**Inelastic scattering spectroscopy**

- We here limit the inelastic processes to energy transfers in the range below 1 eV
- This means that we look at:
  i. Molecular motion and vibration
  ii. Lattice waves (phonons)
  iii. Molecular diffusion and reorientation
- Two experimental techniques are considered:
  i. Inelastic neutron scattering
  ii. Inelastic X-ray scattering
Thermal diffuse scattering

- A time dependent scattering density including small fluctuations in the positions of the atoms is given by:

\[ \rho(x,t) = \rho_0(x) + \frac{\partial \rho}{\partial x} \Delta(x,t) + \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2} \Delta^2(x,t) + \ldots \]

- The fluctuations \( \Delta(x,t) \) can be described as waves with form:

\[ \Delta(x_n, t) = A_q e^{i(\omega_q t - qx_n)} \]

- The inelastic scattering function for harmonic lattice waves scattered by thermal neutrons or X-rays can now be shown to take the following expression:

\[ S(Q, \omega) = N \left| F_{inel}(Q) \right|^2 \frac{(2\pi)^3}{V_c} \sum_G \left\{ \delta(Q + \bar{q} - \bar{G}) \delta(\omega + \omega_q) + \delta(Q - \bar{q} - \bar{G}) \delta(\omega - \omega_q) \right\} \]

- In general:
  - \( Q \) gives information about structure
  - \( \omega \) gives information about dynamics (motion)

- We can extract information from elastic, quasielastic and inelastic scattering
The difference between acoustic and optical phonons

**Optical phonons:**

All phonons that have $\omega \neq 0$ at $k = 0$ are optical. For optical phonons the atoms are oscillating in antiphase and in an ionic crystals these charge oscillations create a time-varying electrical dipole moment. They are called optical because in ionic crystals they are excited very easily by light (infrared radiation). Optical phonons can be transversal (TO) or longitudinal (LO)

**Acoustic phonons:**

The atoms oscillate in phase. Acoustic phonons have frequencies that become small for long wavelengths, and correspond to sound waves in the lattice. Longitudinal and transverse acoustic phonons are often abbreviated as LA and TA phonons, respectively.

Go to this link for animations of transverse and acoustic phonons as a function of mass and k-vector:
http://dept.kent.edu/projects/ksuviz/leeviz/phonon/phonon.html
Phonons in Ge along the [111] direction at $T = 80$ K

- **Inelastic neutron scattering** can be used to study the phonons as a function of direction (represented by the [111] direction in Ge on the fig.)

- Raman scattering and infra-red absorption spectrosocphies are alternative methods of studying phonons. However, these techniques only give information at the zone center ($k = 0$); i.e. long wavelength excitations.

There are 3 acoustic and 3 optical branches.

The transverse branches are two-fold degenerate.
- Inelastic neutron scattering is the technique to apply if one wants derive the full dispersion relation (relationship between the phonon energy and the wave-vector)

- The dispersion relation contains all information about the lattice dynamics and the elastic couplings in the material

- Based on the dispersion relation several physical properties can be derived. These include:
  
  i. Lattice contributions to the specific heat
  
  ii. Thermal expansion coefficients
  
  iii. Thermal conductivity

Phonon dispersion in MgB$_2$ determined by inelastic neutron scattering
Coherent versus incoherent scattering

The scattering function $S(Q, \omega)$ has contributions from single-particle scattering (incoherent) and from multiple-particle scattering (coherent)

- **Incoherent signal:** $S_{\text{inc}}(Q, \omega)$ is the Fourier transform in space and time of the self correlation function. Tells us how individual atoms behave independent of other atoms. Incoherent scattering is therefore angle-independent.

- **Coherent signal:** $S_{\text{coh}}(Q, \omega)$ is the Fourier transform in space and time of the pair correlation function. Tells us how atoms behave in relation to other atoms. Coherent scattering is therefore highly angle dependent!
If an atom is moving, the neutrons which scatter from it may gain or lose a small amount of energy.

Quasi-elastic scattering is applied to determine diffusion rates, molecular reorientation motion, order-disorder transitions etc.

Random diffusion

\[ P(t) = e^{-t/\tau} \]

\[ S(\omega) = \frac{1}{\pi} \frac{1}{1 + (\omega \tau)^2} \]
Inelastic X-ray scattering

- Typical X-ray energies are in the range 5 – 20 keV. Thus, phonons with energies in the range far below 1 eV give rise to relative energy shifts in the range $10^{-5} – 10^{-6}$.

- The use of monochromator crystals, such as Si, at very high scattering angles can give the required ultra-high energy resolution to resolve phonons.

- The spectrum in the figure was acquired at ESRF. The X-ray beam was monochromatized by a cryogenically cooled silicon (111) crystal and by a very high energy resolution monochromater, operating in backscattering geometry and using the Si (888) reflection order. An energy resolution of 3.9 meV was achieved.

- The experiment was performed on a polycrystalline sample of iron at 28 GPa. Iron transforms from the low pressure bcc structure to a hcp structure between 12 and 15 GPa.

Acoustic peak from the diamond anvils