Frontiers of Experimental Condensed Matter Physics

- Part A Scattering:

  Section 2: Dynamical structures

  - Example: thermal excitation.
  - A simple model – uncorrelated motion - illustrates the two main effects
    - Reduction in intensity of diffraction features. The Debye Waller effect.
    - Emergence of diffuse scattering.
  - A more realistic model of scattering from phonons.
    - Structure of the diffuse scattering
    - Conservation laws for Energy and crystal momentum
    - Phonon dispersion measurement

"Einstein" model for thermal vibrations

- Each atom vibrates independently
  - Assume each atom has a Gaussian spread function.
  - In 1-D, the time averaged scattering density is given by the following convolutions

$$\langle \rho(x) \rangle = \rho_o(x) * \left(\pi b^2\right)^{-1/2} \exp\left\{-x^2/b^2\right\} * \sum_n \delta(x - na)$$

Atom density | Gaussian spread | Perfect lattice

  - Fourier transform, of this time-independent function leads to elastic scattering

$$F(u,0) = F_o(u)\exp\left(-\pi^2 b^2 u^2\right)\sum_h \delta(u - h/a)$$

    (for the Fourier transforms see Cowley Ch.2 eq. (49) and (61))
  - The observed intensity is

$$|F(u,0)|^2 = |F_o(u)|^2 \exp\left(-2\pi^2 b^2 u^2\right)\sum_h \delta(u - h/a)$$

    - Elastic intensity only at positions corresponding to the average lattice
    - Diffracted intensity reduced by a factor depending on b^2, where b is the rms atom displacement.

Debye Waller factor

Classical 1-D harmonic oscillator

- Equipartition of energy gives mean potential energy = $k_BT/2$.

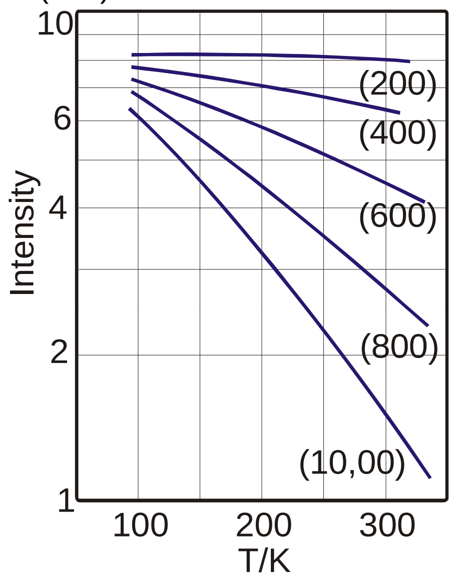
Spring constant

$$\langle U\rangle = \frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_BT$$

- $<x^2> \sim b^2$, hence $b^2 \sim$ T and $\left|F(u,0)\right|^2 \propto \exp\left(-Tu^2\right)$

Debye Waller factor

(n00) reflections for aluminium



- Note:
- Dependence on T;
- Dependence on u through n in (n00).
- ~as predicted

Redrawn from *Phys Rev* 152 591 (1966)

Diffuse scattering

Where does the lost intensity go?

- To calculate the total scattering (all energy changes) we need to determine

$$\int\left|F(\mathbf{u},\nu)\right|^2 \mathrm{d}\nu = \int \mathrm{d}\nu \int\int P(\mathbf{r},t)\exp(2\pi i(\mathbf{u}.\mathbf{r}+\nu t))\,\mathrm{d}\mathbf{r}\,\mathrm{d}t$$

- Performing the integration over ν first, note

$$\int \exp(2\pi i\,\nu t)\,\mathrm{d}\nu = \delta(t)$$

- Total scattering is

$$I(\mathbf{u}) = \int\int P(\mathbf{r},t)\exp(2\pi i\mathbf{u}.\mathbf{r})\delta(t)\,\mathrm{d}\mathbf{r}\,\mathrm{d}t$$

$$= \int P(\mathbf{r},0)\exp(2\pi i\mathbf{u}.\mathbf{r})\,\mathrm{d}\mathbf{r}$$

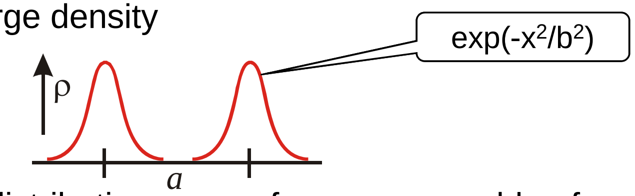
i.e. the Fourier transform of Patterson function with $t = 0$.

- What does the Patterson function look like?
- Consider, first, the average charge density of two δ-fn atoms with a thermal spread given as above

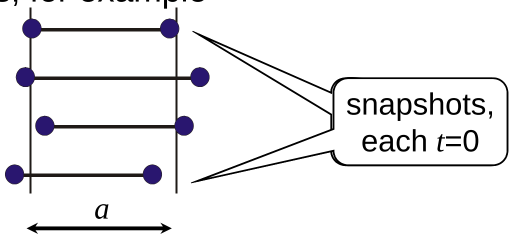
$$\langle\rho(x)\rangle = \{\delta(x)+\delta(x-a)\} * \left\{(\pi b^2)^{-1/2}\exp\{-x^2/b^2\}\right\}$$

Spatial correlation at t=0

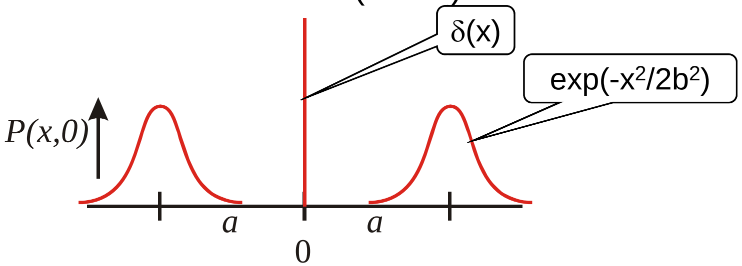
- Charge density



- the distribution comes from an ensemble of snapshots, for example



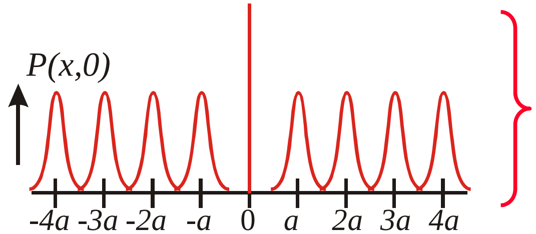
- The correlation function (at t=0) looks like



Note the central peak is a δ-function. Each atom "sees" itself at rest. The Gaussian peaks at ± *a* are broadened by convolution.

Result for a 1-D lattice

- Similar arguments give, for a 1-D lattice:



- The full expression, including the atomic charge density is

$$P(x,0)) = \rho_o(x) * \rho_o(-x)$$

$$* \left\{ \delta(x) + \sum_{n\neq 0} \delta(x-na) * \left(2\pi b^2\right)^{-1/2} \exp\left\{-x^2/2b^2\right\} \right\}$$

- Rearranging gives

$$= \rho_o(x) * \rho_o(-x) * \left[\sum_{all\ n} \delta(x-na) * \left(2\pi b^2\right)^{-1/2} \exp\left\{-x^2/2b^2\right\} \right]$$

$$+ \delta(x) - \delta(x) * \left(2\pi b^2\right)^{-1/2} \exp\left\{-x^2/2b^2\right\}$$

- Fourier transformation gives the scattered intensity.

$$I(u) = FT[P(x,0))]$$

Diffuse intensity

- The various parts FT as follows:

$$\boxed{\rho_o(x) * \rho_o(-x) \Rightarrow |F_o|^2} \qquad \boxed{\sum_{all\ n} \delta(x - na) \Rightarrow \sum_h \delta(u - h/a)}$$

$$\boxed{(2\pi b^2)^{-1/2} \exp\{-x^2/2b^2\} \Rightarrow \exp\{-2\pi^2 b^2 u^2\}} \qquad \boxed{\delta(x) \Rightarrow 1}$$

- Remember the scattered intensity we are calculating is the intensity (at all energies) as a function of scattering vector u. It is

$$I(u) = \underbrace{|F_o|^2 \times \exp\{-2\pi^2 b^2 u^2\} \times \sum_h \delta(u - h/a)}$$

$$+ \underbrace{|F_o|^2 \left[1 - \exp\{-2\pi^2 b^2 u^2\}\right]}$$

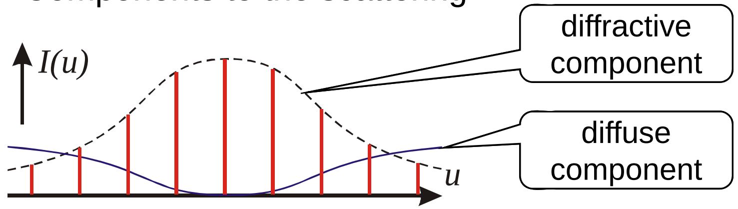
diffuse scattering, i.e. at all u values

diffraction, the average lattice gives discrete peaks, I is as before (Slide 2)

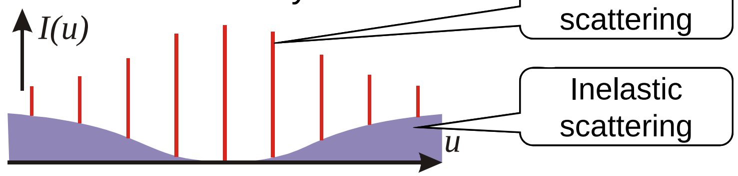
- The two terms correspond to *elastic* and *inelastic* scattering respectively. We know this because the first term is identical to the explicit elastic intensity we determined earlier.

Pictorially

- Components to the scattering



- Measured intensity



- The shape of the diffuse scattering (as well as the energy loss/gain) depends on the detail of the model used. In the present case the diffuse scattering has a Gaussian shape mainly because we took the motion to be uncorrelated and of Gaussian form. (Note the intensity distribution also depends on the atomic form factor, $|F_o|^2$)

Scattering from phonons

- Lattice with a periodic distortion
  - More realistic treatment of thermal properties
  - Emergence of kinematic laws (Conservation of energy and crystal momentum)
- Time dependent distortion

$$\rho(\mathbf{r},t)=\underbrace{\langle\rho(\mathbf{r})\rangle}_{\text{average density, time independent, with lattice periodicity}}+\underbrace{\Delta\rho(\mathbf{r},t)}_{\text{deviation from average does not have the lattice periodicity}}$$

  - The correlation function is

$$P(\mathbf{r},t)=\{\underset{1}{\langle\rho(\mathbf{r})\rangle}+\underset{2}{\Delta\rho(\mathbf{r},t)}\}*\{\underset{3}{\langle\rho(-\mathbf{r})\rangle}+\underset{4}{\Delta\rho(-\mathbf{r},-t)}\}$$

$$= 1*3 + 2*4 + \underbrace{1*4 + 2*3}_{=0}$$

  - To see that the last two terms are zero, consider, for example, 1 * 4 . The argument is not obvious.

- 1 * 4 is

$$\langle\rho(\mathbf{r})\rangle*\Delta\rho(-\mathbf{r},-t)=\overbrace{\overbrace{\langle\rho_o(\mathbf{r})\rangle}^{\text{average atom density}}*\overbrace{\sum_n\delta(\mathbf{r}-\mathbf{R}_n)}^{\text{lattice sites}}}^{\langle\rho(\mathbf{r})\rangle}*\Delta\rho(-\mathbf{r},-t)$$

$$\underbrace{\sum_n\delta(\mathbf{r}-\mathbf{R}_n)*\Delta\rho(-\mathbf{r},-t)}_{A}$$

- The term A is a superposition of $\Delta\rho$ at each lattice site. Since $\Delta\rho$ dos not have the lattice periodicity and its space and time average is (by definition) zero, the superposition result in zero, everywhere.
- Returning to the non-zero terms in the correlation function

$$P(\mathbf{r},t)=\underbrace{\langle\rho(\mathbf{r})\rangle*\langle\rho(-\mathbf{r})\rangle}_{\text{periodic and time independent}}+\underbrace{\Delta\rho(\mathbf{r},t)*\Delta\rho(-\mathbf{r},-t)}_{*}$$

- As before, we have two terms. The first term gives elastic, diffraction; the second term is the diffuse, inelastic scattering (calculated below).

Phonon displacements

- Model the phonon as a longitudinal wave travelling in the x-direction.
$$\Delta = A\cos 2\pi\left(lx - \nu_l t\right)$$
- For an atom displaced from an average site at $x=X$, density ρ follows from a Taylor expansion
$$\rho_{atom}(x,t) = \rho_o(X+\Delta,t)$$
$$= \rho_o(X) + \Delta(X,t)\rho_o'\big|_{x=X} + \cdots$$
- For the lattice, as a whole, the density deviation is
$$\Delta\rho(x,t) = \left\{\rho_o'(x) * \sum_n \delta(x-na)\right\} A\cos 2\pi\left(lx-\nu_l t\right)$$
- We can now determine the diffusive, inelastic scattering contribution from the time dependent term, $\boxed{*}$, in the correlation function on the previous page
$$P_d(x,t) = \Delta\rho * \Delta\rho =$$
$$\rho_o'(x)*\sum_n\delta(x-na)A\cos 2\pi\left(lna-\nu_l t\right)$$
$$* \rho_o'(-x)*\sum_m \delta(x+ma)A\cos 2\pi\left(lma-\nu_l t\right)$$

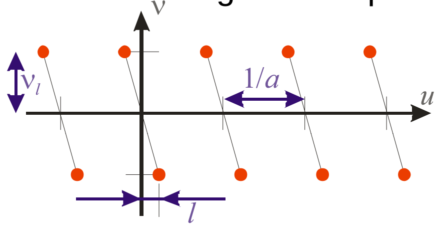
diffuse

- rearranging gives
$$P_d(x,t)=\sum_n\sum_m A^2\cos 2\pi\{l(n-m)a-\nu_l t\}$$
$$\times\left[\rho_o'(x)*\rho_o'(-x)*\delta(x-(n-m)a)\right]$$
which depends only on n-m, so the double sum can be replaced with a single sum,
$$P_d(x,t) = NA^2\underbrace{\left(\rho_o'(x)*\rho_o'(-x)\right)}$$
$$* \underbrace{\sum_n\delta(x-na)} \times \underbrace{\cos 2\pi\{lx-\nu_l t\}}$$
- Fourier transformation of this correlation function leads to the scattered intensity.
$$|F(u,\nu)|^2 \propto$$
$$|2\pi uF(u)|^2 \underbrace{\sum_h \delta((u-h/a),\nu)} * \underbrace{\delta(u\pm l,\nu\pm\nu_l)}$$
  - the δ-fn comb is at $\nu=0$ (no time dependence in that term of the correlation function).
  - we have used the general result for the FT of a derivative: FT[$f'(x)$]=-2$\pi iuF(u)$.

Kinematics: phonon scattering

Energy & crystal momentum conservation

- The expression shows we only get scattered intensity at discrete values of scattering vector, u, and at discrete changes in frequency, ν_l.



- We have demonstrated, explicitly, the conventional laws of conservation in a periodic system. i.e. Energy and crystal momentum conservation. They are more often expressed as

$$E_f = E_i \pm \hbar\omega$$

phonon angular frequency

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{G} \pm \mathbf{q}$$

phonon wave-vector

where f is the final state of the scattered particle and i is the initial state. Note momentum conservation is usually expressed in term of the wave vector (related to momentum by $\mathbf{p} = \hbar\mathbf{k}$).

  - $\mathbf{G}$ is a reciprocal lattice vector
  - ± describes phonon creation and annihilation.

Notes:

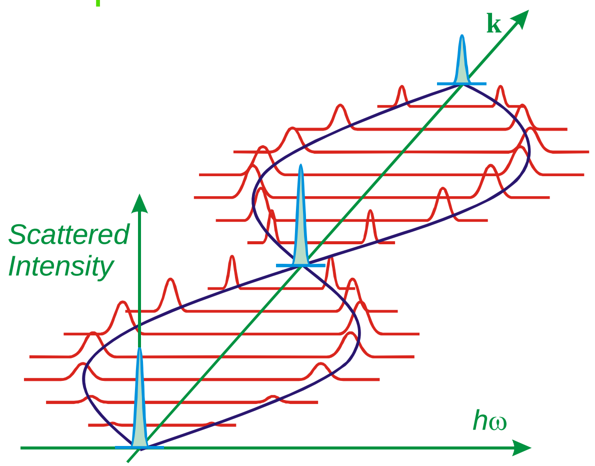
- We have calculated the “diffuse” scattering (i.e. that deriving from time-dependence of the scatterers). Scattering, in the case of single phonons, is not diffuse but discrete.

- It is instructive to compare the result with our earlier, less realistic, treatment of thermal effects (result on p.7). Note: uncorrelated motion (earlier case) leads to scattering in at all values of $\mathbf{u}$.

- We have discovered that correlations (in x and t) of the scatterers are exhibited directly in the distribution of the scattered particles.
  - Spatial correlations manifest themselves at specific scattering vectors (u_x,u_y,u_z)
  - Temporal correlations manifest themselves at specific energies ($\Delta E = \pm\hbar\omega$).

Phonon inelastic scattering

- Schematic spectrum for acoustic branch

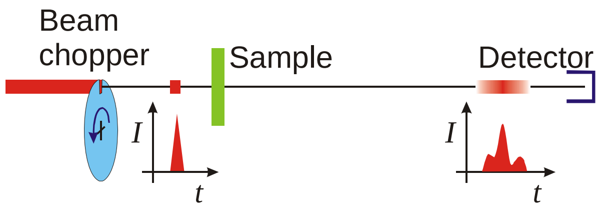


- A branch of acoustic phonons is sketched above:
  - Elastic diffraction peaks (light blue) have been added (NB calculation above, was only inelastic)
  - Inelastic peaks (red) follow the phonon dispersion (dark blue)

Detail:
  - Form factor for inelastic scattering ~$\mathbf{k}^2$ for small $\mathbf{k}$. It decreases with F at larger $\mathbf{k}$.
  - Energy loss (ω<0, "Stokes line") is usually stronger than energy gain (ω>0, "anti-Stokes line").

Illustration: surface phonons

- Surface phonons
  - Vibrations localised at a surface require a probe that scatters strongly from the surface.
  - Low energy electrons and atoms are the main candidates.
  - Helium atoms are "light" and scatter mainly elastically or through single phonon scattering.
  - The interaction is only with the outermost surface layer and are exclusively sensitive to the surface motion.
  - Techniques are similar (though usually cruder) than the corresponding neutron technology.
  - Eg. Energy changes are usually measured by time of flight methods.
    - Incident beam converted to pulse with a mechanical chopper
    - Time to reach detector measured



Phonons on NiO(100)

- kinematics

$$E_f = E_i + \Delta E$$

$$\Delta E = E_i\left(\left(k_f / k_i\right)^2 - 1\right)$$

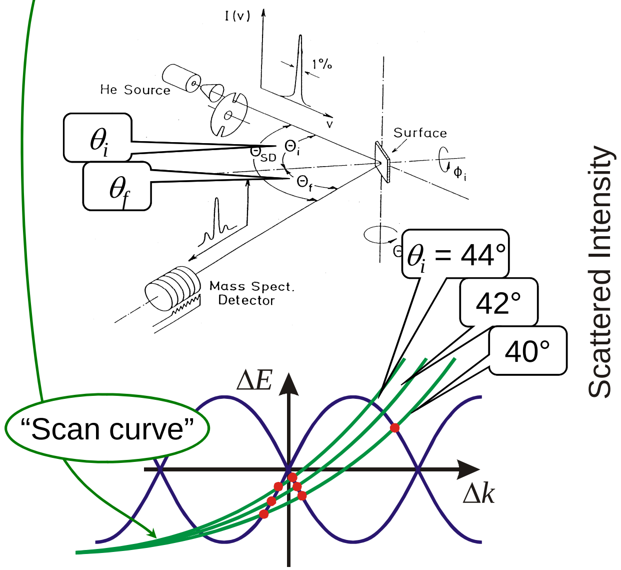
Parallel to surface

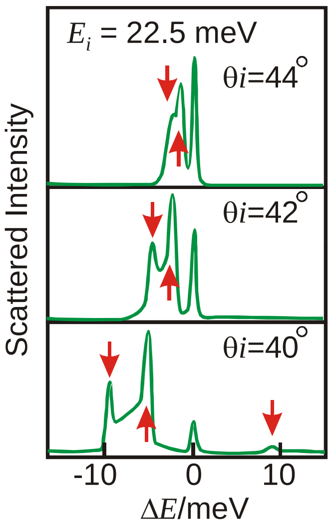
$$\Delta K = k_f \sin\theta_f - k_i \sin\theta_i$$

$$k_f / k_i = \frac{\sin\theta_i + \Delta K / k_i}{\sin\theta_f}$$

$$\Delta E = E_i\left(\left(\frac{\sin\theta_i + \Delta K / k_i}{\sin\theta_f}\right)^2 - 1\right)$$

Experiment Schematic





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