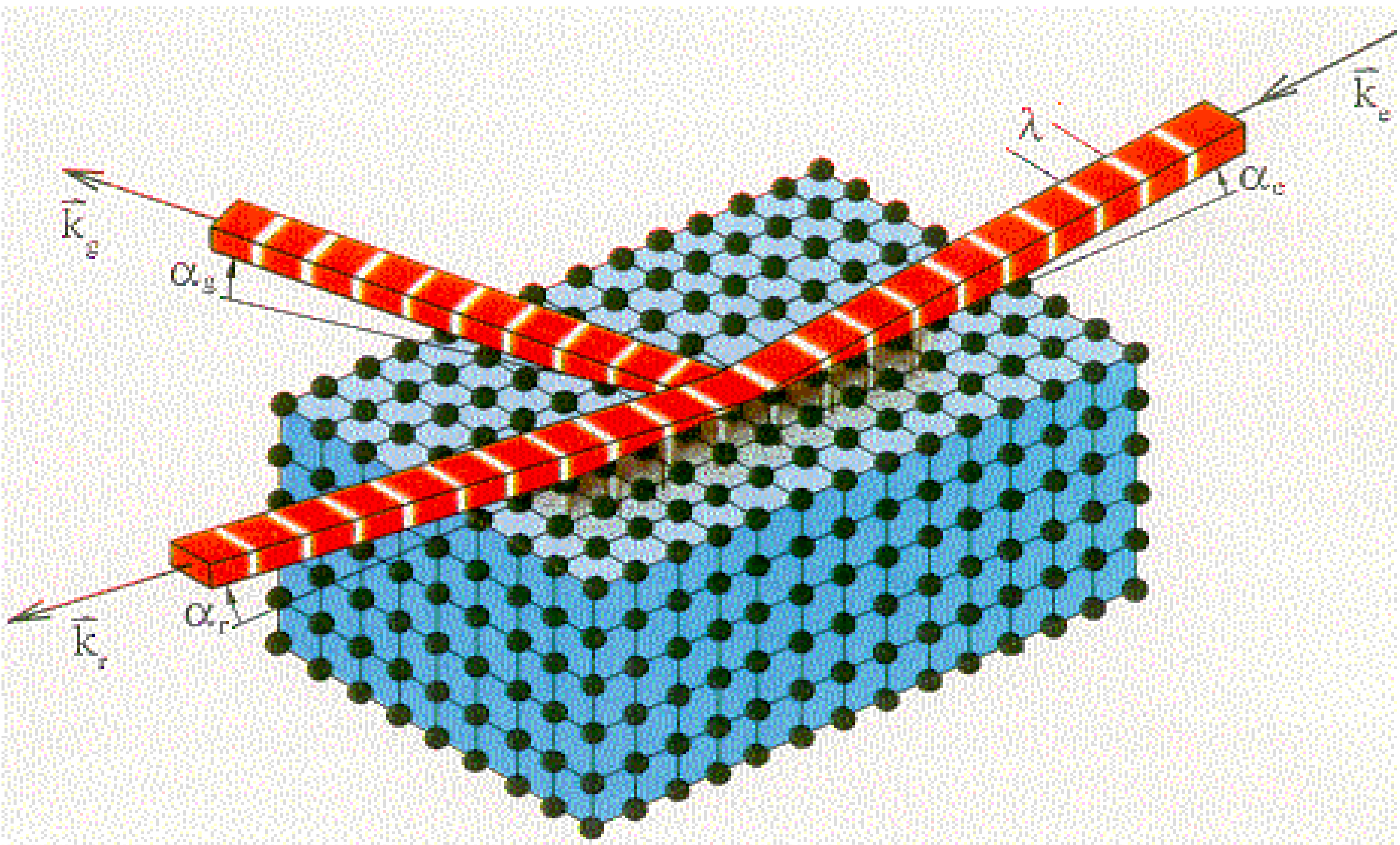
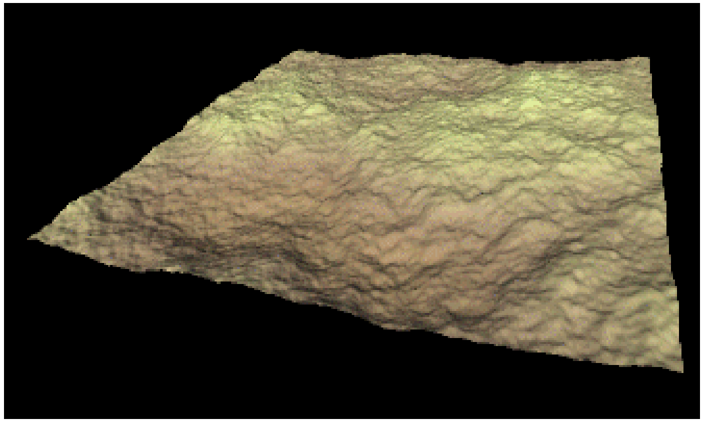
Grazing-Incidence-Diffraction

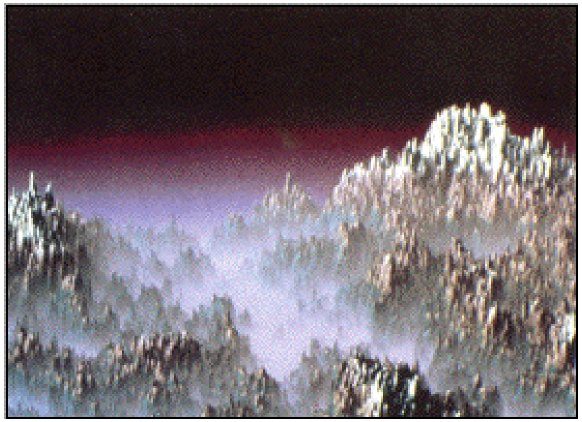


What do Specular and Off-specular scattering measure?

- **Specular reflectivity** measures variations in scattering density normal to surface (averaged over x,y plane)
- **Off-specular scattering** measures (x,y) variations of scattering density, e.g. due to roughness, magnetic domains, etc.

Almost all real surfaces are rough!





Self-Affine Fractal Surfaces

Let $\delta z(\mathbf{r})$ be height fluctuation about average surface at point $\mathbf{r}$ in 2D plane.

R.m.s. roughness σ is defined by

$\sigma^2 = < [\delta z(\mathbf{r})]^2 >$

Consider quantity

$$G(\mathbf{R}) = < [\delta z(\mathbf{r}) - \delta z(\mathbf{r}+\mathbf{R})]^2 >$$

For self-affine surfaces,

$$G(\mathbf{R}) = AR^{2h} \qquad 0<h<1$$

h is called the roughness exponent.

For real surfaces, there must be a cutoff length ξ.

$$G(\mathbf{R}) = 2\sigma^2(1 - \exp(-[R/ \xi]^{2h})$$

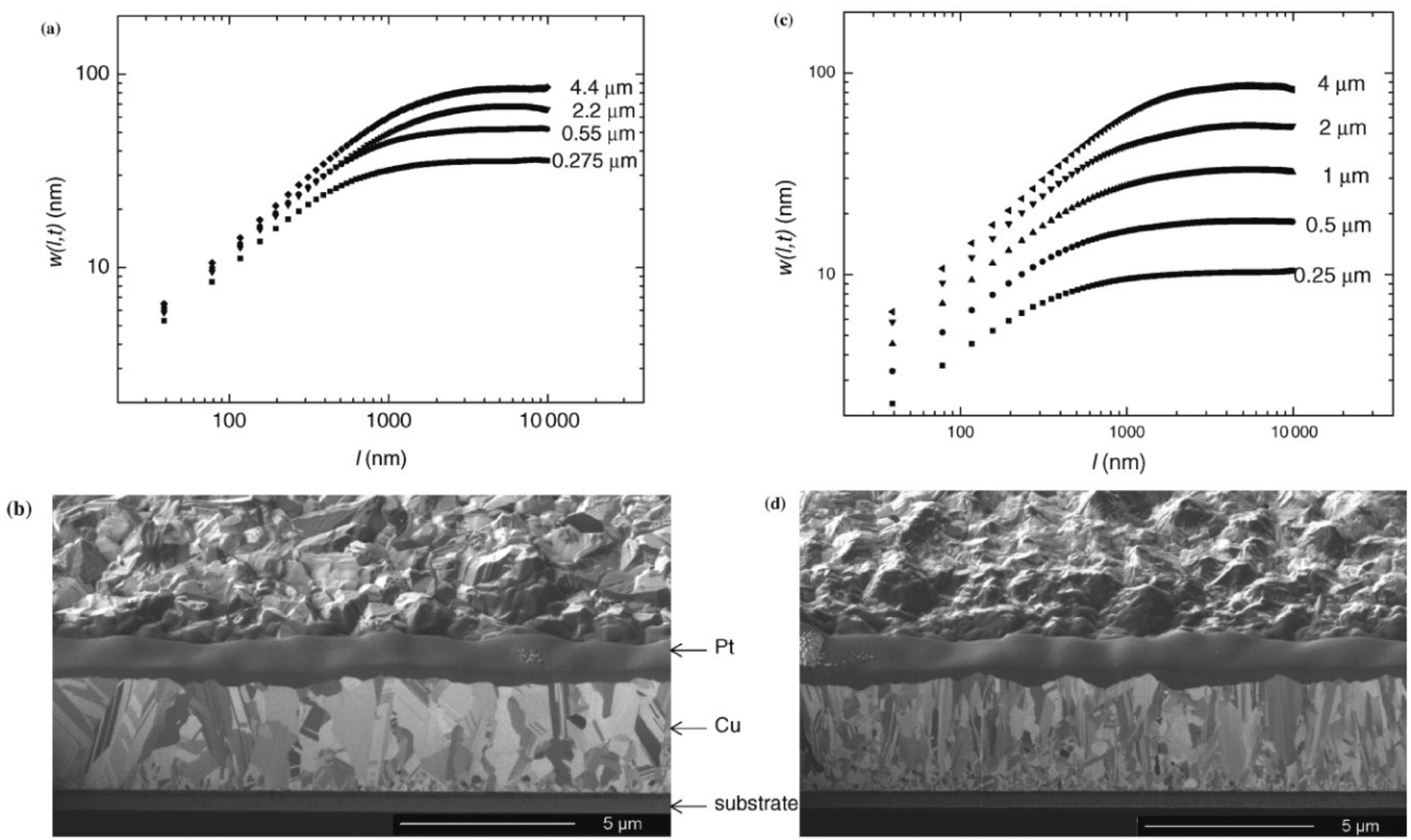
This implies that the **height-height correlation function**

$C(\mathbf{R})= <\delta z(\mathbf{r})\delta z(\mathbf{r}+\mathbf{R})> = \sigma^2\exp(-[R/ \xi]^{2h})$

AFM/FIB Studies-Electrodeposition

M.C. Lafouresse et al., PRL 98, 236101 (2007)

Cu Films



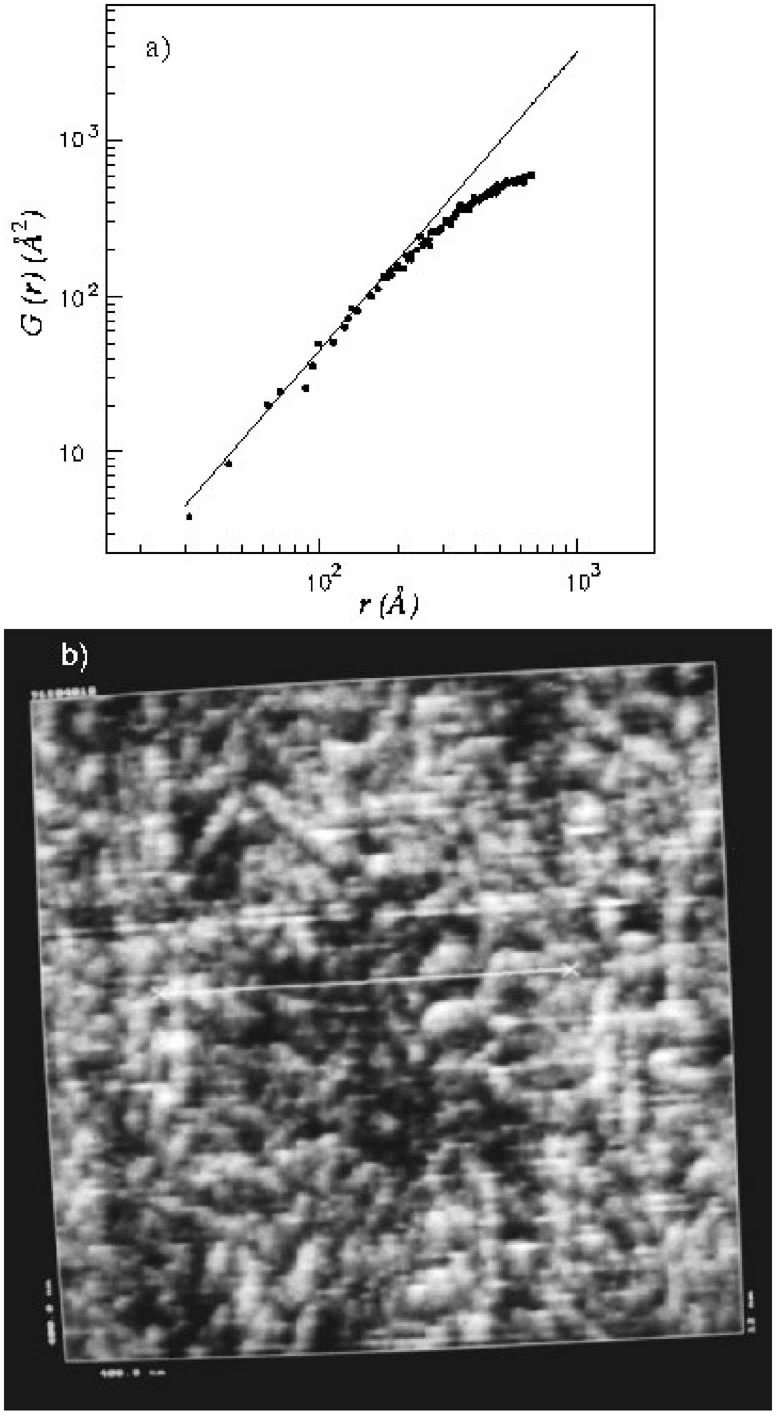
Scattering from a Self-Affine Fractal Surface

$$S(\vec{q}) = (Ar_0^2 / q_z^2)e^{-q_z^2\sigma^2} \iint dXdYe^{q_z^2 C(R)} e^{-i(q_x X + q_y Y)}$$

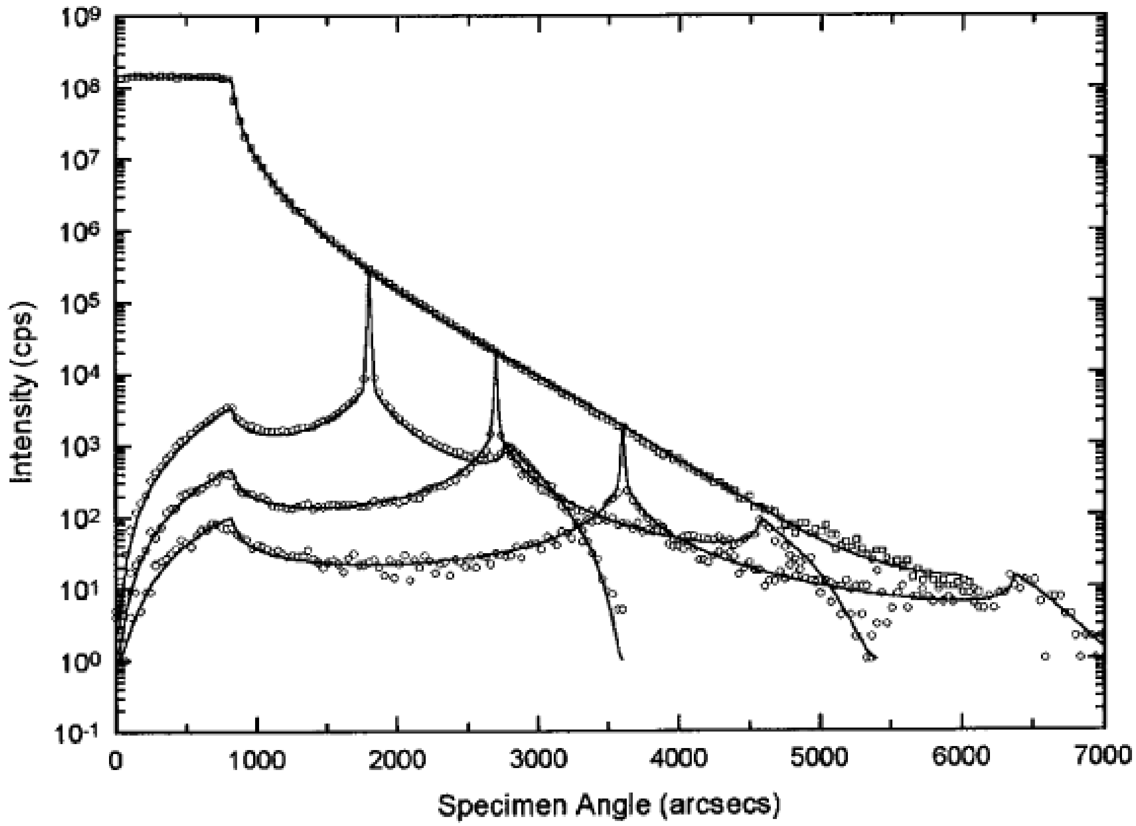
SKS et al., Phys. Rev. B 38, 2297 (1988)

Jun Wang et al., Europhys. Lett, 42 283-288 (1998)

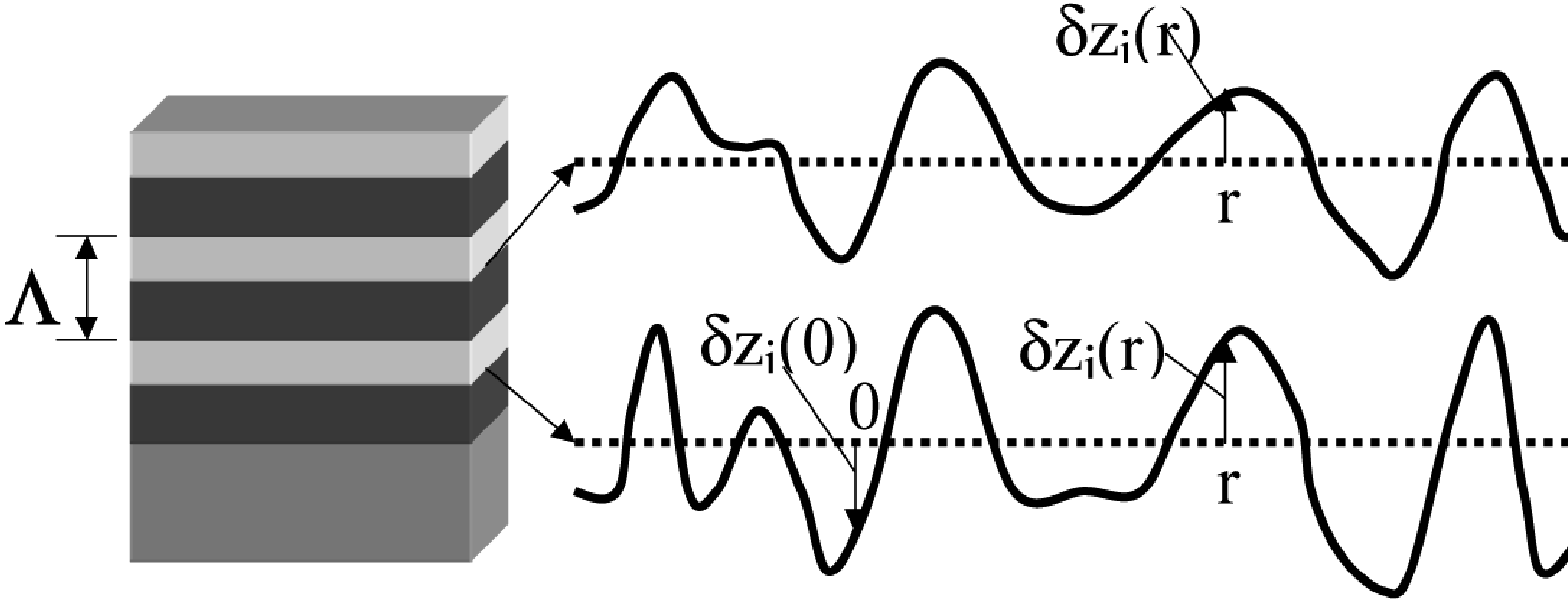
Mo layers



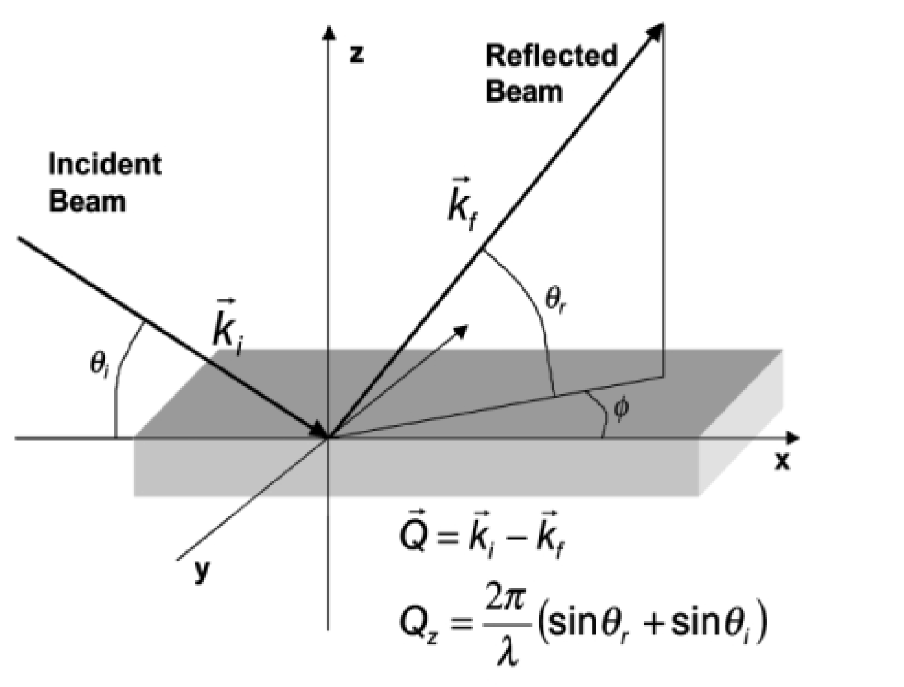
Example of Diffuse Scattering of X-Rays from a single rough surface



Multilayers



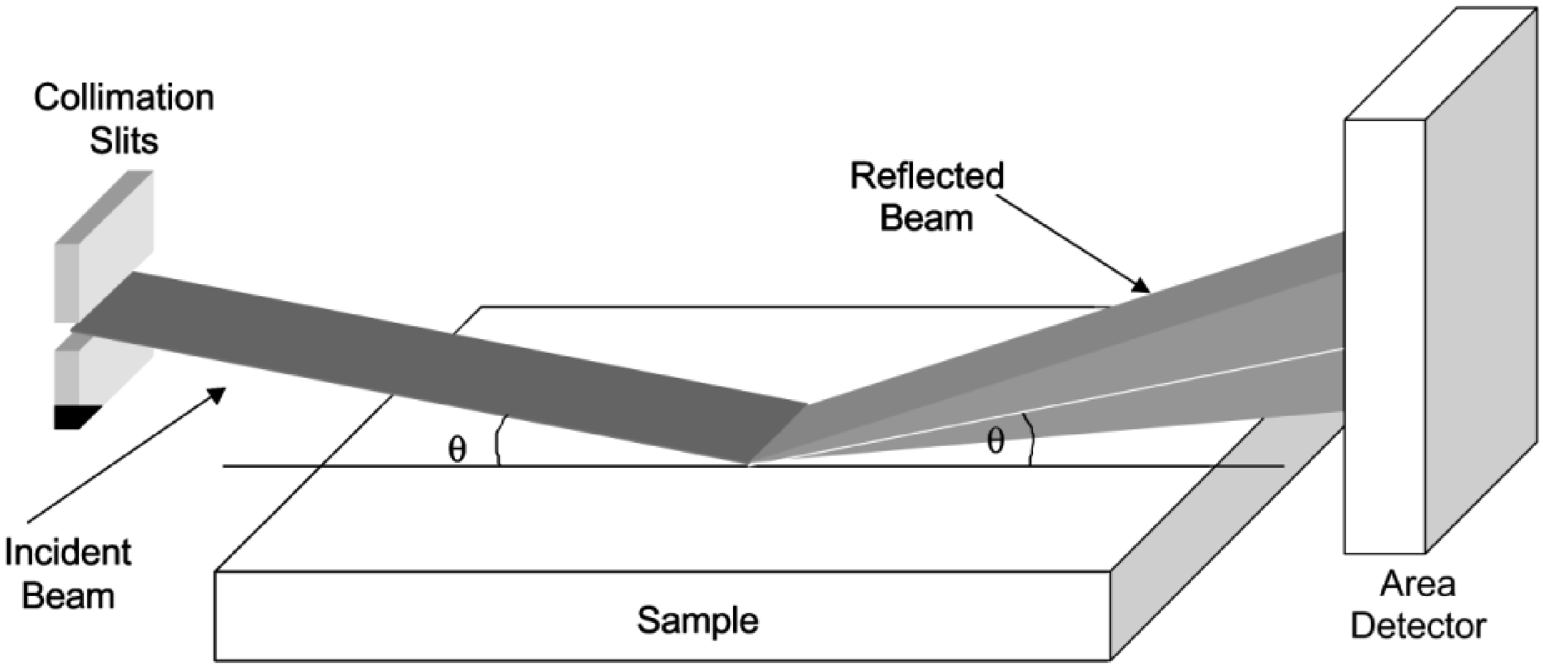
Vector Diagram for **Q** in GISAXS



$Q_y = (2\pi/\lambda)\mathrm{Cos}\theta_f \mathrm{Sin}\ \phi$

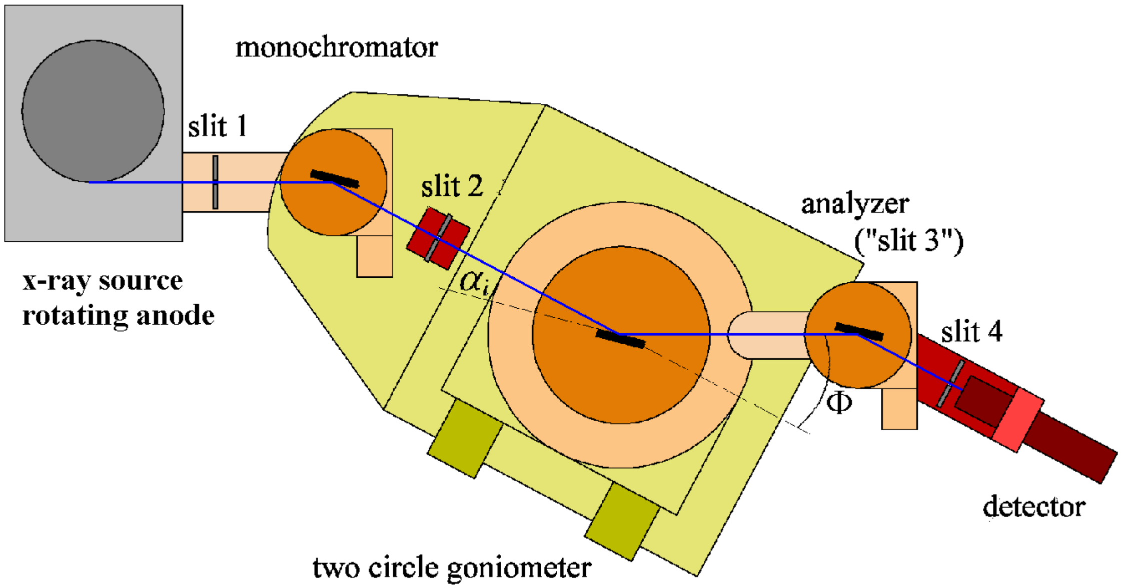
$Q_x = (2\pi/\lambda)(\mathrm{Cos}\ \theta_f \mathrm{Cos}\phi - \mathrm{Cos}\ \theta_i)$

Measurement of GISAXS



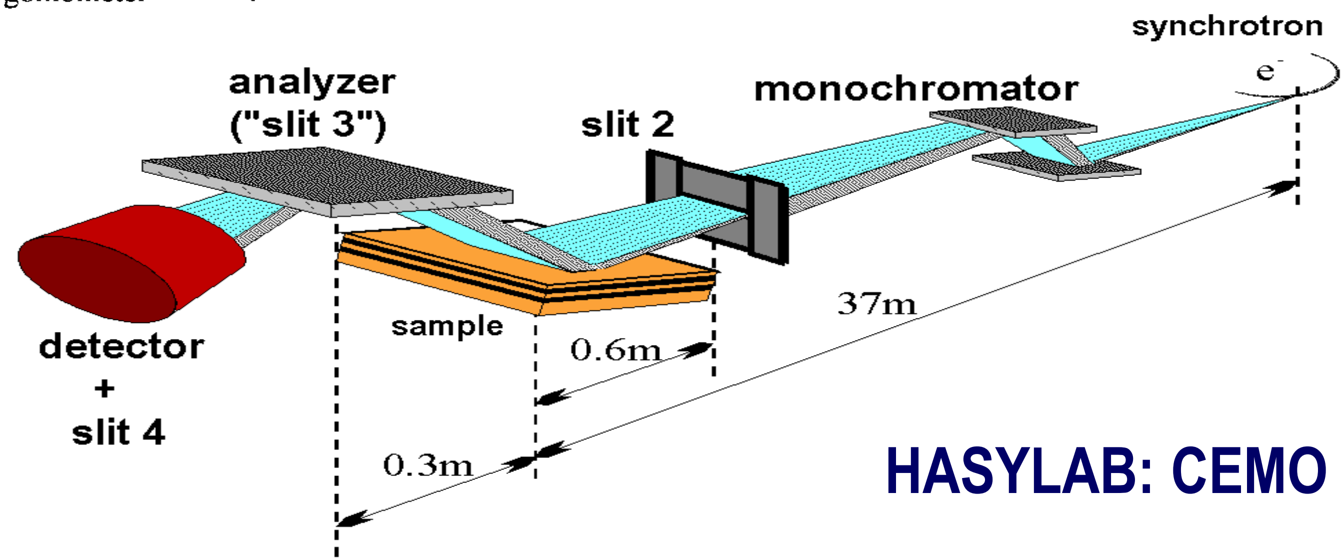
g. 2. A schematic diagram of an off-specular reflectivity experiment. A collimated polychromatic or monochromatic ribbon shaped beam is cident on the sample surface at angles of typically $\leq 2°$. The beam is reflected from the surface producing a diffuse signal about the specular rection. Multiwire or multielement detectors may be used as detectors or a single element detector may be scanned.

X-Ray Reflectometers



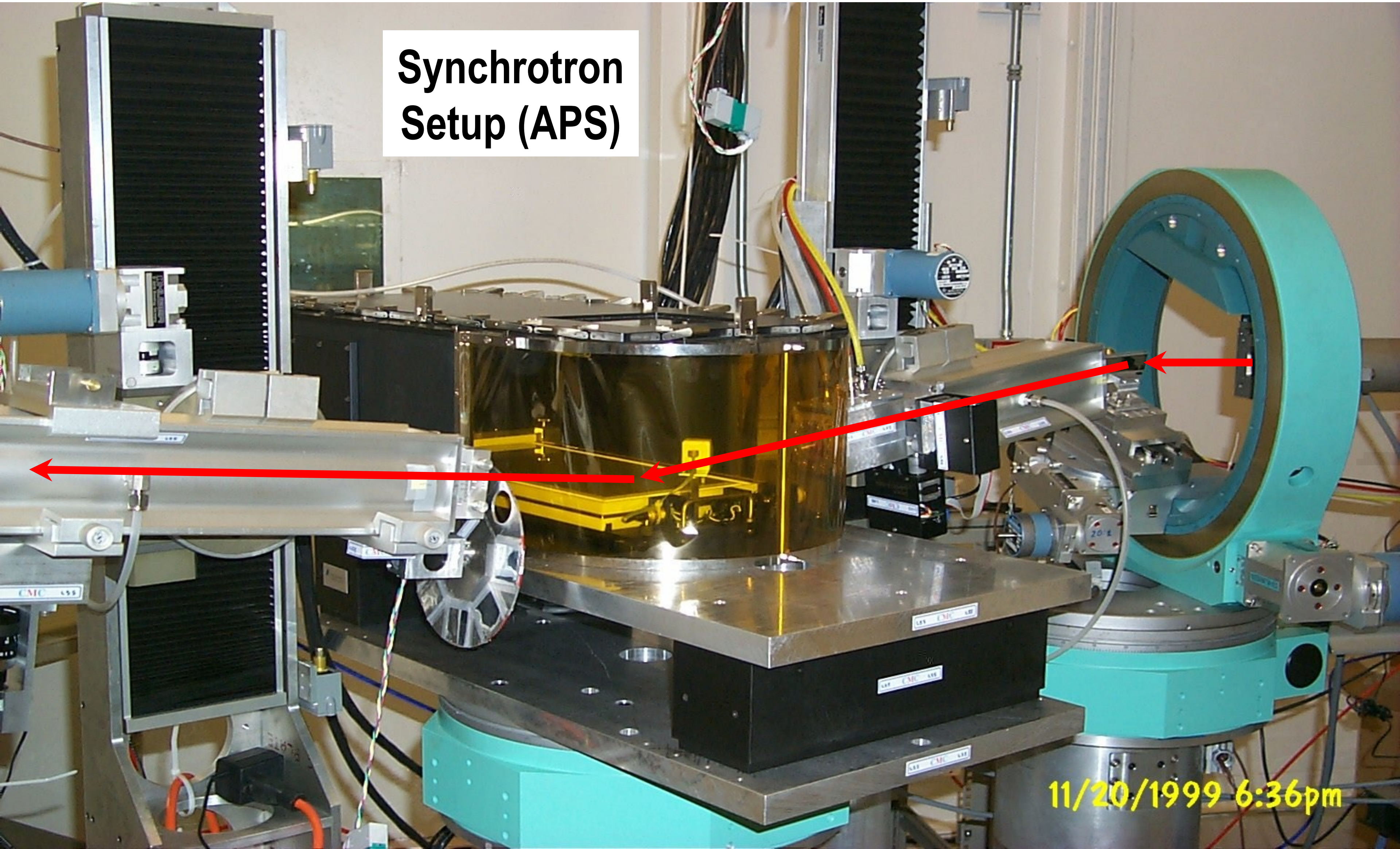
Laboratory Setup

Synchrotron Setup

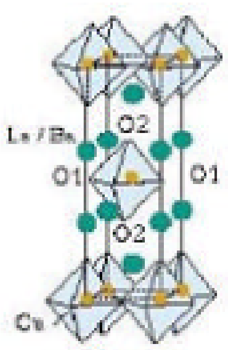


HASYLAB: CEMO

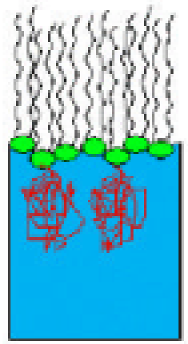
Reflectivity from Liquids I

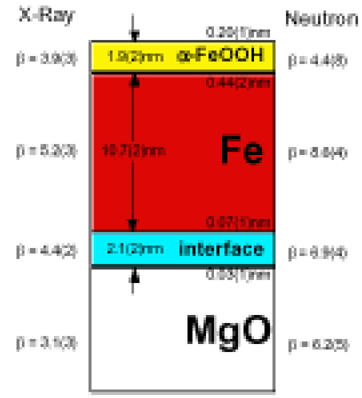


We Have Seen How Neutron Scattering Can Determine a Variety of Structures

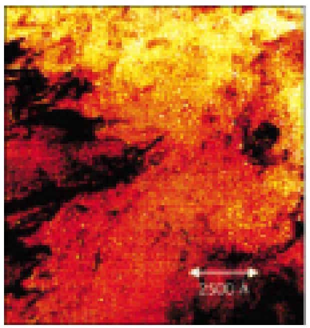


crystals

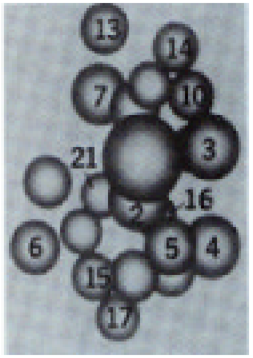




surfaces & interfaces

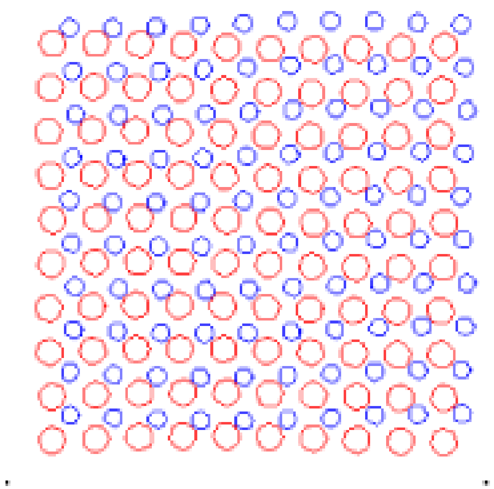


disordered/fractals



biomachines

but what happens when the atoms are moving?



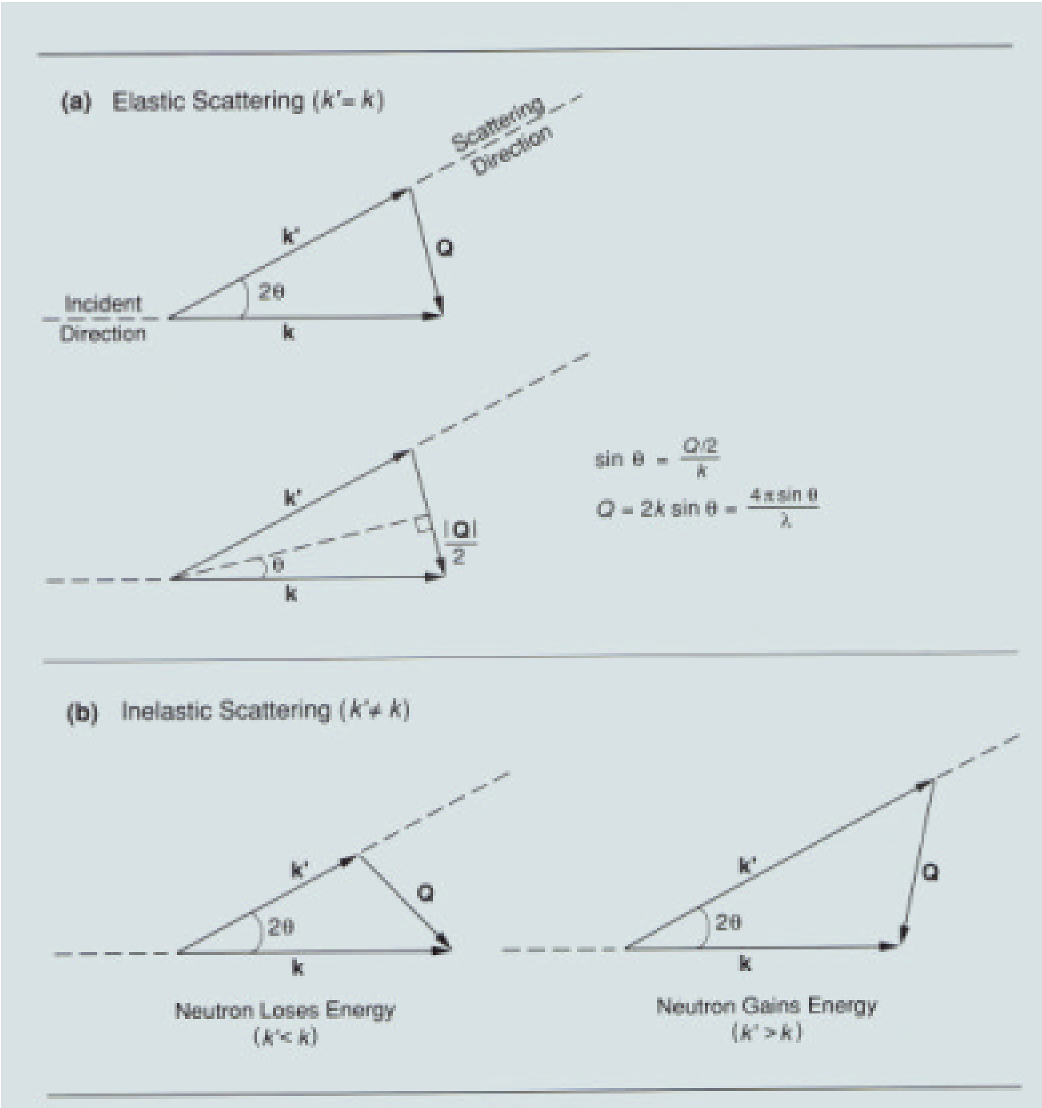
Can we determine the directions and time-dependence of atomic motions?

Can well tell whether motions are periodic?

Etc.

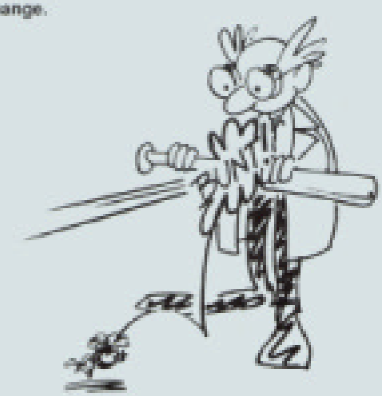
These are the types of questions answered by inelastic neutron scattering

The Neutron Changes Both Energy & Momentum When Inelastically Scattered by Moving Nuclei



inelastic scattering

Scattering in which exchange of energy and momentum between the incident neutron and the sample causes both the direction and the magnitude of the neutron's wave vector to change.



The Elastic & Inelastic Scattering Cross Sections Have an Intuitive Similarity

- The intensity of 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

- The intensity of 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*.

- For 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

The Inelastic Scattering Cross Section

Recall that $\left(\frac{d^2\sigma}{d\Omega . dE}\right)_{coh} = b_{coh}^2 \frac{k'}{k} NS(\vec{Q},\omega)$ and $\left(\frac{d^2\sigma}{d\Omega . dE}\right)_{inc} = b_{inc}^2 \frac{k'}{k} NS_i(\vec{Q},\omega)$

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

and the correlation functions that are intuitively similar to those for the elastic scattering case:

$G(\vec{r},t) = \frac{1}{N}\int\left\langle \rho_N(\vec{r},0)\rho_N(\vec{r}+\vec{R},t)\right\rangle d\vec{r}$ and $G_s(\vec{r},t) = \frac{1}{N}\sum_j \int\left\langle \delta(\vec{r}-\vec{R}_j(0))\delta(\vec{r}+\vec{R}-\vec{R}_j(t))\right\rangle d\vec{r}$

The evaluation of the correlation functions (in which the ρ's and δ - functions have to be treated as non - commuting quantum mechanical operators) is mathematically tedious. Details can be found, for example, in the books by Squires or Marshal and Lovesey.

Examples of $S(Q,\omega)$ and $S_s(Q,\omega)$

- Expressions for $S(Q,\omega)$ and $S_s(Q,\omega)$ can be worked out for a number of cases e.g:
  - Excitation or absorption of one quantum of lattice vibrational energy (phonon)
  - Various models for atomic motions in liquids and glasses
  - Various models of atomic & molecular translational & rotational diffusion
  - Rotational tunneling of molecules
  - Single particle motions at high momentum transfers
  - Transitions between crystal field levels
  - Magnons and other magnetic excitations such as spinons
- Inelastic neutron scattering reveals details of the shapes of interaction potentials in materials

A Phonon is a Quantized Lattice Vibration

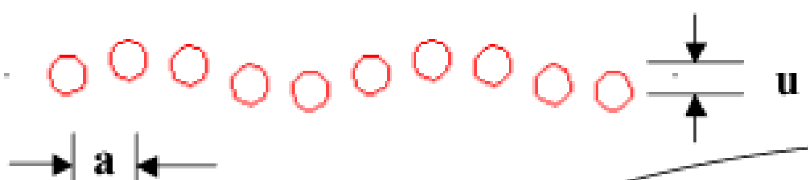
- Consider linear chain of particles of mass M coupled by springs. Force on n'th particle is

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

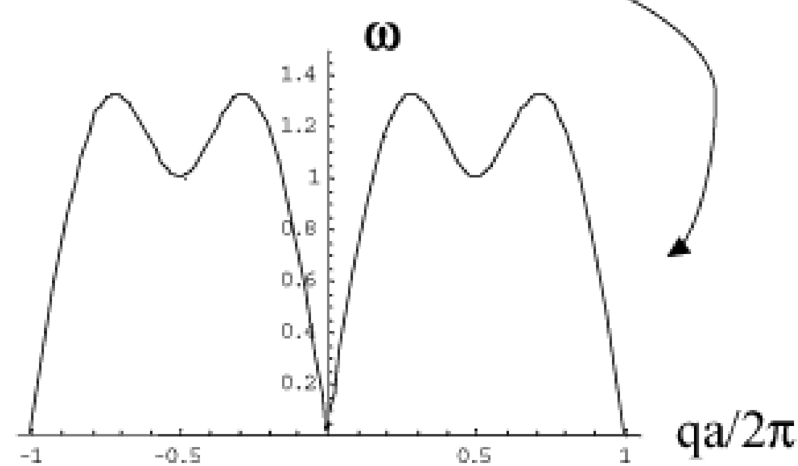
First neighbor force constant; displacements

- Equation of motion is $F_n = M\ddot{u}_n$
- Solution is: $u_n(t) = A_q e^{i(qna - \omega t)}$ 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



Inelastic Magnetic Scattering of Neutrons

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

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

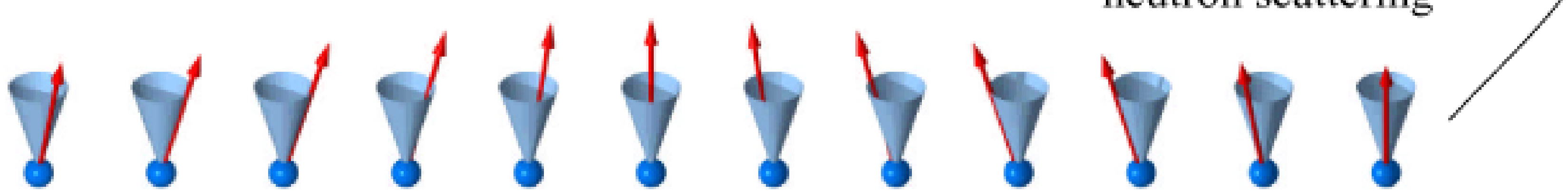
exchange coupling — ground state energy — spin waves (magnons)

with

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

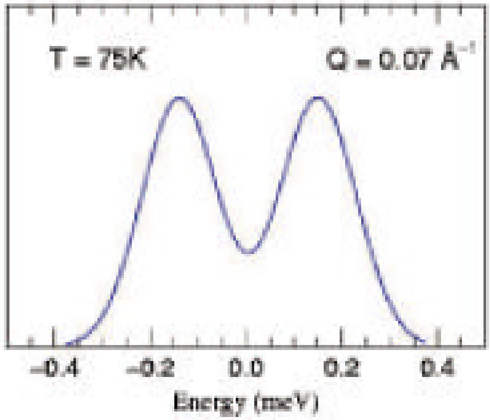
$\hbar\omega_q = Dq^2$ is the dispersion relation for a ferromagnet

Fluctuating spin is perpendicular to mean spin direction => spin-flip neutron scattering

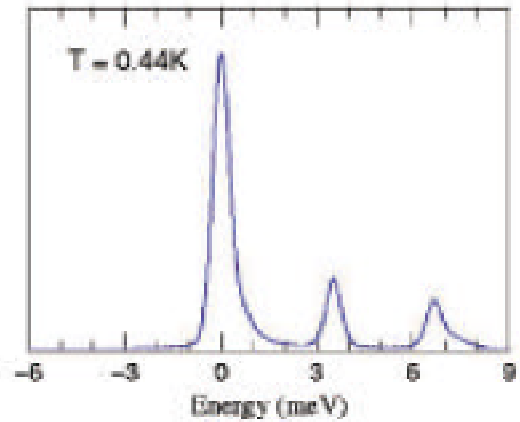


Spin wave animation courtesy of A. Zheludev (ORNL)

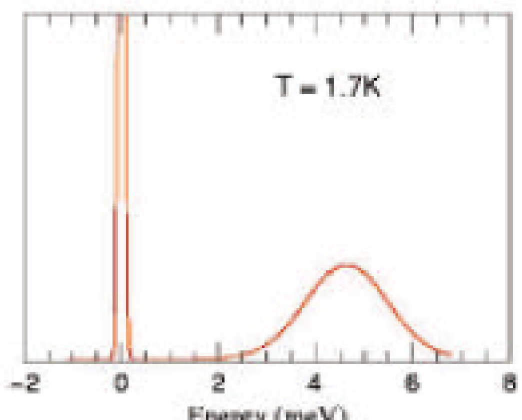
Measured Inelastic Neutron Scattering Signals in Crystalline Solids Show Both Collective & Local Fluctuations*



Spin waves – collective excitations



Crystal Field splittings ($HoPd_2Sn$) – local excitations

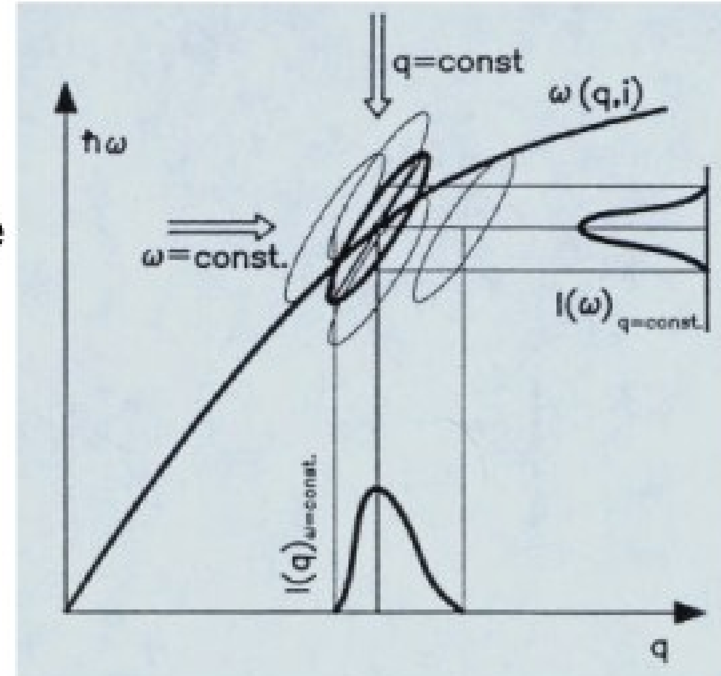


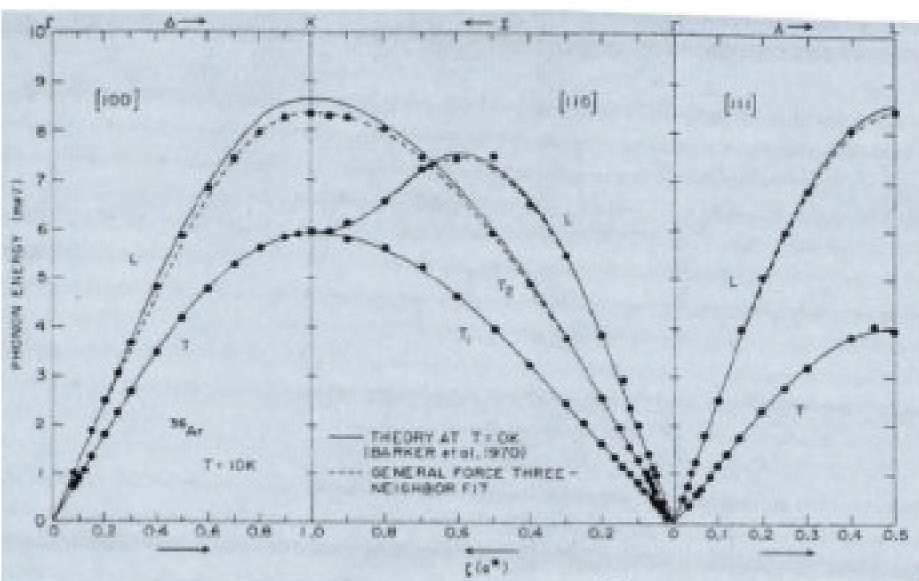
Local spin resonances (e.g. $ZnCr_2O_4$)

* Courtesy of Dan Neumann, NIST

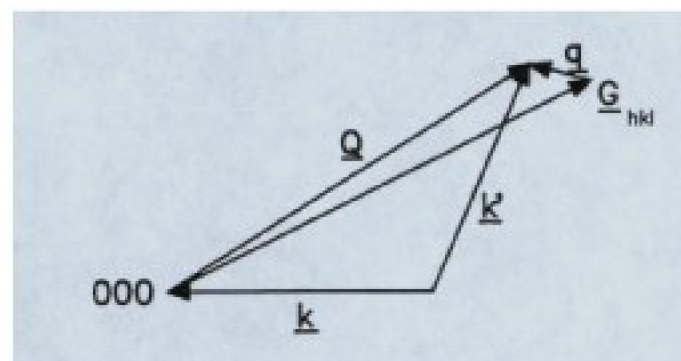
Triple Axis Spectrometers Have Mapped Phonons Dispersion Relations in Many Materials

- Point by point measurement in (Q,E) space
- Usually keep either k_I or k_F fixed
- Choose Brillouin zone (I.e. G) to maximize scattering cross section for phonons
- Scan usually either at constant-Q (Brockhouse invention) or constant-E

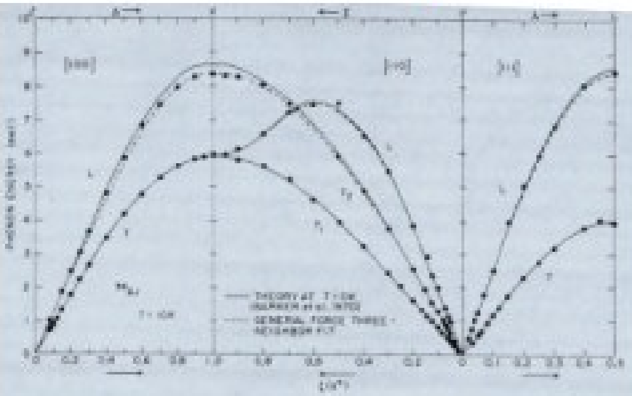




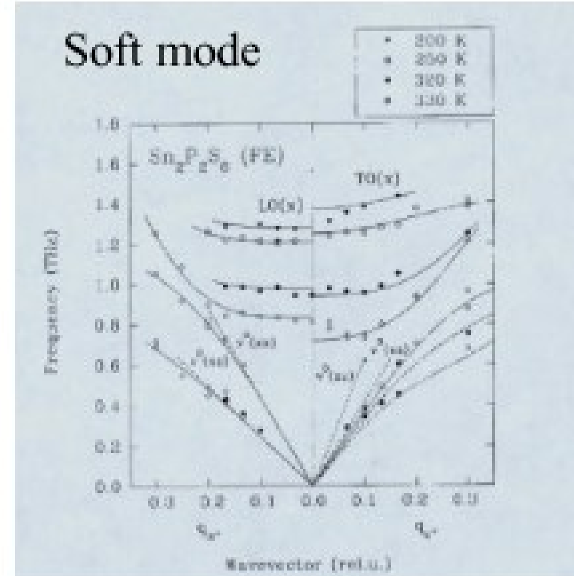
Phonon dispersion of ^{36}Ar

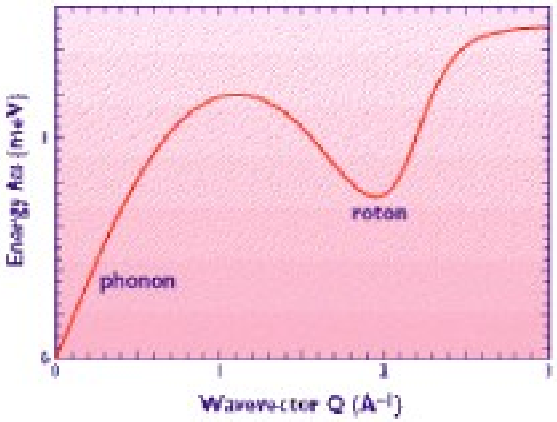


Examples of Phonon Measurements

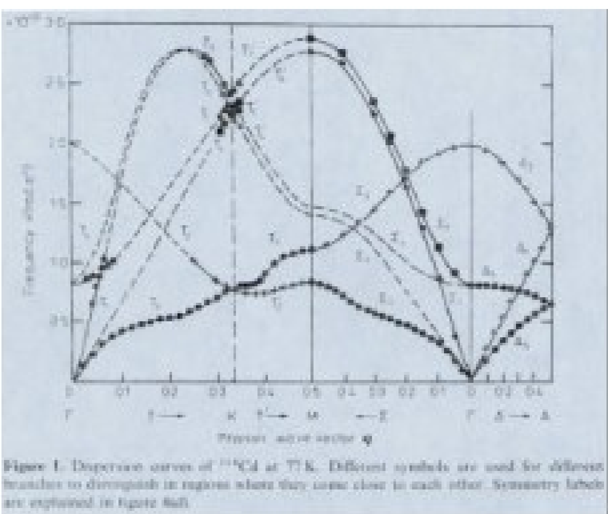


Phonons in ^{36}Ar – validation of LJ potential

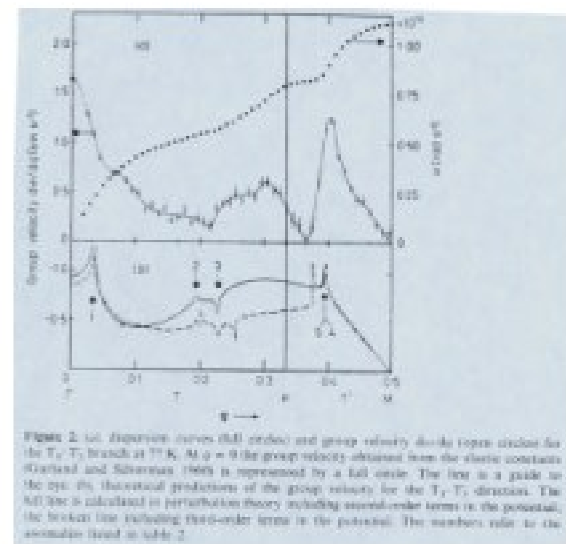




Roton dispersion in ^{4}He

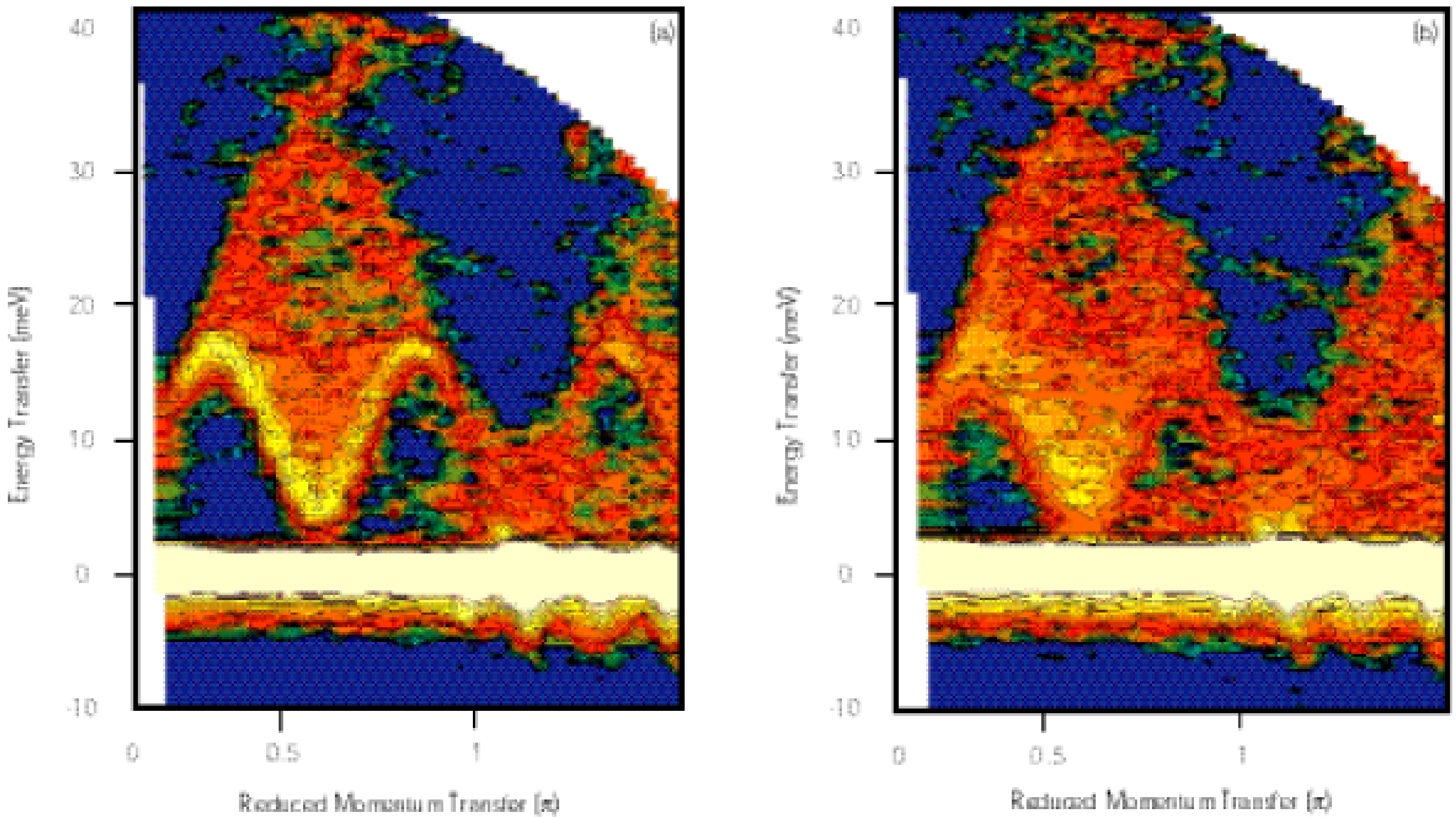


Phonons in ^{110}Cd



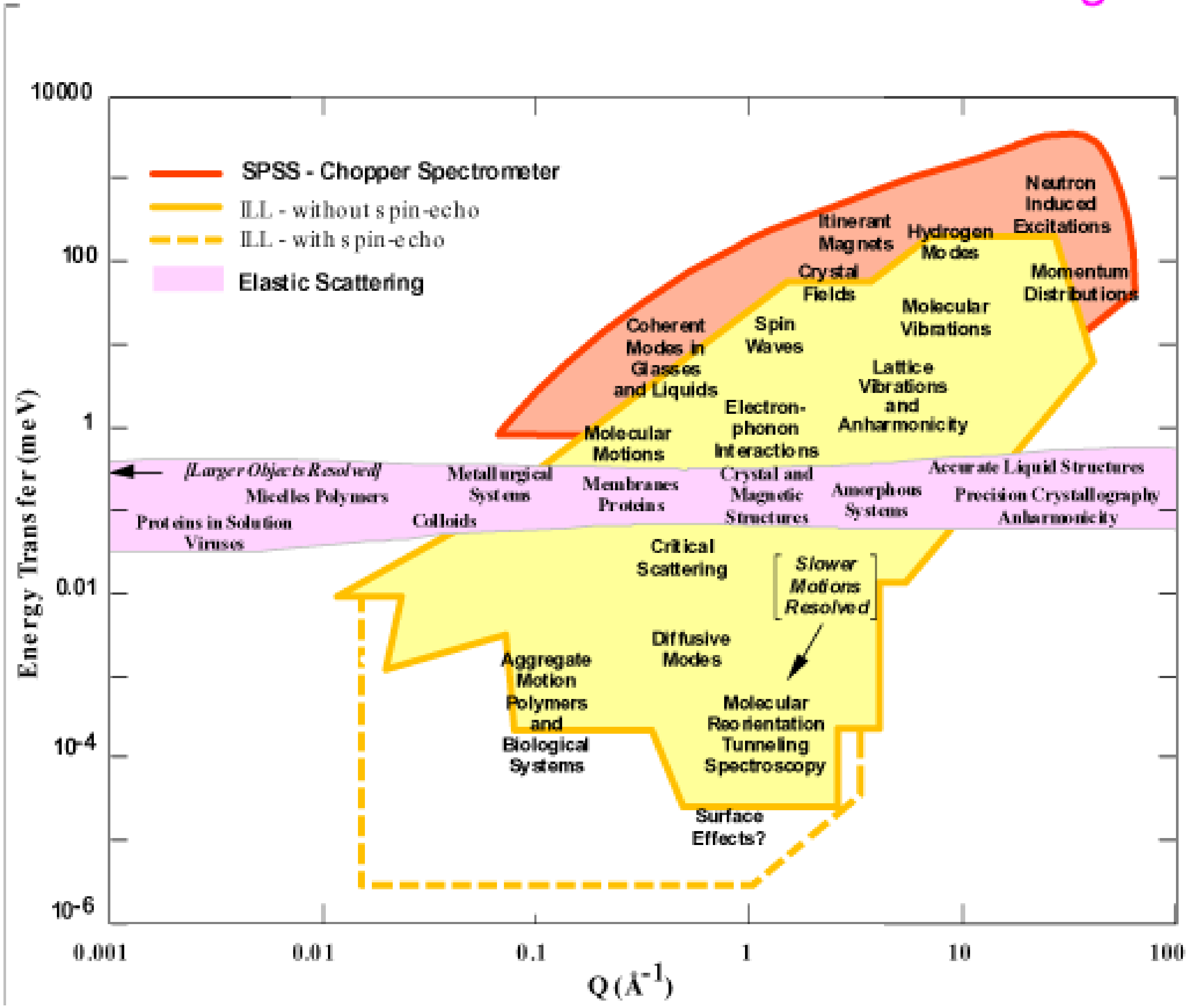
Kohn anomalies in ^{110}Cd

Time-of-flight Methods Can Give Complete Dispersion Curves at a Single Instrument Setting in Favorable Circumstances



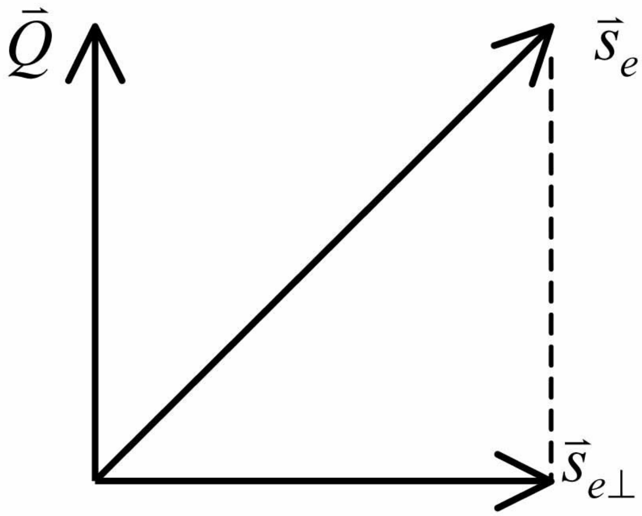
$CuGeO_3$ is a 1-d magnet. With the unique axis parallel to the incident neutron beam, the complete magnon dispersion can be obtained

Much of the Scientific Impact of Neutron Scattering Has Involved the Measurement of Inelastic Scattering



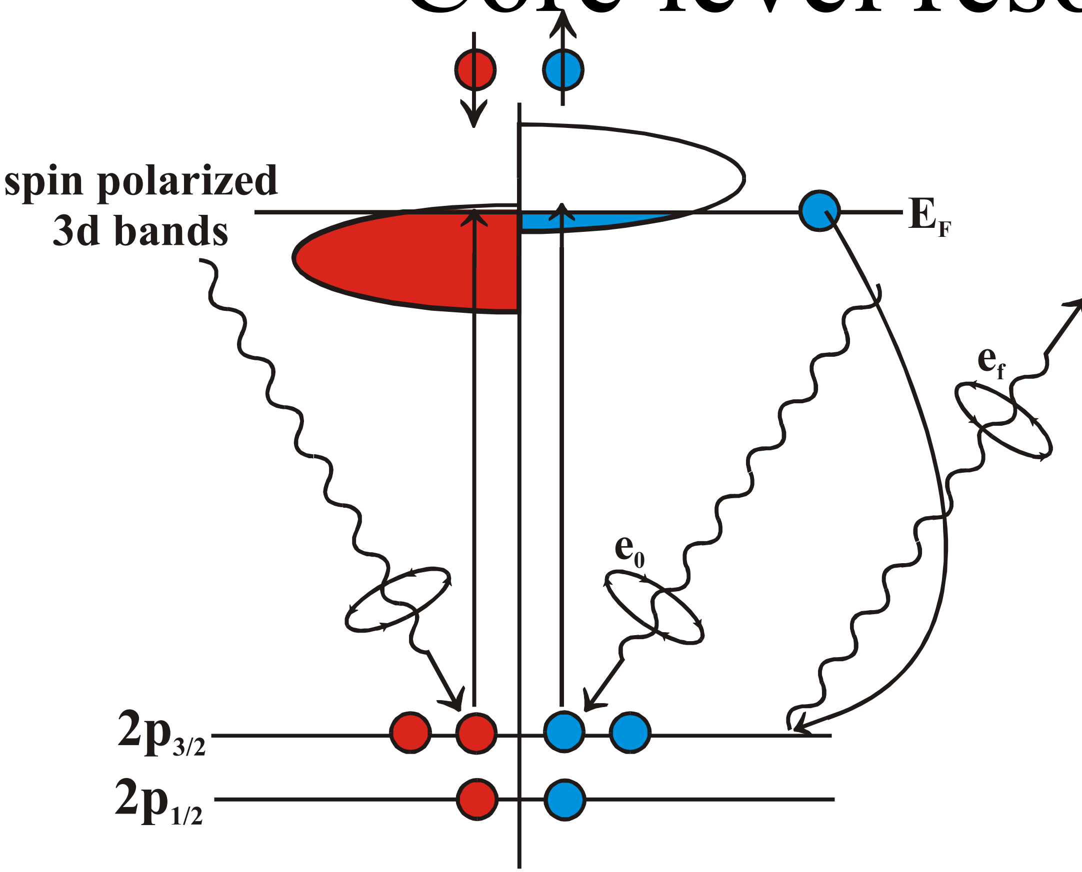
Energy & Wavevector Transfers accessible to Neutron Scattering

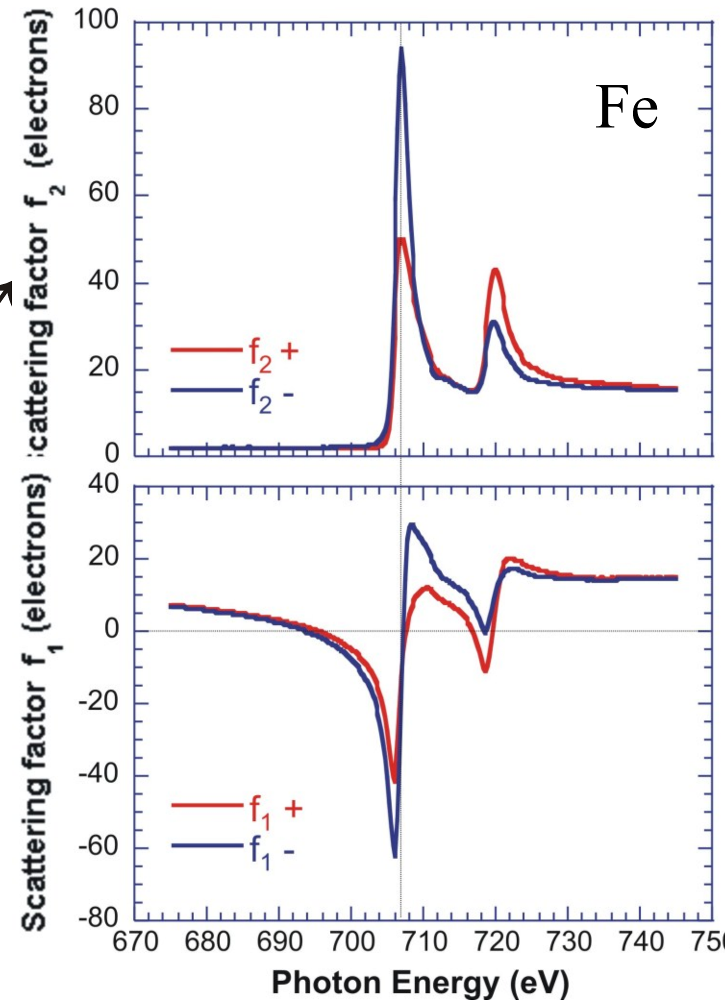
Magnetic Neutron Scattering



Resonant Magnetic X-ray Scattering

Core level resonances





$$f = f_1 + if_2$$

Kortright *et al.*, Phys. Rev. B **65**, 12216 (2000)

NEUTRONS:

$$R_{++}(Q_z) - R_{--}(Q_z) \sim M_{xy,parallel}(Q_z)\, n(Q_z)$$

,

$$R_{+-}(Q_z) = R_{-+}(Q_z) \sim \langle M_{xy,\, perp}(Q_z) \rangle^2$$

X-RAYS:

$$R_{+}(Q_z) - R_{-}(Q_z) \sim M_{x}(Q_z)\, n(Q_z)$$

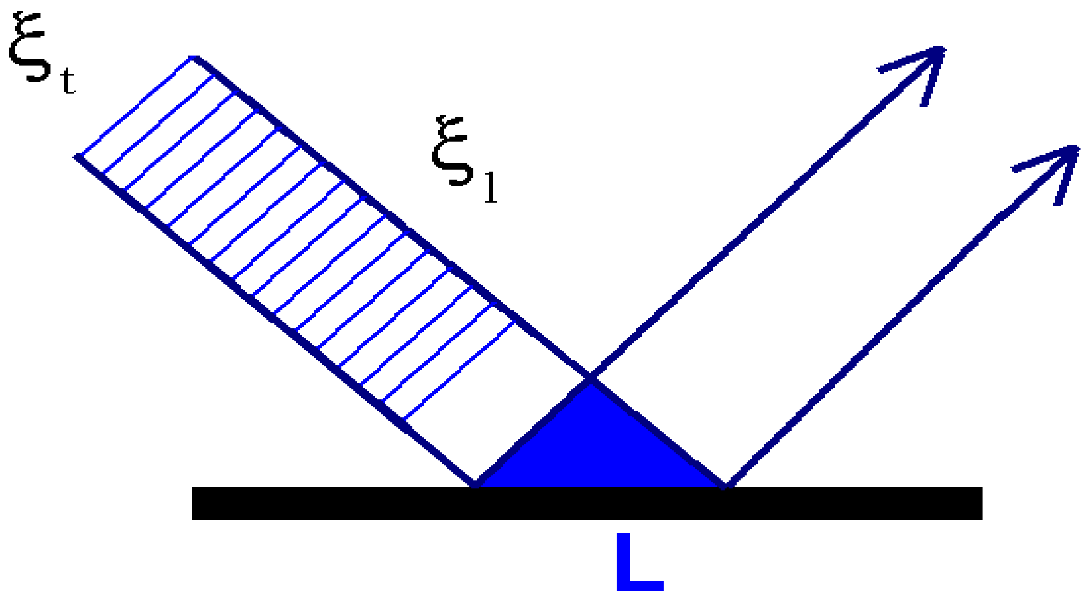
Coherence Lengths

$\xi_l = \lambda^2 / \otimes L$

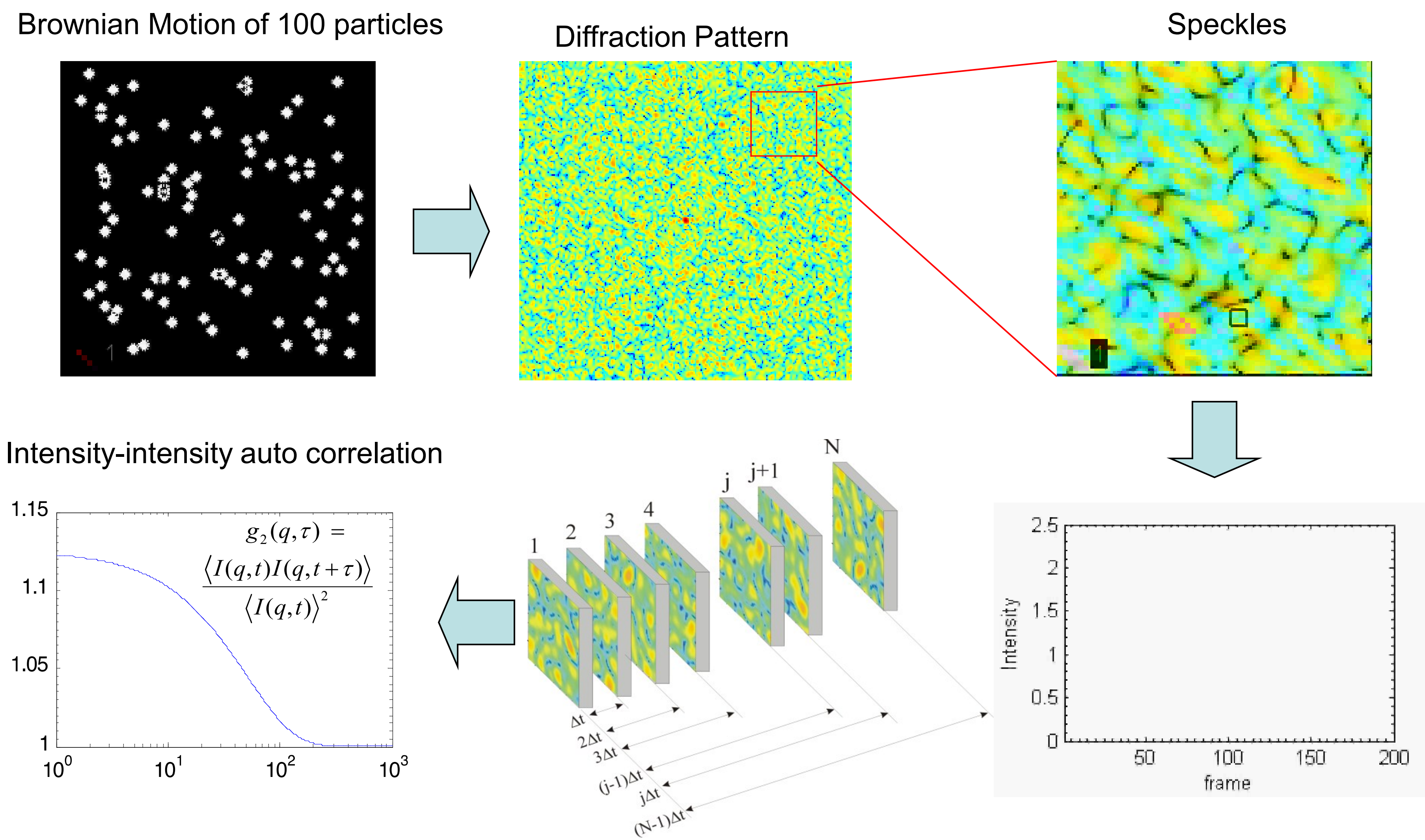
$= \lambda(\Delta\lambda / L\,)^{-1}$

$\xi_t = \lambda R / s$

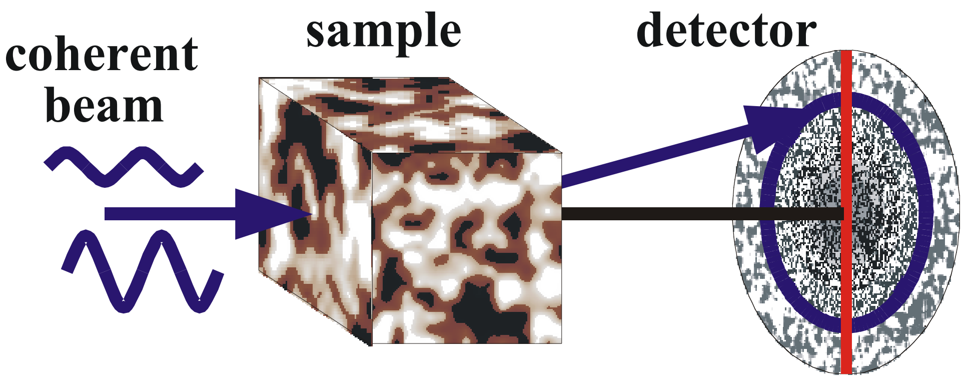
$(\xi_{hor.}, \xi_{vert.})$



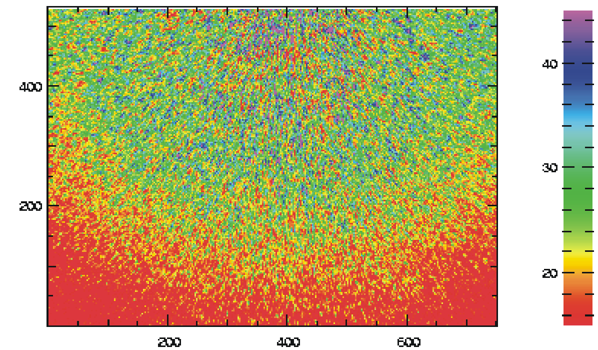
Photon Correlation Spectroscopy□

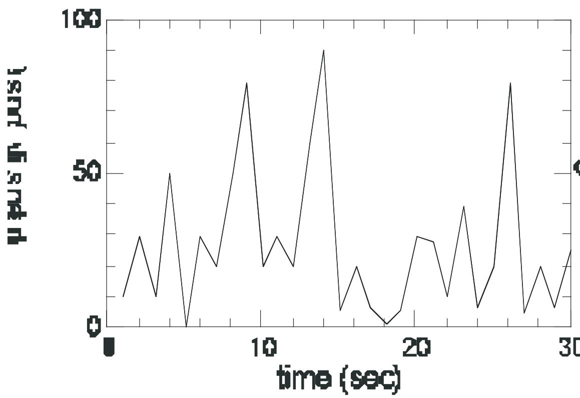


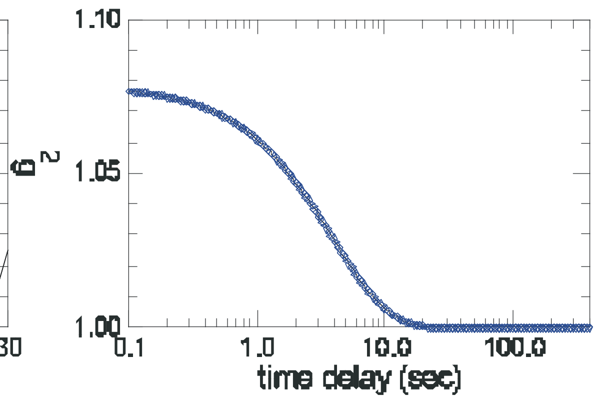
Photon Correlation Spectroscopy



X-ray speckle pattern from a static silica aeroge







$$g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t)\rangle}{\langle I(q,t')\rangle^2}$$

$$g_2(t) = 1 + \beta \exp(-2\Gamma t)$$
$$= 1 + \beta \exp(-2t/\tau)$$

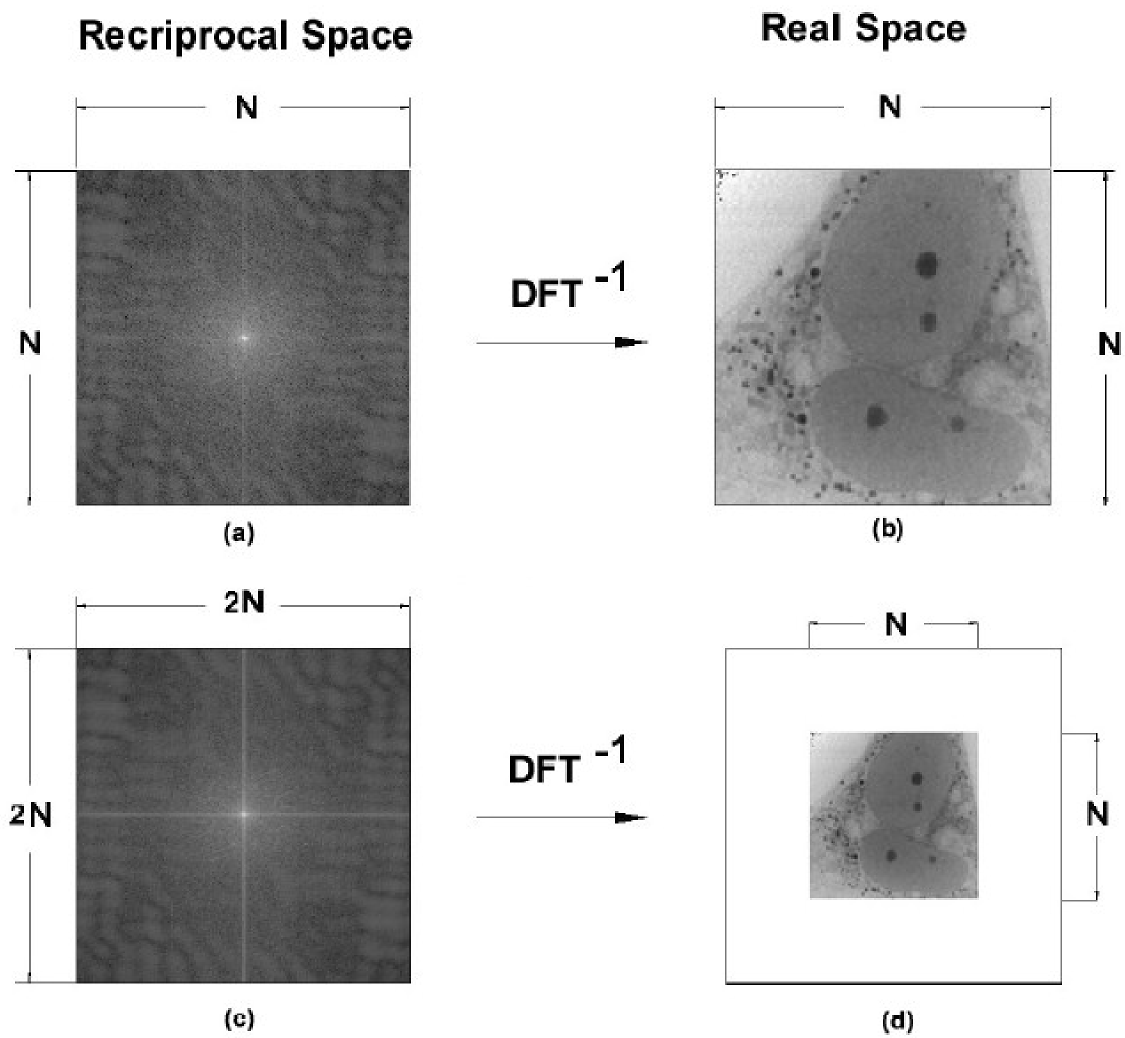
β:speckle contrast

“Oversampling”:

Non-crystals:
pattern continuous,
can do finer sampling
of intensity

Finer sampling;
larger array;
smaller transform;
“finite support”

(area around specimen
must be clear!)

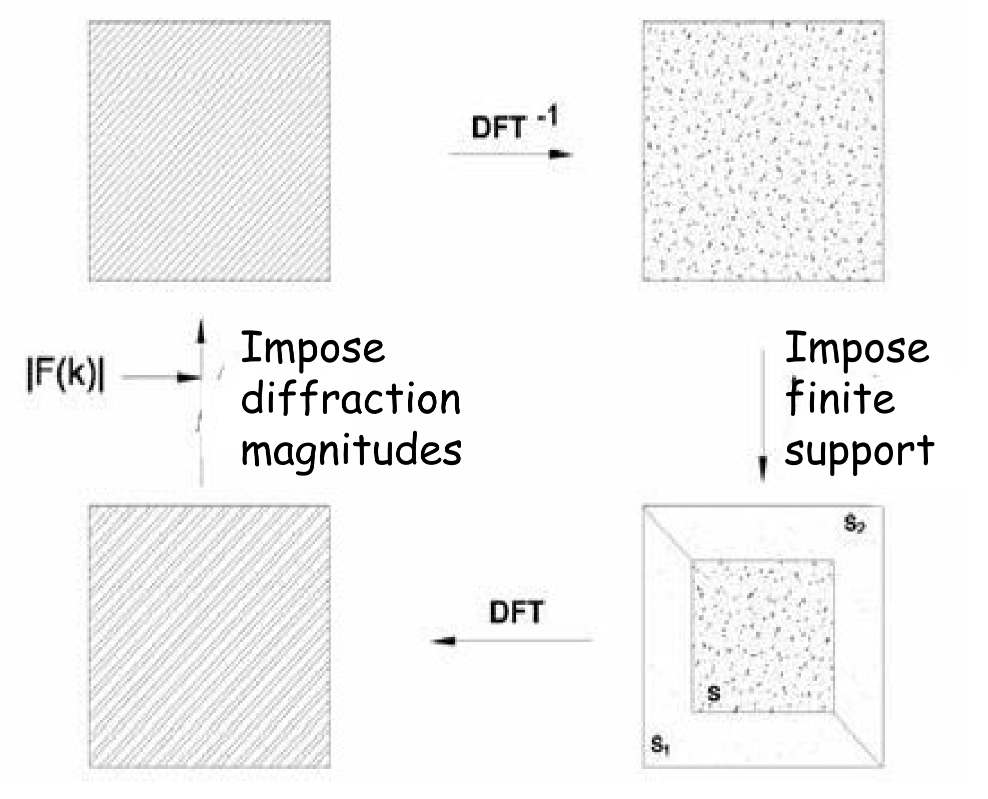


Reconstruction

Equations can still not be solved analytically

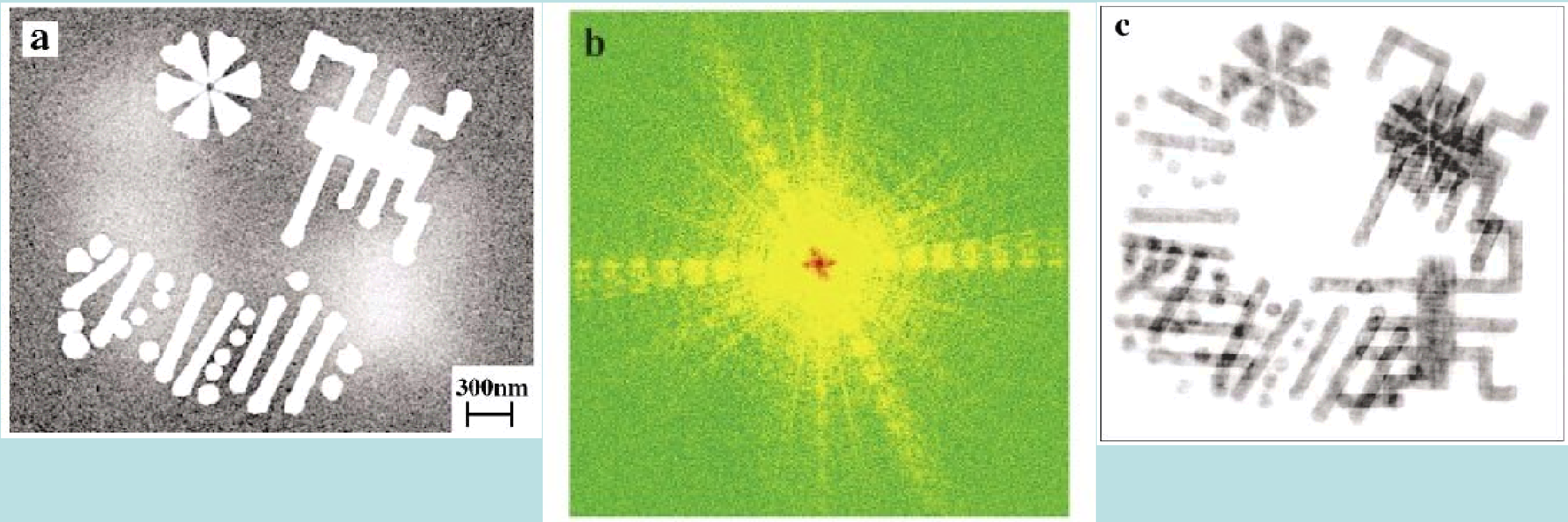
Fienup iterative algorithm

Reciprocal space Real space



•Positivity of electron density helps!

DIFFRACTION IMAGING BY J. MIAO ET AL

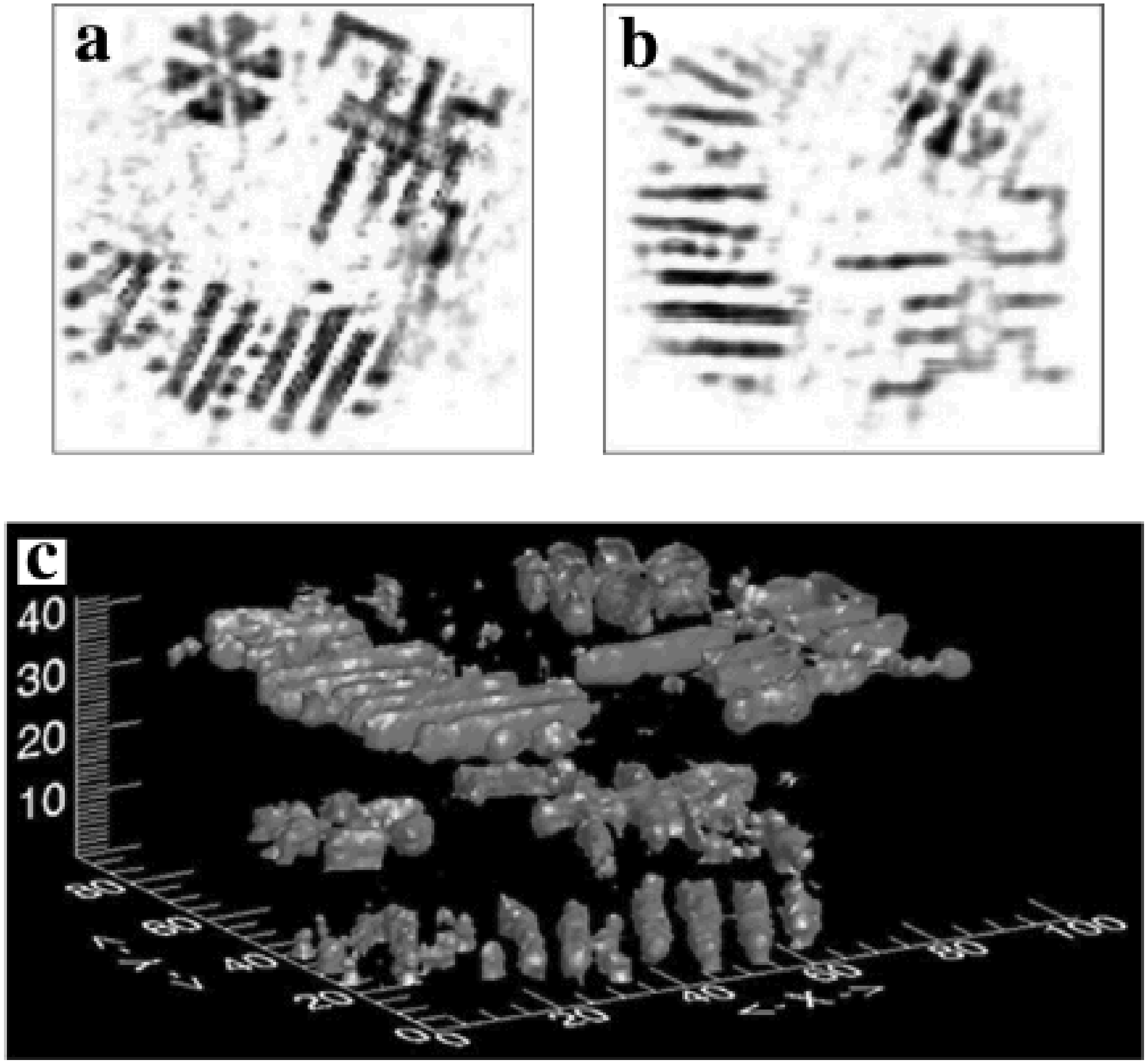


- From Miao, Ishikawa, Johnson, Anderson, Lai, Hodgson PRL Aug 2002
- SEM image of a 3-D Ni microfabricated object with two levels 1 µm apart
- Only top level shows to useful extent

- Diffraction pattern taken at 2 Å wavelength at SPring 8

- 2-D reconstruction with Fienup-type algorithm
- Both levels show because the depth of focus is sufficient
- <u>Resolution = 8 nm (new record)</u>

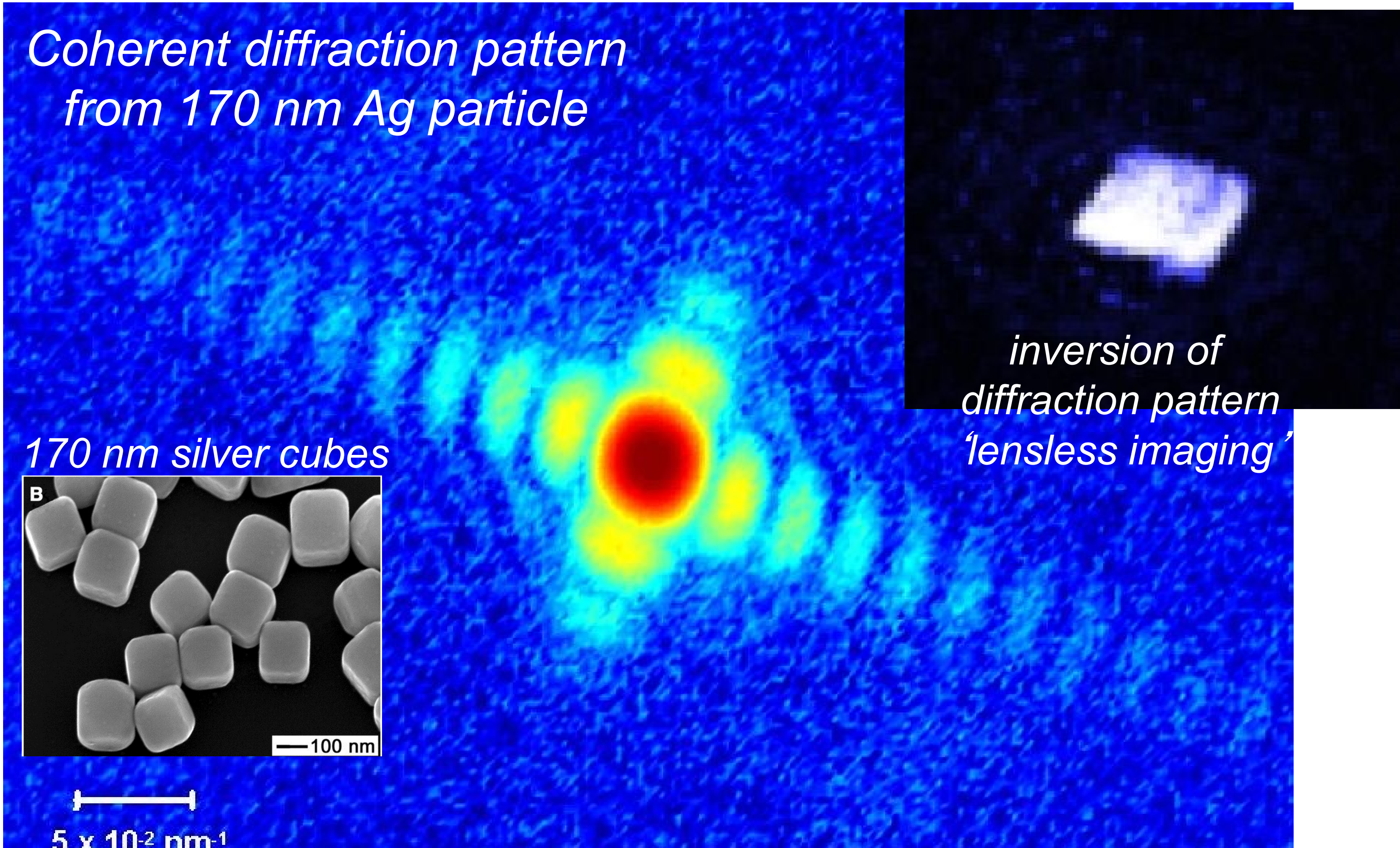
MIAO ET AL 3-D RECONSTRUCTIONS



- Miao et al 3-D reconstruction of the same object pair
- a and b are sections through the *image*
- c is 3-D density
- Resolution = 55 nm

Imaging of individual nanoparticles at the APS

Ross Harder, University of Illinois, Champaign



I.K. Robinson, et al., Science 298 2177 (2003)

Formal Theory of Scattering

Neutrons

ψ_k incident neutron wave fn.

χ_λ initial sample wave fn.

$\psi_{k'}$ scattered neutron wave fn.

$\chi_{\lambda'}$ final sample wave fn.

$$\left(\frac{d\sigma}{d\Omega}\right)_{\lambda\to\lambda'} = \frac{1}{\Phi}\frac{1}{d\Omega}\sum_{k'}^{d\Omega} W_{\vec{k}\lambda\to\vec{k}'\lambda'} \qquad (1)$$

$W_{k\lambda\to k'\lambda'}$ = Number of transitions $k\lambda \to k'\lambda'$ per second

Use Fermi's Golden Rule:

$$\sum_{k'}^{d\Omega} W_{\vec{k}\lambda\to\vec{k}'\lambda'} = \frac{2\pi}{\hbar}\nu_{k'}\left|\langle \vec{k}'\lambda'|V|\vec{k}\lambda\rangle\right|^2 \qquad (2)$$

$\nu_{k'}$ = Number of neutron momentum states in $d\Omega$ per unit energy range at $\vec{k}'$.

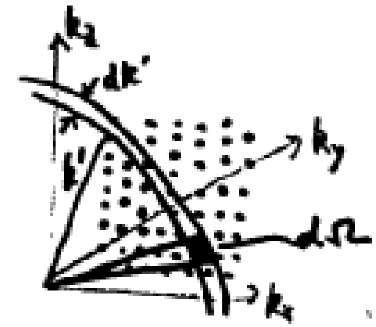
V = Interaction potential of neutron with the sample.

$$H = H_{neutrons}\left(\frac{P_N^2}{2m_N}\right) + H_{sample} + V$$

Quantize states in box of side L with periodic boundary conditions:

$$\vec{k} = \frac{2\pi}{L}\left(n_x, n_y, n_z\right)$$

Density of k-pts / unit vol. of k-space = $\frac{L^3}{(2\pi)^3}$



$$E' = \frac{\hbar^2}{2m}k'^2$$

$$dE' = \frac{\hbar^2}{m}k'dk$$

Now $\nu_{k'}dE'$ = Number of k-pts inside $d\Omega$ with energy between E', and $E' + dE'$

$$= (k')^2\, dk'd\Omega \frac{L^3}{(2\pi)^3}$$

$$\therefore \nu_{k'} = \frac{L^3}{(2\pi)^3}\frac{m}{\hbar^2}k'd\Omega$$

Incident neutron wave fn. $\psi_k = L^{-3/2} e^{i\bar{k}\cdot\bar{r}}$

Incident flux $\Phi = v|\psi_k|^2 = \frac{\hbar}{m} k \frac{1}{L^3}$

Thus, by Eqs. (1), (2),

$$\left(\frac{d\sigma}{d\Omega}\right)_{\lambda\to\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 L^6 \left|\langle \bar{k}'\lambda' | V | \bar{k}\lambda \rangle\right|^2 \qquad (3)$$

Use energy conservation law,

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda\to\lambda'} = \frac{k'}{k}\left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\langle k'\lambda' | V | k\lambda \rangle\right|^2 L^6 \, \delta(E_\lambda - E_{\lambda'} + E - E') \qquad (4)$$

Formally represent interaction between neutron and nucleus by a delta-fn. (Fermi pseudopotential)

$V(r_n - R_i) = a\,\delta(\bar{r}_n - \bar{R}_i)$

Consider elastic scattering again from a single fixed nucleus:

Elastic $\begin{matrix} k' = k \\ \lambda' = \lambda \end{matrix} \langle k'\lambda' | V | k\lambda \rangle = a$

(3) gives $\frac{d\sigma}{d\Omega} = \left(\frac{m}{2\pi\hbar^2}\right)^2 a^2$

Comparing this with the result $\frac{d\sigma}{d\Omega} = b^2$

$$a = \left(\frac{2\pi\hbar^2}{m}\right) b$$

Thus $V(r) = \left(\frac{2\pi\hbar^2}{m}\right) b\,\delta(\bar{r})$ is the <u>effective</u> interaction between a neutron at $\bar{r}$ and a fixed nucleus at the origin.

Scattering by an assembly of nuclei:

$$V(\bar{r}) = \left(\frac{2\pi\hbar^2}{m}\right)\sum_{j=1}^{N} b_j\,\delta\left(\bar{r} - \bar{R}_j\right) \text{ for neutron at } \bar{r}.$$

$$\left\langle k'\lambda' \middle| V \middle| \bar{k}\lambda \right\rangle = \frac{1}{L^3}\int d\bar{r}\, e^{-i\left(\bar{k}'-\bar{k}\right)\cdot\bar{r}} \int\ldots\iint dR_1\ldots dR_N \\ \chi_{\lambda'}^{*}\chi_{\lambda}\sum_{j=1}^{N} b_j\,\delta\left(\bar{r}-\bar{R}_j\right)\times\left(\frac{2\pi\hbar^2}{m}\right) \\ = \frac{1}{L^3}\left(\frac{2\pi\hbar^2}{m}\right)\sum_{j=1}^{N} b_j \left\langle \lambda' \middle| e^{-i\bar{q}\cdot\bar{R}_j} \middle| \lambda \right\rangle$$

Thus from Eq. (4)

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\lambda\to\lambda'} = \frac{k'}{k}\sum_{i,j=1}^{N} b_i b_j \left[\left\langle \lambda \middle| e^{-i\bar{q}\cdot\bar{R}_i} \middle| \lambda' \right\rangle \left\langle \lambda' \middle| e^{i\bar{q}\cdot\bar{R}_j} \middle| \lambda \right\rangle\right] \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right) \quad (5)$$

where

$\hbar\omega = E - E'$ = Neutron energy loss

Summing over all possible final states λ' of the sample and averaging over all initial states λ, we obtain

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \frac{k'}{k}\sum_{ij} b_i b_j \sum_{\lambda\lambda'} P_\lambda \left\langle \lambda \middle| e^{-i\bar{q}\cdot\bar{R}_i} \middle| \lambda' \right\rangle \left\langle \lambda' \middle| e^{i\bar{q}\cdot\bar{R}_j} \middle| \lambda \right\rangle \delta\left(E_\lambda - E_{\lambda'} + \hbar\omega\right)$$

$$P_\lambda = Z^{-1} e^{-E_\lambda/kT} \qquad Z = \sum_\lambda e^{-E_\lambda/kT}$$

b_i depends on nucleus (isotope, spin relative to neutron ↑↑ or ↓↓), etc. Even for a monatomic system

$b_i = \langle b\rangle + \delta b_i$ ← random sample

$$b_i b_j = \langle b\rangle^2 + \langle b\rangle\left[\delta b_i + \delta b_j\right] + \delta b_i \delta b_j$$

(the bracketed term → zero; $\delta b_i \delta b_j$ → zero unless $i = j$)

$$\left\langle \delta b_i^2 \right\rangle = \left\langle b^2 \right\rangle - \langle b\rangle^2$$

So $$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} + \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}}$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} = \frac{k'}{k}\langle b\rangle^2 \sum_{\lambda\lambda'} P_\lambda \left\langle \lambda \left| \sum_i e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| \sum_j e^{i\vec{q}\cdot\vec{R}_j} \right| \lambda \right\rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

$\langle b\rangle^2 \rightarrow \sigma_{\text{coh}}/4\pi$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}} = \frac{k'}{k}\left[\langle b^2\rangle - \langle b\rangle^2\right] \sum_{\lambda\lambda'} P_\lambda \sum_i \left\langle \lambda \left| e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \times \left\langle \lambda' \left| e^{i\vec{q}\cdot\vec{R}_i} \right| \lambda \right\rangle \times \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

$\langle b^2\rangle - \langle b\rangle^2 \rightarrow \sigma_{\text{inc}}/4\pi$

Write it as

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} = \frac{k'}{k}\frac{\sigma_{\text{coh}}}{4\pi} N S_{\text{coh}}(\vec{q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc}} = \frac{k'}{k}\frac{\sigma_{\text{inc}}}{4\pi} N S_{\text{inc}}(\vec{q},\omega)$$

$$S_{\text{coh}}(\vec{q},\omega) = \frac{1}{N}\sum_{\lambda\lambda'} P_\lambda \left\langle \lambda \left| \sum_i e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| \sum_j e^{i\vec{q}\cdot\vec{R}_j} \right| \lambda \right\rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \quad (6)$$

$$S_{\text{inc}}(\vec{q},\omega) = \frac{1}{N}\sum_{\lambda\lambda'} P_\lambda \sum_i \left\langle \lambda \left| e^{-i\vec{q}\cdot\vec{R}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| e^{i\vec{q}\cdot\vec{R}_i} \right| \lambda \right\rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

Heisenberg Time-Dependent Operators

If A is any operator, and H is the system Hamiltonian

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar}$$

is the corresponding time-dependent Heisenberg operator.

$A(0) = A$.

Write $\delta(E_\lambda - E_{\lambda'} + \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} e^{i(E_{\lambda'} - E_\lambda)t/\hbar}$

Then

$$\sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle e^{i(E_{\lambda'} - E_\lambda)t/\hbar}$$

$$\left[e^{-iHt/\hbar} |\lambda\rangle = e^{-iE_\lambda t/\hbar} |\lambda\rangle \right]$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle \lambda | A(0) B(t) | \lambda \rangle$$

$$\sum_{\lambda} P_\lambda \langle \lambda | A(0) B(t) | \lambda \rangle \equiv \langle A(0) B(t) \rangle$$ ← T.D. Correlation function

Thus, by (6),

$$S_{\mathrm{coh}}(\bar{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{\lambda}P_{\lambda}\left\langle\lambda\left|\sum_{i}e^{-i\bar{q}\cdot\bar{R}_i(0)}\right.\right.$$

$$\left.\left.\times\sum_{j}e^{i\bar{q}\cdot\bar{R}_j(t)}\right|\lambda\right\rangle$$

$$=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\sum_{ij}e^{-i\bar{q}\cdot\bar{R}_i(0)}e^{i\bar{q}\cdot\bar{R}_j(t)}\right\rangle$$

$$S_{\mathrm{inc}}(\bar{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\sum_{i}P_{\lambda}\left\langle\lambda\left|e^{-i\bar{q}\cdot\bar{R}_i(0)}e^{i\bar{q}\cdot\bar{R}_i(t)}\right|\lambda\right\rangle$$

$$=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\sum_{i}e^{-i\bar{q}\cdot\bar{R}_i(0)}e^{i\bar{q}\cdot\bar{R}_i(t)}\right\rangle$$

Let $\rho_N(\bar{r})$ be density fn. of nuclei,

$$\rho_N(\bar{r})=\sum_{i}\delta(\bar{r}-\bar{R}_i)$$

It's Fourier Transform

$$\rho_N(\bar{q})=\int d\bar{r}\,e^{-i\bar{q}\cdot\bar{r}}=\sum_{i}e^{-i\bar{q}\cdot\bar{R}_i}$$

Thus,

$$S_{\mathrm{coh}}(\bar{q}\cdot\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\rho_N(\bar{q},0)\rho_N^{+}(\bar{q},t)\right\rangle \tag{7}$$

$$\left\langle\rho_N(\bar{q},0)\rho_N^{+}(\bar{q},t)\right\rangle=\int d\bar{r}\,e^{-i\bar{q}\cdot\bar{r}}G(\bar{r},t)$$

$$G(\bar{r},t)=\sum_{ij}\int d\bar{r}'\left\langle\delta\left(\bar{r}-\bar{r}'-\bar{R}_i(0)\right)\delta\left(\bar{r}'+\bar{R}_j(t)\right)\right\rangle$$

⇓

Van-Hove space-time correlation function of system

$$\boxed{S_{\mathrm{coh}}(\bar{q},\omega)=\frac{1}{N}\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\int d\bar{r}\,e^{-i\bar{q}\cdot\bar{r}}G(\bar{r},t)} \tag{8}$$

NOTE: $R_i(0)$, $R_j(t)$ are not <u>commuting</u> operators in general, so care must be exercised!

<u>X-rays</u>

$$H = \frac{1}{2m}\sum_i \left(\vec{P}_i + \frac{e}{c}\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i)\right)\cdot\left(\vec{P}_i + \frac{e}{c}\vec{A}(r)\delta(\vec{r}-\vec{r}_i)\right)$$

$$+ \sum_i V(r_i) + V_{\text{int}}^{e-e}$$

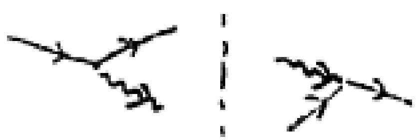
(P_i = electron momentum,
$\vec{A}$ = vector potential

$$= \frac{1}{2m}\sum_i \left(P_i^2 + V(r_i)\right) + V_{\text{int}}^{e-e} \leftarrow H_{e\ell}$$

$$+ \frac{e}{2mc}\sum_i \left\{\vec{P}_i\cdot\vec{A}(\vec{r})\delta(\vec{r}-\vec{r}_i) + \vec{A}(\vec{r})\delta(r-r_i)\cdot\vec{P}_i\right\} \quad \swarrow H_{\text{int}}^{(1)} \tag{9}$$

$$+ \frac{e^2}{2mc^2}\sum_i \delta(\vec{r}-\vec{r}_i)\vec{A}(\vec{r})\cdot\vec{A}(\vec{r}) \leftarrow H_{\text{int}}^{(2)}$$

$$\vec{A}(\vec{r}) = \sum_{\vec{k},\alpha}\left(\frac{\hbar}{\omega_k}\right)^{1/2} c\left\{\vec{\varepsilon}_\alpha a^+_{\vec{k},\alpha} e^{i\vec{k}\cdot\vec{r}} + \vec{\varepsilon}^*_\alpha a_{\vec{k},\alpha} e^{-i\vec{k}\cdot\vec{r}}\right\} \tag{10}$$

$H_{\text{int}}^{(1)} \rightarrow$ 

In 1st order $\rightarrow$ 1-photon absorption, emission

In 2nd order $\rightarrow$ scattering

$H_{\text{int}}^{(2)} \rightarrow$ 

In 1st order $\rightarrow$ scattering

Using $H_{\text{int}}^{(2)}$,

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\substack{\vec{k}\alpha\rightarrow\vec{k}'\beta \\ \lambda\rightarrow\lambda'}} = \left(\frac{e^2}{mc^2}\right)^2 \left|\vec{\varepsilon}_\alpha\cdot\vec{\varepsilon}^*_\beta\right|^2 \left\langle \lambda\left|\sum_i e^{-i\vec{q}\cdot\vec{r}_i}\right|\lambda'\right\rangle \left\langle \lambda'\left|\sum_j e^{i\vec{q}\cdot\vec{r}_j}\right|\lambda\right\rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \tag{11}$$

"Thomson" Scattering

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \left(\frac{e^2}{mc^2}\right)^2 S_{e\ell}(\vec{q},\omega)\left|\vec{\varepsilon}_\alpha\cdot\vec{\varepsilon}^*_\beta\right|^2$$

$$S_{e\ell}(\bar{q},\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\langle\rho_{e\ell}(\bar{q},0)\rho_{e\ell}^{+}(\bar{q},t)\right\rangle \tag{12}$$

Elastic Scattering: $\omega = 0 \rightarrow$ "Infinite time average."

Often what we measure is $\int\frac{d^2\sigma}{d\Omega dE'}dE'=\frac{d\sigma}{d\Omega}$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}}=\frac{\hbar}{2\pi\hbar}\int d\omega e^{-i\omega t}\int_{-\infty}^{\infty}dt\left\langle\rho(\bar{q},0)\rho^{+}(\bar{q},t)\right\rangle \begin{cases}\times\frac{k'}{k}\langle b\rangle^2\rightarrow\text{neutrons}\\ \times\left(\frac{e^2}{mc^2}\right)^2\left|\bar{\varepsilon}_\alpha\cdot\bar{\varepsilon}_\beta^*\right|^2\rightarrow\text{x-rays}\end{cases} \tag{13}$$

$$\int d\omega e^{-i\omega t}=2\pi\delta(t)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{wh}=S(\bar{q})\begin{cases}\times\langle b\rangle^2\rightarrow\text{neutrons}\\ \times\left(\frac{e^2}{mc^2}\right)\left|\bar{\varepsilon}_\alpha\cdot\bar{\varepsilon}_\beta^*\right|^2\rightarrow\text{x-rays}\end{cases} \tag{14}$$

$$S(q)=\left\langle\rho(q,0)\rho^{+}(q,0)\right\rangle\equiv\left\langle\rho(q)\rho^{+}(q)\right\rangle$$

(Equal-Time Correlation Function)

General References

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