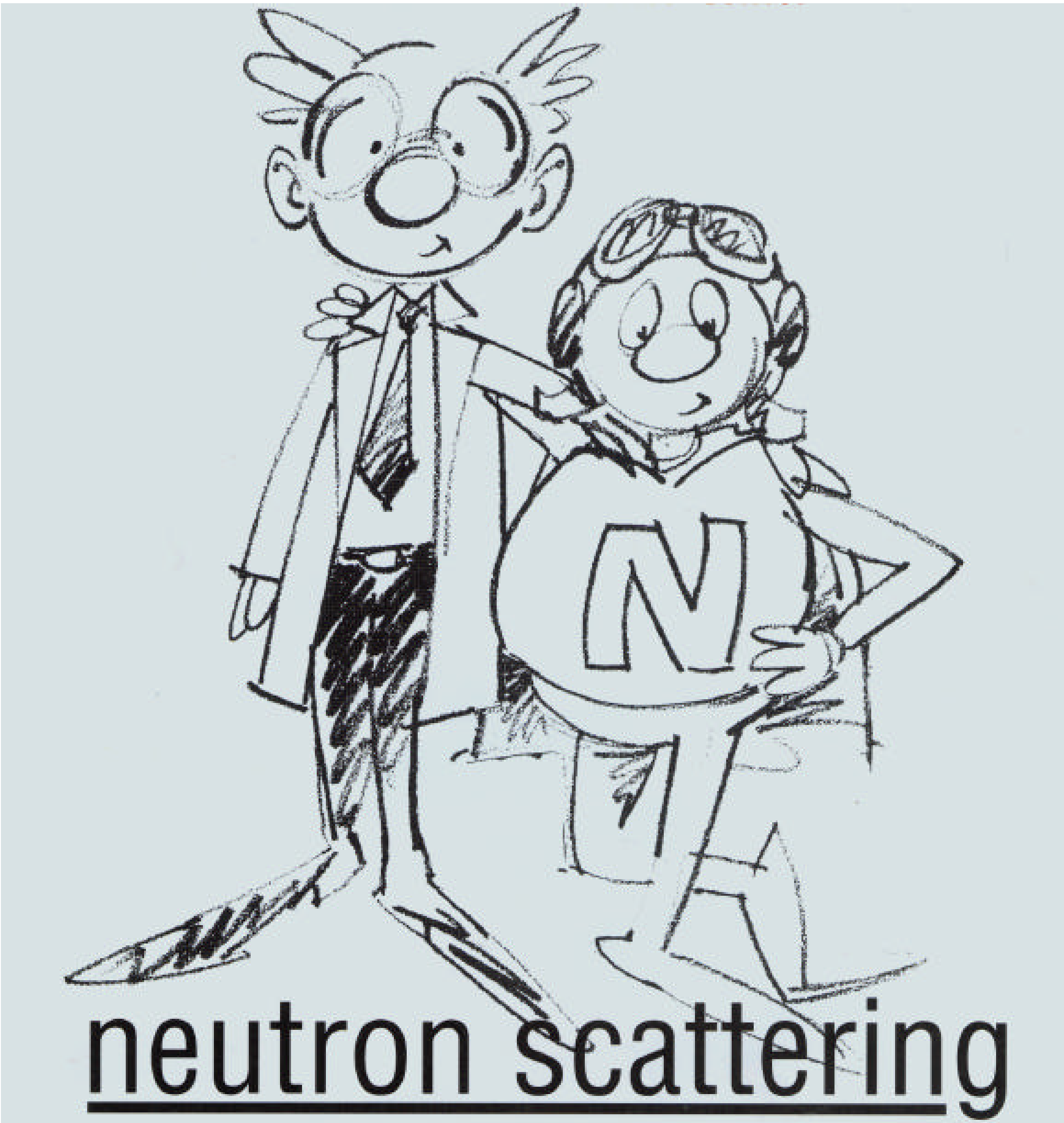


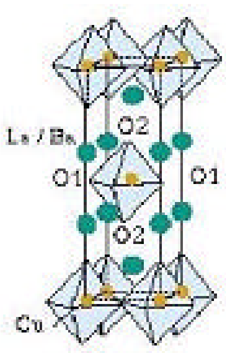
LECTURE 6: Inelastic Scattering

by

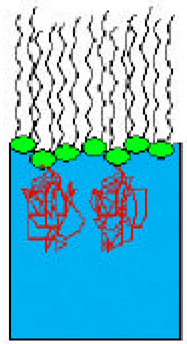
Roger Pynn

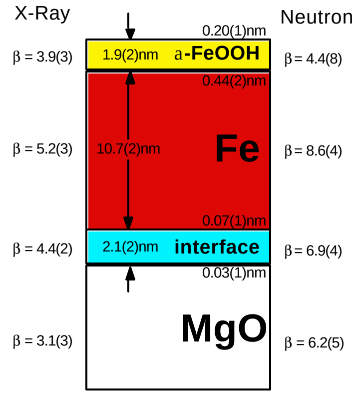
Los Alamos
National Laboratory

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

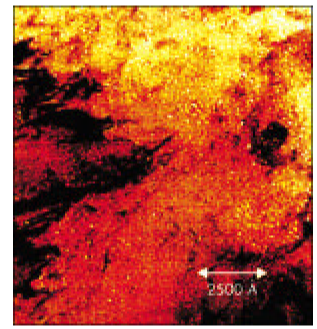


crystals

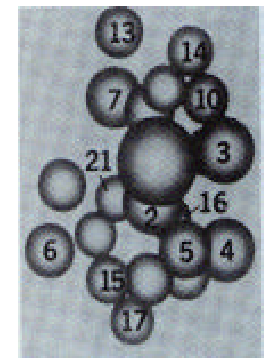




surfaces & interfaces

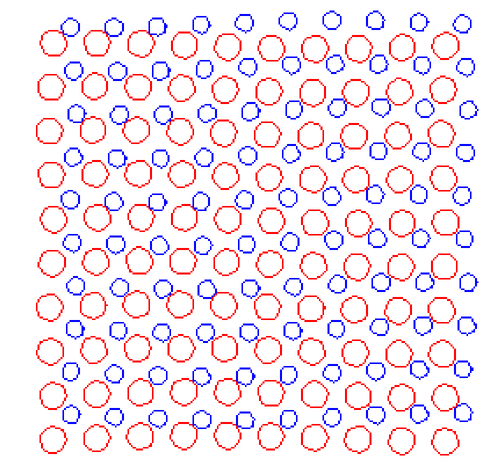


disordered/fractals



biomachines

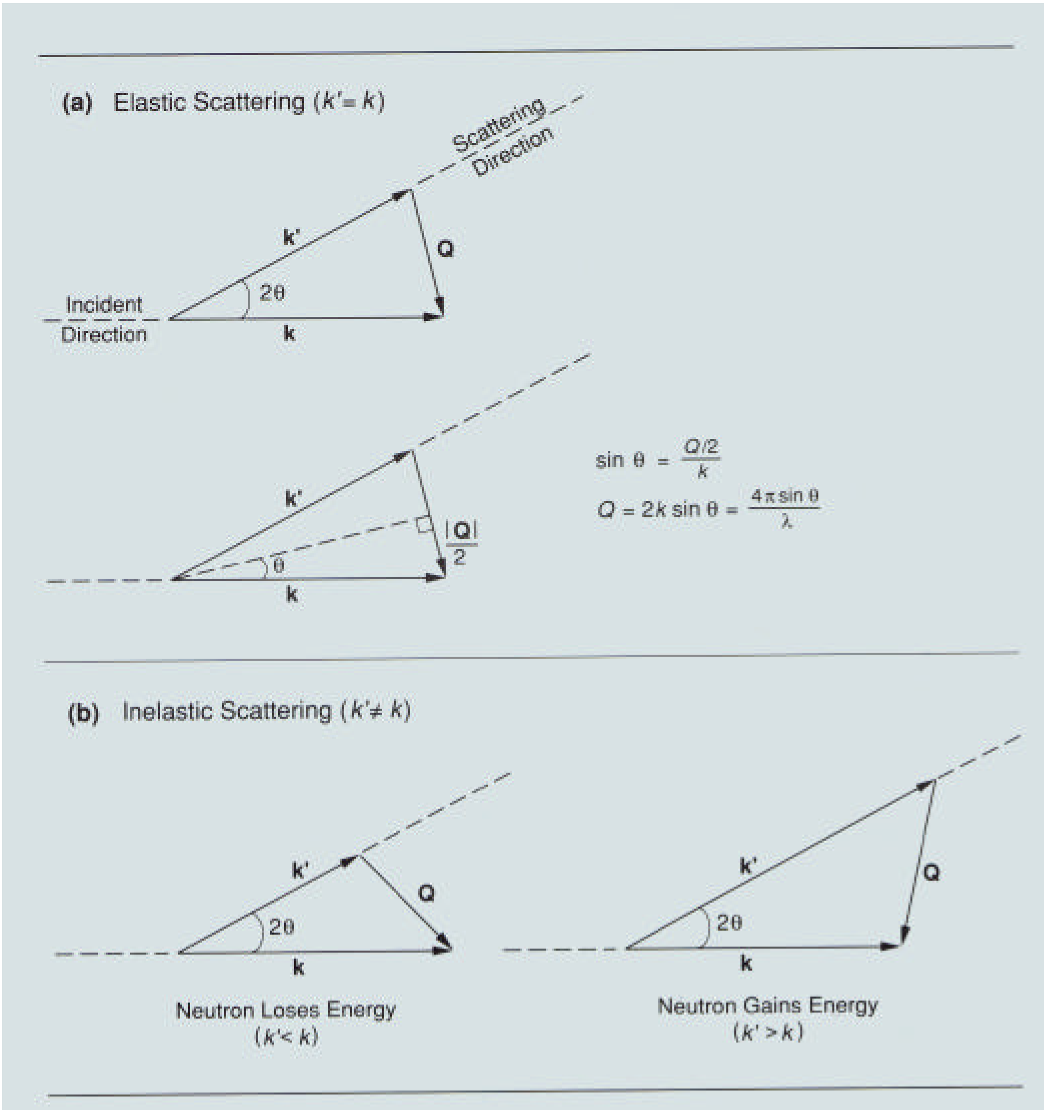
but what happens when the atoms are moving?



Can we determine the directions and time-dependence of atomic motions?
Can well tell whether motions are periodic?
Etc.

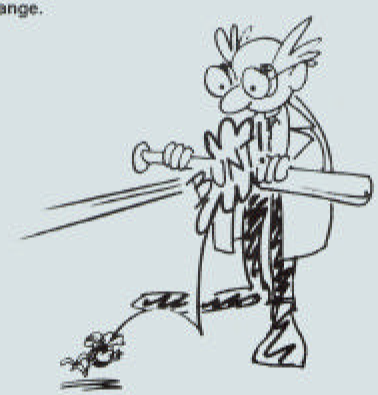
These are the types of questions answered by inelastic neutron scattering

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 *<u>and time</u>* Fourier Transforms of the *<u>time-dependent</u>* pair correlation function function, G(r,t) = probability of finding a particle at position r *<u>at time t</u>* when there is a particle at r=0 and *<u>t=0</u>*.

- For inelastic *<u>incoherent</u>* scattering, the intensity is proportional to the space and time Fourier Transforms of the *<u>self-correlation</u>* function, $G_s(r,t)$ I.e. the probability of finding a particle at position r at time t when *<u>the same</u>* particle was at r=0 at t=0

The Inelastic Scattering Cross Section

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

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

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

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

The evaluation of the correlation functions (in which the r's and d-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

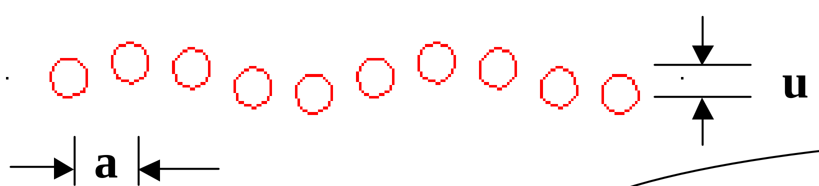
$$F_n = a_0 u_n + a_1(u_{n-1} + u_{n+1}) + a_2(u_{n-2} + u_{n+2}) + \ldots$$

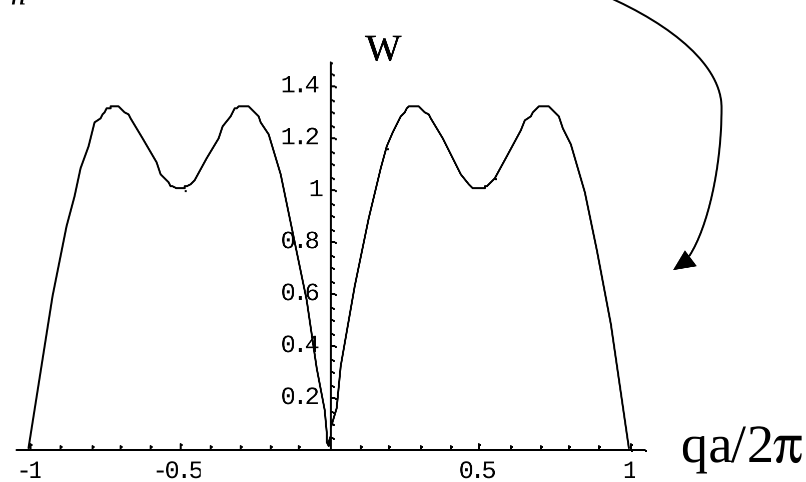
First neighbor force constant

displacements

- Equation of motion is $F_n = M\ddot{u}_n$
- Solution is: $u_n(t) = A_q e^{i(qna - wt)}$ with $w_q^2 = \dfrac{4}{M}\sum_n a_n \sin^2(\frac{1}{2}nqa)$

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





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

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

exchange coupling

ground state energy

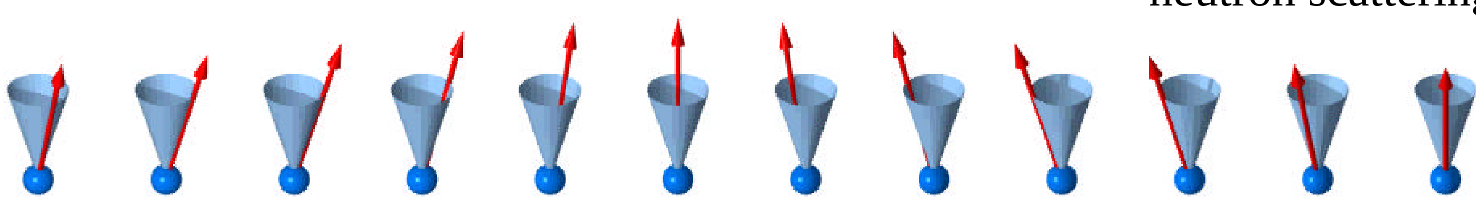
spin waves (magnons)

with

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

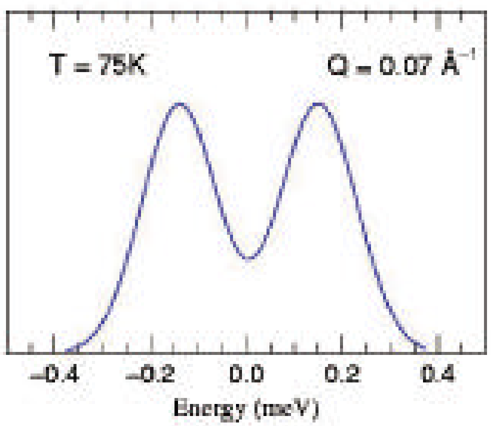
$\hbar w_q = Dq^2$ is the dispersion relation for a ferromagnet

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

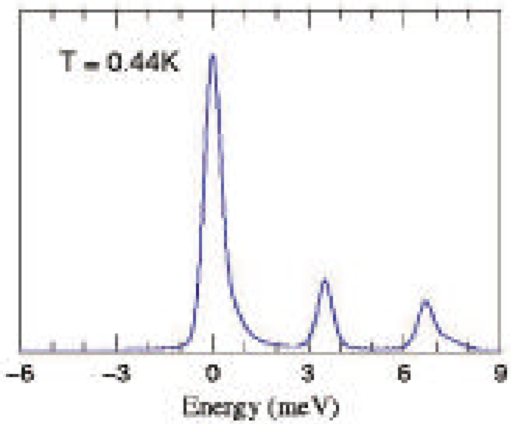


Spin wave animation courtesy of A. Zheludev (ORNL)

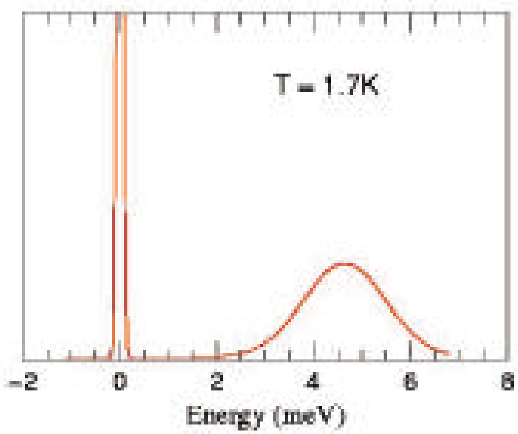
Measured Inelastic Neutron Scattering Signals in Crystalline Solids Show Both Collective & Local Fluctuations*



Spin waves – collective excitations



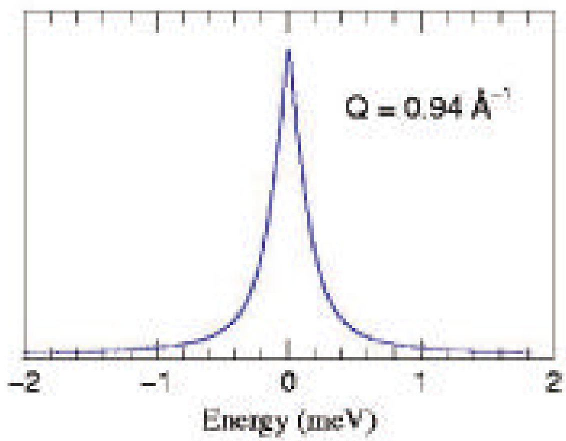
Crystal Field splittings ($HoPd_2Sn$) – local excitations



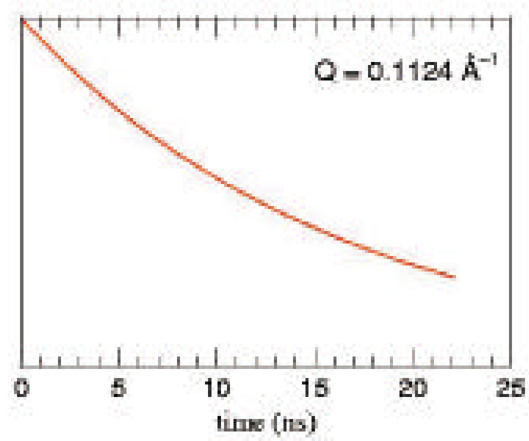
Local spin resonances (e.g. $ZnCr_2O_4$)

* Courtesy of Dan Neumann, NIST

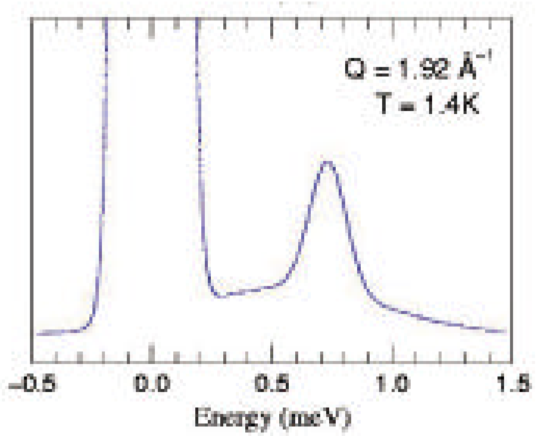
Measured Inelastic Neutron Scattering Signals in Liquids Generally Show Diffusive Behavior



"Simple" liquids (e.g. water)

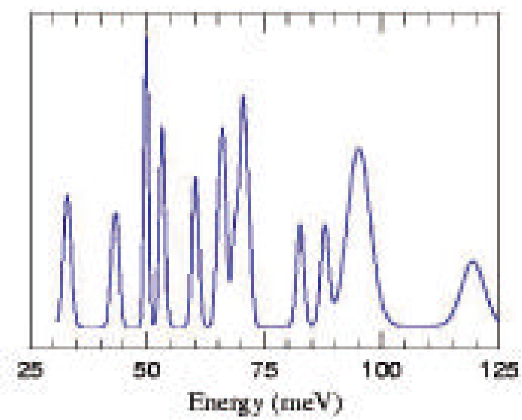


Complex Fluids (e.g. SDS)

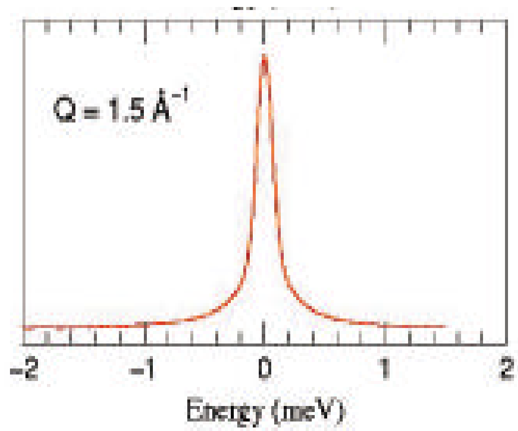


Quantum Fluids (e.g. He in porous silica)

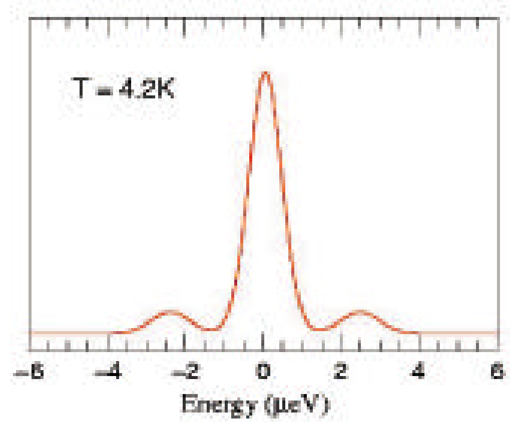
Measured Inelastic Neutron Scattering in Molecular Systems Span Large Ranges of Energy



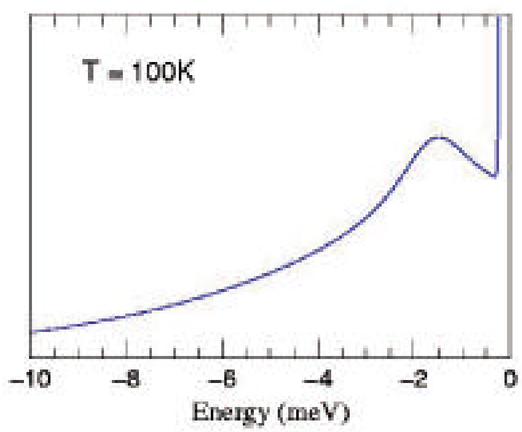
Vibrational spectroscopy
(e.g. C_{60})



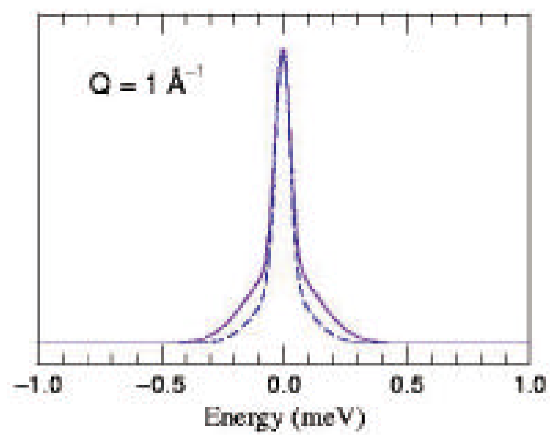
Molecular reorientation
(e.g. pyrazine)



Rotational tunneling
(e.g. CH_3I)



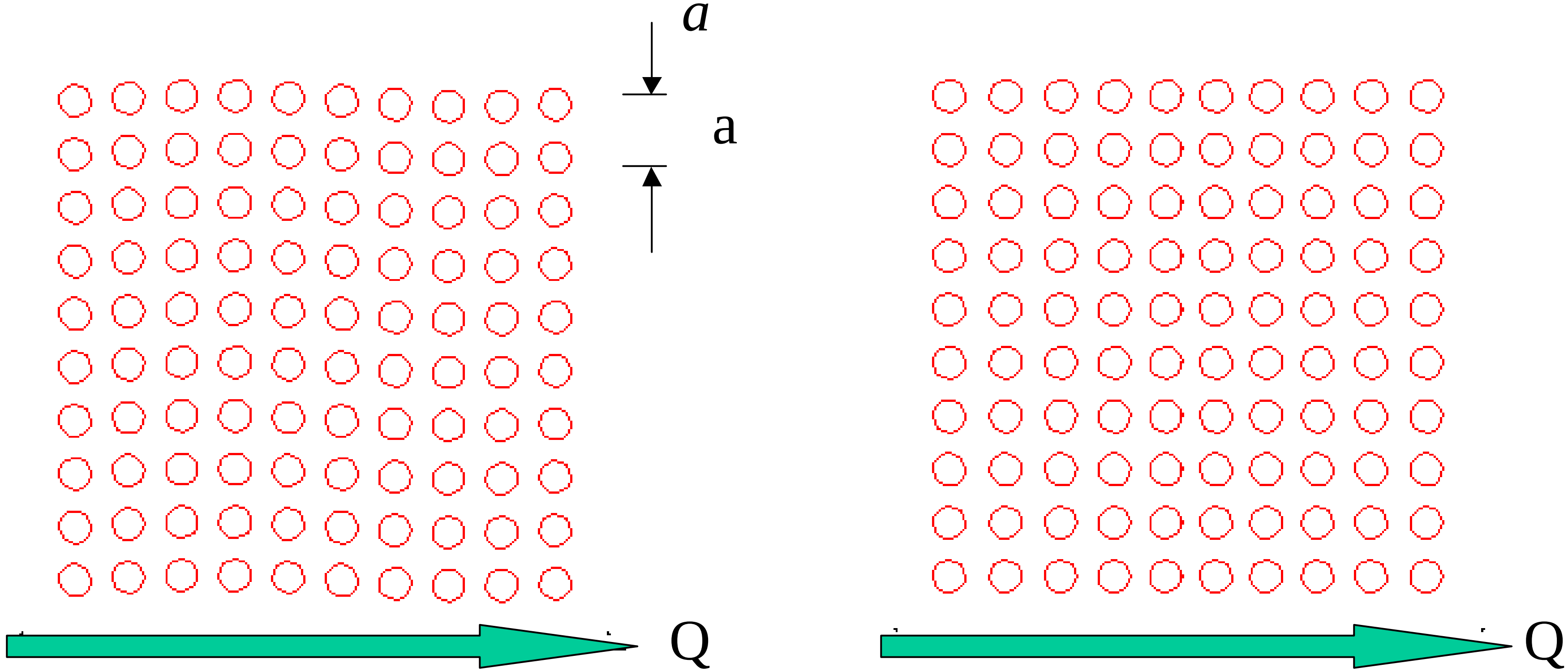
Polymers



Proteins

Atomic Motions for Longitudinal & Transverse Phonons

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



Transverse phonon

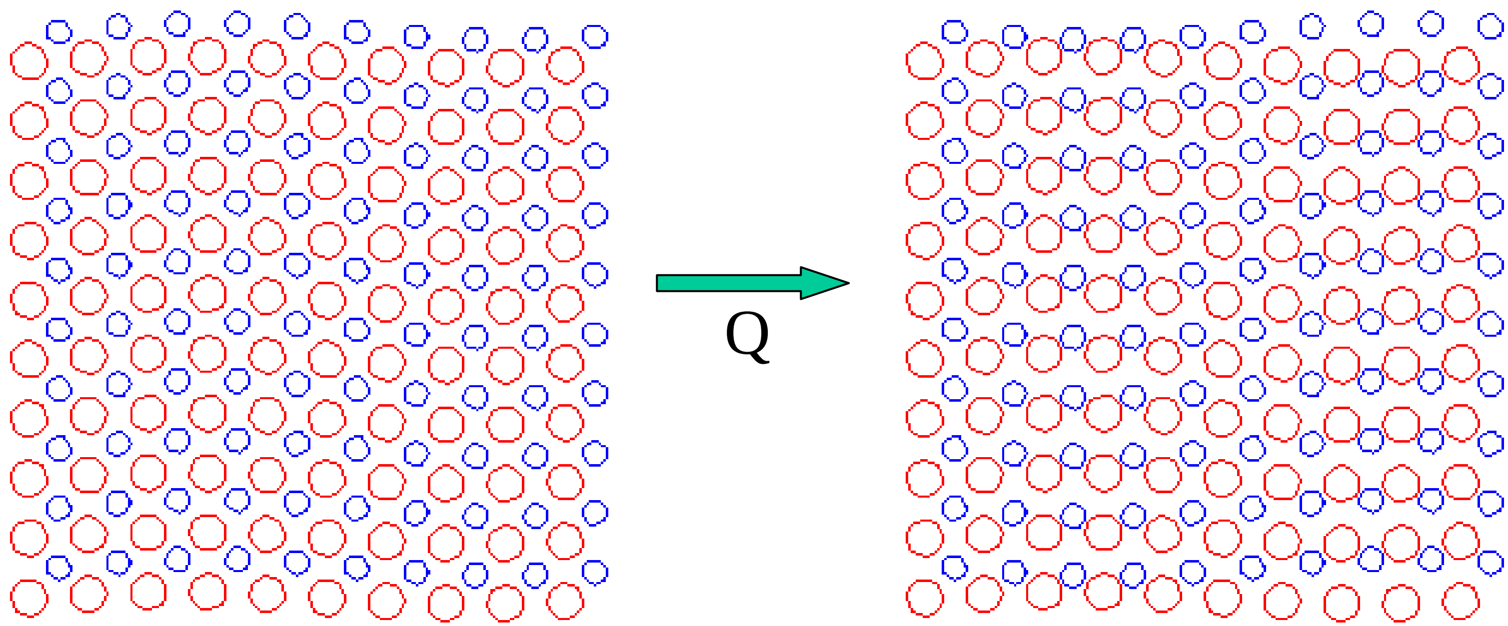
$$\vec{e}_T = (0,0.1,0)a$$

Longitudinal phonon

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

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

Transverse Optic and Acoustic Phonons



Acoustic

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

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

Optic

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

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

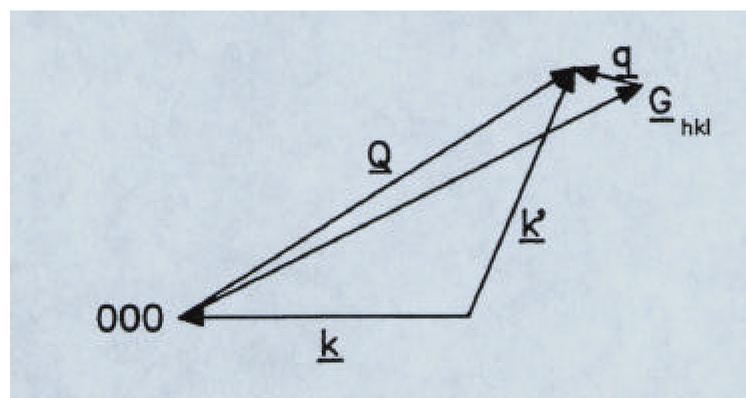
$$\vec{R}_{lk} = \vec{R}^{0}_{lk} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - wt)}$$

Phonons – the Classical Use for Inelastic Neutron Scattering

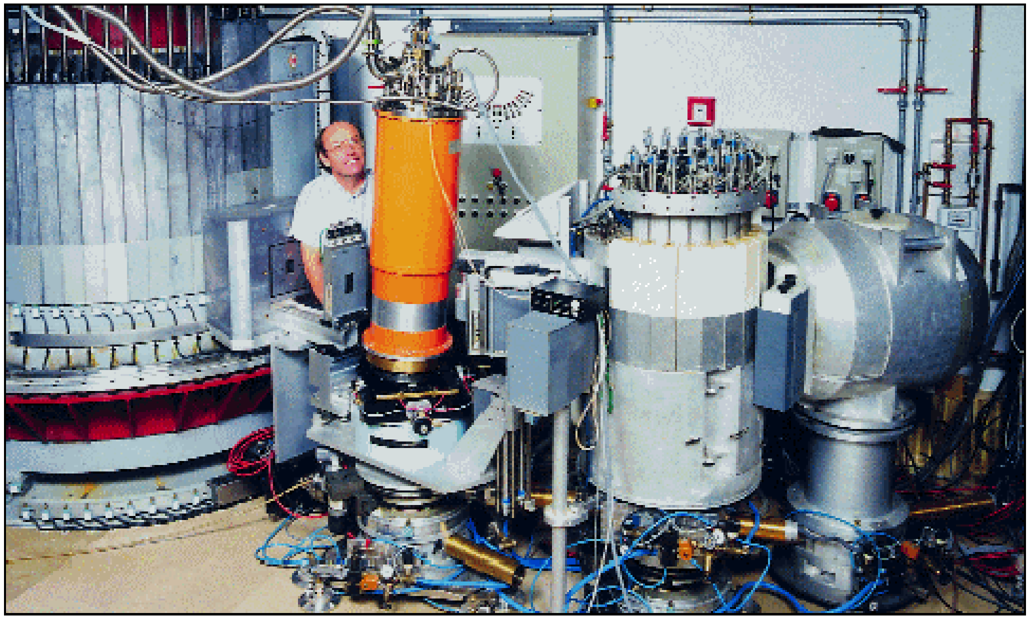
- Coherent scattering measures scattering from single phonons

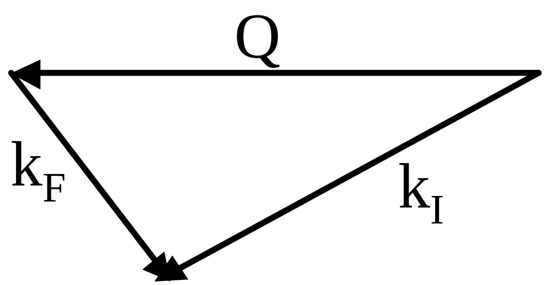
$$\left(\frac{d^{2}s}{d\Omega dE}\right)_{coh\pm1} = s_{coh}\frac{k'}{k}\frac{p^{2}}{MV_{0}}e^{-2W}\sum_{s}\sum_{G}\frac{(\vec{Q}.\vec{e}_{s})^{2}}{w_{s}}(n_{s}+\frac{1\pm1}{2})d(w\mp w_{s})d(\vec{Q}-\vec{q}-\vec{G})$$

- Note the following features:
  - Energy & momentum delta functions => see single phonons (labeled *s*)
  - Different thermal factors for phonon creation (n_s+1) & annihilation (n_s)
  - Can see phonons in different Brillouin zones (different recip. lattice vectors, ***G***)
  - Cross section depends on relative orientation of ***Q*** & atomic motions ($\boldsymbol{e}_s$)
  - Cross section depends on phonon frequency (ω_s) and atomic mass (M)
  - In general, scattering by multiple excitations is either insignificant or a small correction (the presence of other phonons appears in the Debye-Waller factor, W)

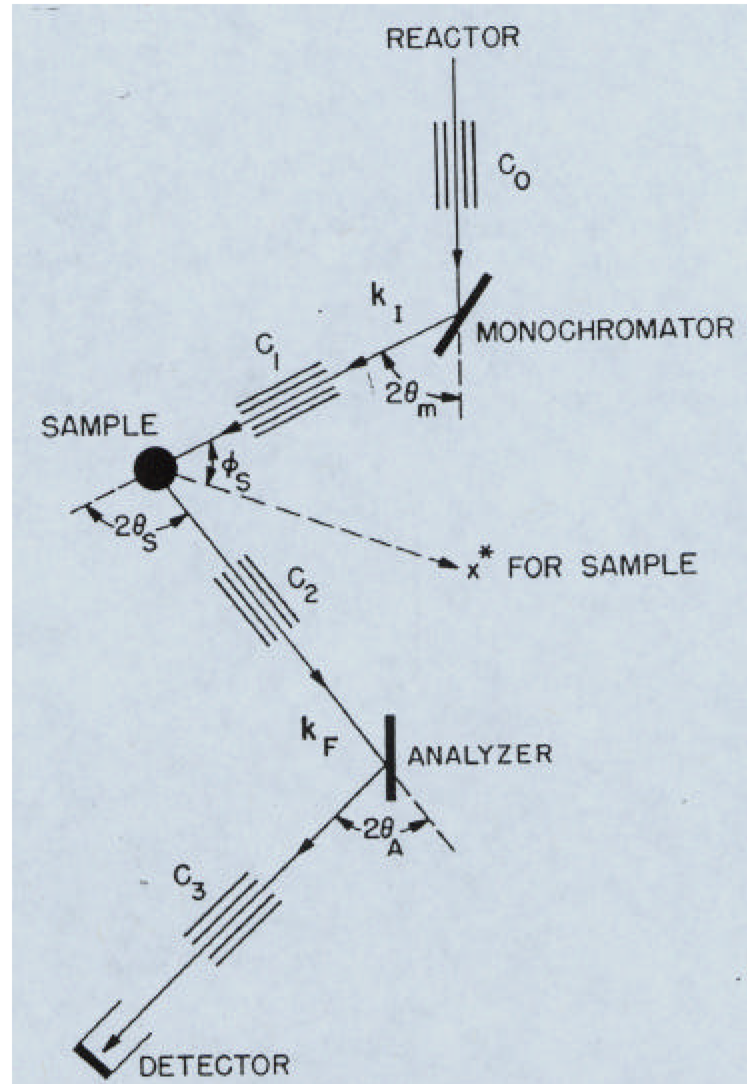


The Workhorse of Inelastic Scattering Instrumentation at Reactors Is the Three-axis Spectrometer



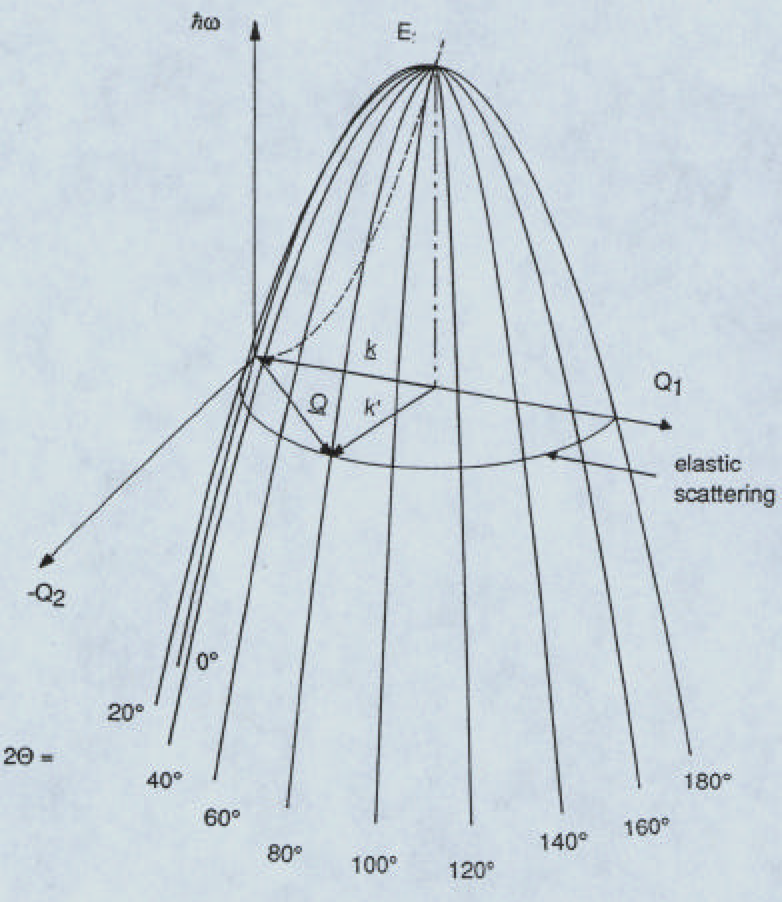


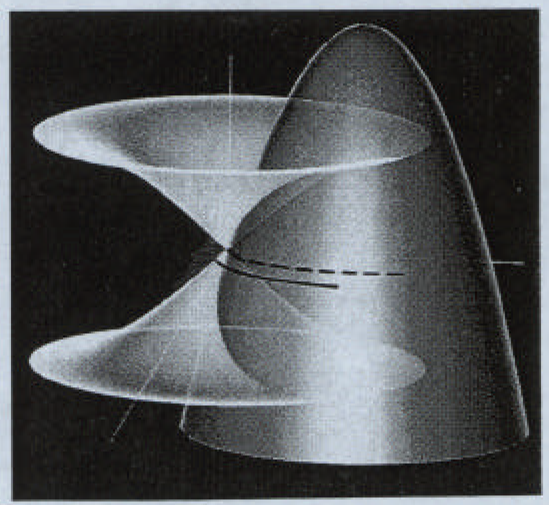
“scattering triangle”



The Accessible Energy and Wavevector Transfers Are Limited by Conservation Laws

- Neutron cannot lose more than its initial kinetic energy & momentum must be conserved

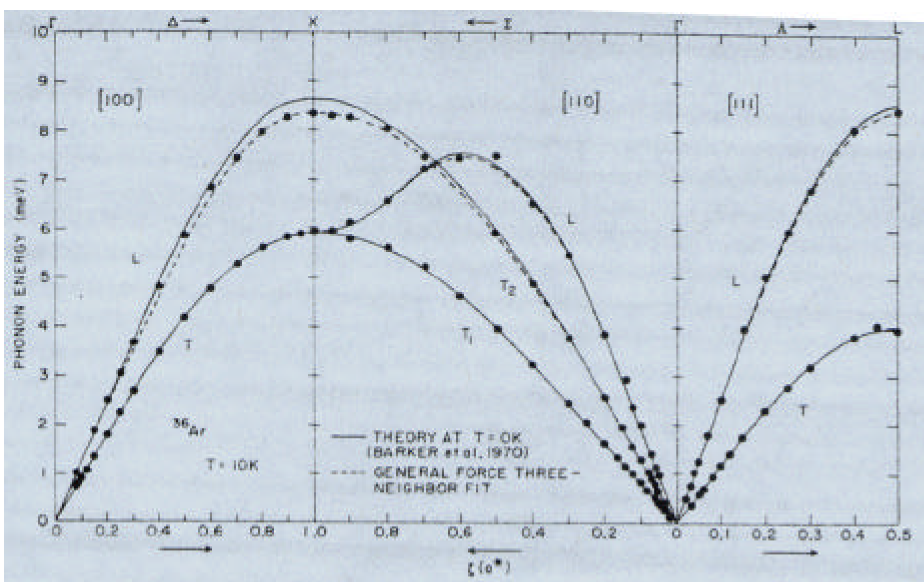




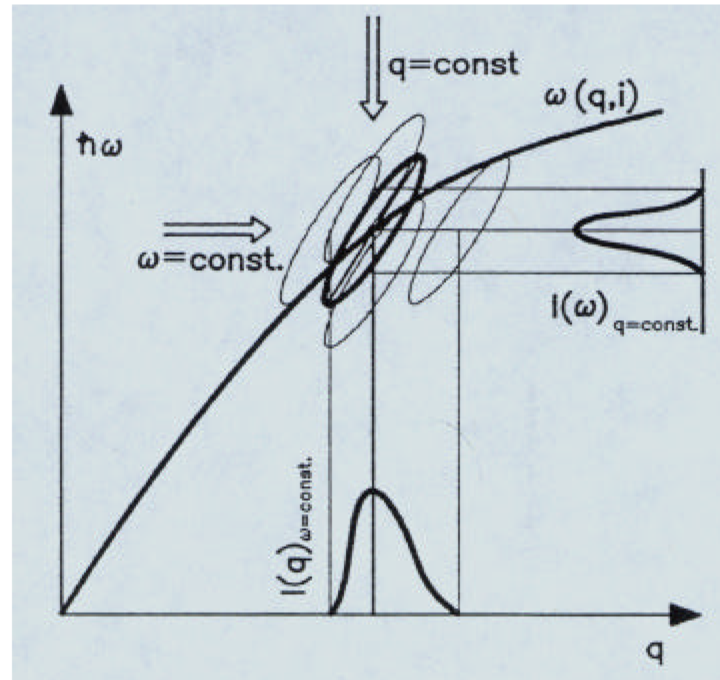
Intersection of the dynamical range surface (paraboloid) with a (rotationally symmetric) dispersion surface. The projection of the lines of intersection into the Q-plane are different for energy gain and energy loss

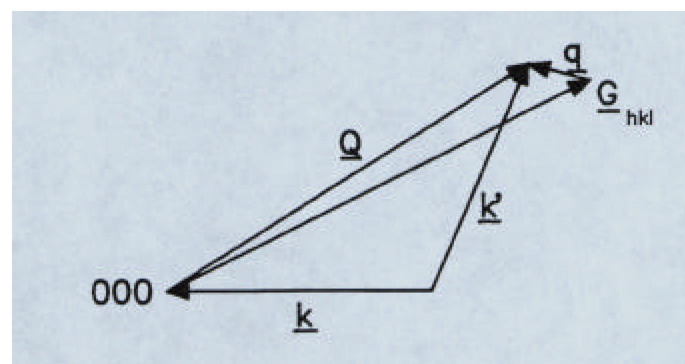
Triple Axis Spectrometers Have Mapped Phonons Dispersion Relations in Many Materials

- 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





What Use Have Phonon Measurements Been?

- Quantifying interatomic potentials in metals, rare gas solids, ionic crystals, covalently bonded materials etc

- Quantifying anharmonicity (I.e. phonon-phonon interactions)

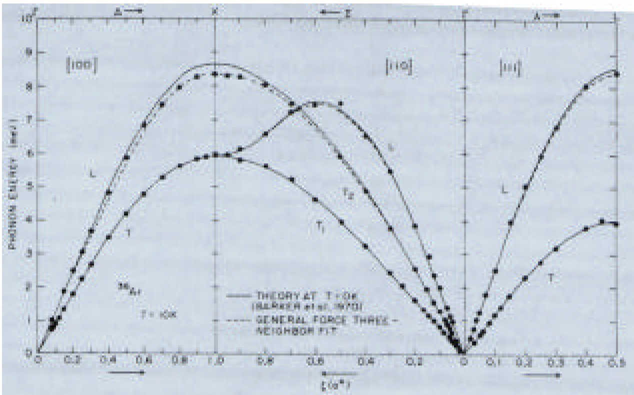
- Measuring soft modes at 2^{nd} order structural phase transitions

- Electron-phonon interactions including Kohn anomalies

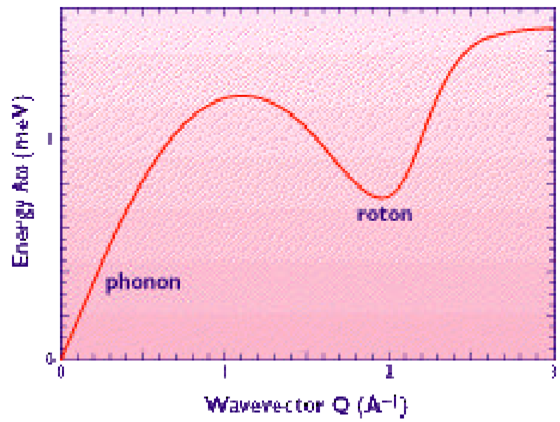
- Roton dispersion in liquid He

- Relating phonons to other properties such as superconductivity, anomalous lattice expansion etc

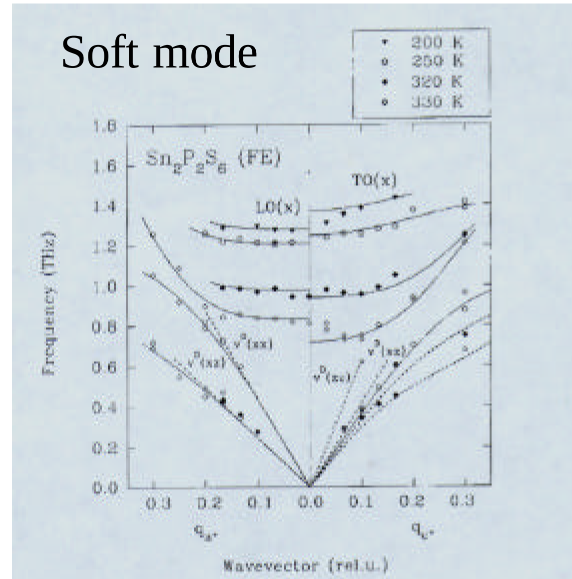
Examples of Phonon Measurements



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



Roton dispersion in ^{4}He



Soft mode

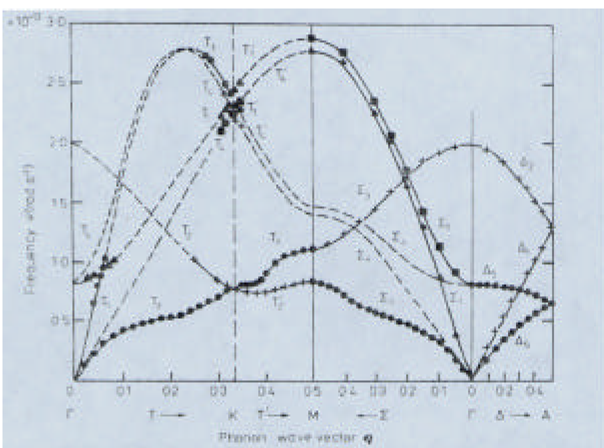


Figure 1. Dispersion curves of ^{110}Cd at 77 K. Different symbols are used for different branches to distinguish in regions where they come close to each other. Symmetry labels are explained in figure 6(a).

Phonons in ^{110}Cd

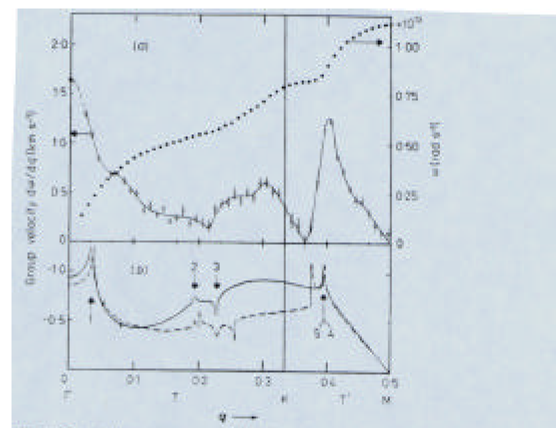
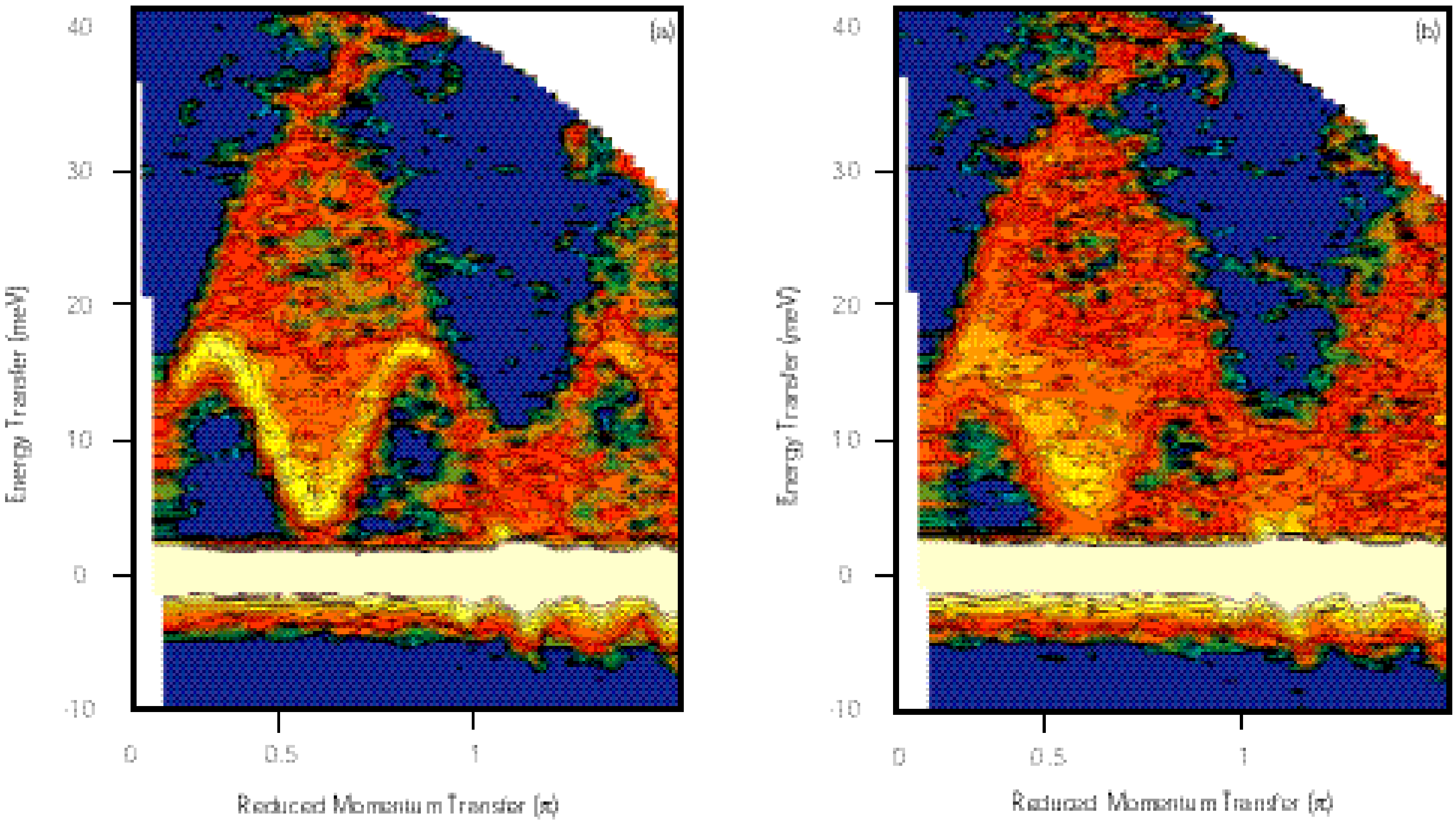


Figure 2. (a) dispersion curves (full circles) and group velocity dω/dq (open circles) for the T_1-T_1 branch at 77 K. At q = 0 the group velocity obtained from the elastic constants (Garland and Silverman 1960) is represented by a full circle. The line is a guide to the eye. (b) theoretical predictions of the group velocity for the T_1-T_1 direction. The full line is calculated in perturbation theory including second-order terms in the potential; the broken line including third-order terms in the potential. The numbers refer to the anomalies listed in table 2.

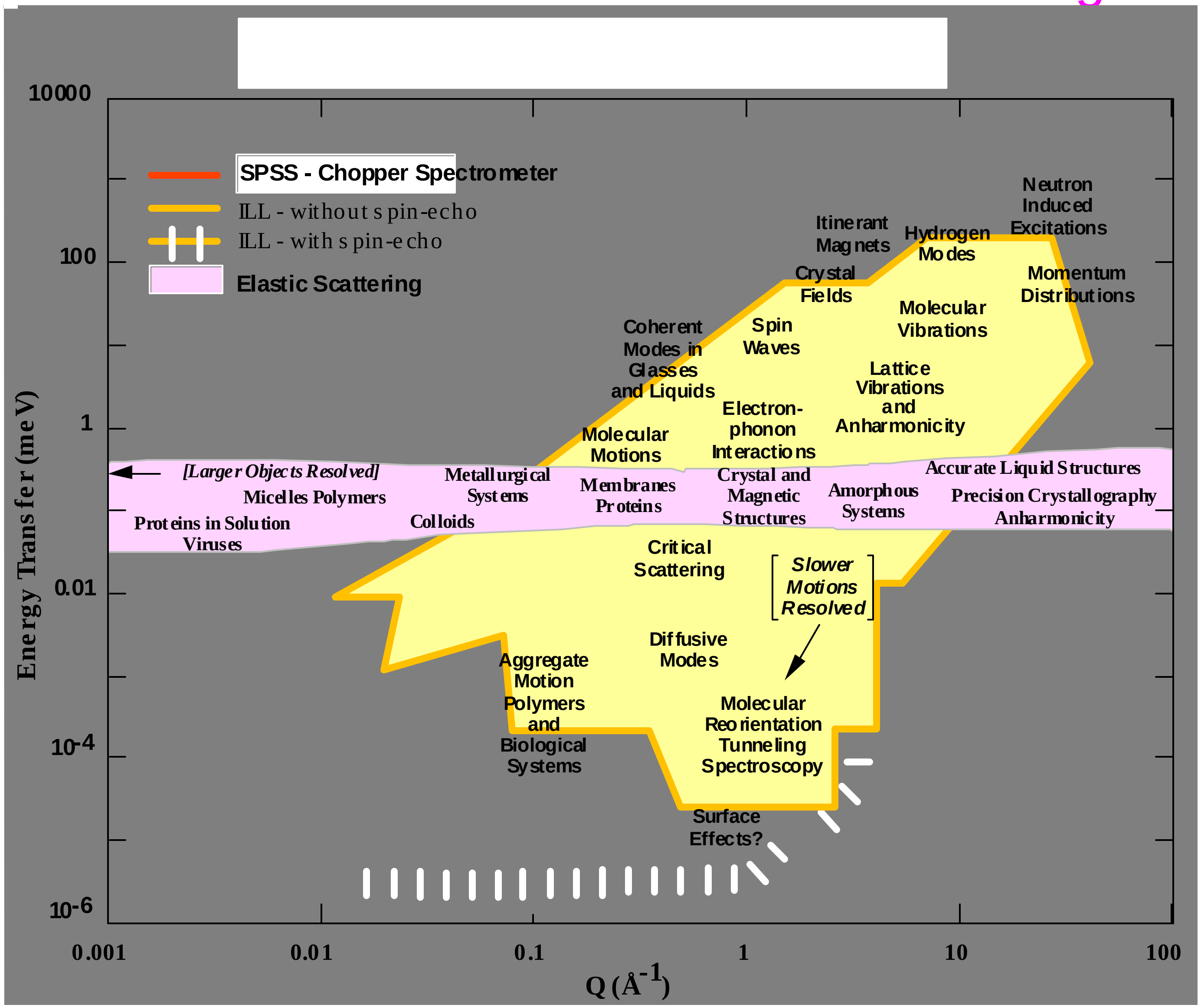
Kohn anomalies in ^{110}Cd

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