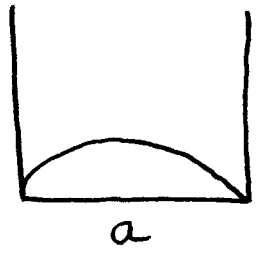


3D Debye Model

Peter Debye reasoned that the vibrational modes can be approximated as elastic waves, or standing waves that vanish at the endpoints. We can ^{also} do the calculation for photons and then let $c \rightarrow v$.

Standing Wave Approach



elastic waves: disturbances subject linear restoring forces.

standing waves: linear combinations

$$n_x (\lambda_x/2) = a \quad n_y (\lambda_y/2) = a$$

$$n_z (\lambda_z/2) = a$$

n_x, n_y, n_z define modes.

$$\frac{2a}{\lambda_x} = n_x \quad \frac{2a}{\lambda_y} = n_y \quad \frac{2a}{\lambda_z} = n_z$$

$$4a^2 \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2} \right) = n_x^2 + n_y^2 + n_z^2$$

$$\frac{4a^2}{\lambda^2} \left(\underbrace{\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma}_1 \right) = n_x^2 + n_y^2 + n_z^2$$

$$4a^2 / \lambda^2 = n_x^2 + n_y^2 + n_z^2$$

$$v = \lambda \nu \quad 4a^2 \frac{\nu^2}{v^2} = r^2$$

$$\begin{aligned} \text{No. modes (0-r)} &= \frac{1}{8} \frac{4}{3} \pi r^3 = M(r) \\ &= \pi r^3 / 6 \end{aligned}$$

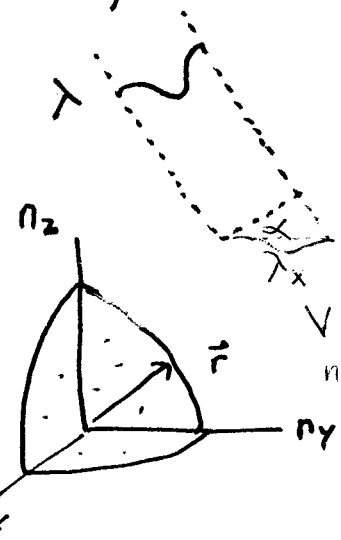
$$r = \frac{2a\nu}{v}$$

$$M(\nu) = \frac{\pi}{6} \left(\frac{2a\nu}{v} \right)^3 = \frac{4}{3} \pi V \nu^3 / v^3$$

$$N(\nu) = \frac{dM}{d\nu}$$

$$\text{density of modes } N(\nu) d\nu = \frac{4\pi V}{v^3} \nu^2 d\nu$$

also same as density states calc. in particle in a box

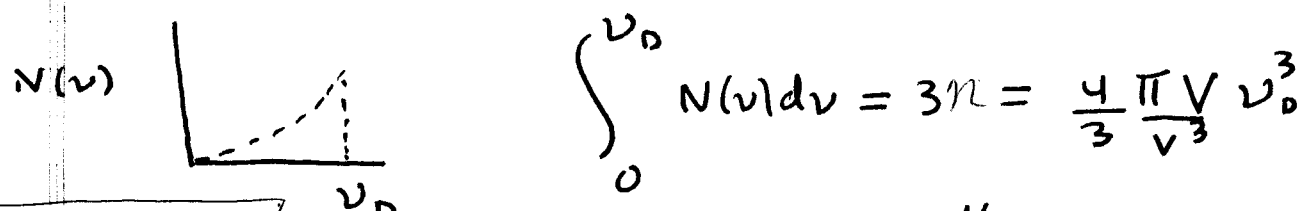


$$\lambda_x \cos \alpha = \lambda$$

$V =$ no. combos n_x, n_y, n_z through



$3N$ modes where N : no. of bases no. rotation, translation



"acoustic waves" & "optical waves"

$\therefore v_0 = v \left\{ \frac{9N}{4\pi V} \right\}^{1/3}$

$v_{\text{metal}} \sim 2 \times 10^5 \text{ cm s}^{-1}$
 (sound speed) (300K)
 $N/V \sim 4 \times 10^{22} \text{ cm}^{-3}$
 $v_0 = 6 \times 10^{12} \text{ s}^{-1}$
 $\tilde{\nu}_0 = v_0/c = 200 \text{ cm}^{-1}$

In terms of v_0 :

$N(v) dv = \frac{9N}{v_0^3} v^2 dv$

The Debye frequency, albeit artificial, can be obtained by measurements on the surface (elastic properties, C_v)

Note: intramolecular vibrations can be detected if $> v_0$.

Often, instead of v_0 or ω_0 , one sees the Debye temperature:

$\frac{\hbar \omega_0}{k_B} \equiv \Theta_D \equiv \frac{\hbar v_0}{k_B} = \frac{v_0/c}{k_B/hc} = \frac{\tilde{\nu}_0}{\tilde{k}_B} \quad \tilde{k}_B = 0.695 \frac{\text{cm}^{-1}}{\text{K}}$

Substance	$\tilde{\nu}_D (\text{cm}^{-1})$	$\Theta_D (\text{K})$
Ag	156	225
Pt	167	240
W	278	400
C (graphite)	528	760
C (diamond)	1550	2230

The higher the Θ_D the more rigid the surface.

What is the average energy per mode?

$\langle E \rangle_{\text{mode}} = \frac{\sum_i E_i e^{-E_i/kT}}{q_{\text{vib}}} = k_B T^2 \frac{\partial \ln q_{\text{vib}}}{\partial T}$

$q_{\text{vib}} = \sum e^{-E_i/kT}$

— 2
 — 1
 — 0

$$E_{TOTAL} \Rightarrow C_V$$

$$\langle E \rangle_{mode} = \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$$

zero-point energy

$$\langle E \rangle_{mode} = \hbar \omega \bar{n}_\omega$$

excluding zero pt energy

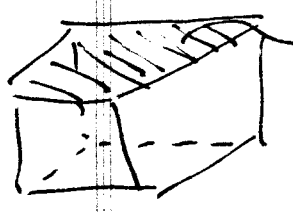
photon occupation number

$$\bar{n}_\omega = \frac{1}{e^{\hbar \omega / kT} - 1}$$

Bose-Einstein distribution law for phonons (equivalent to photons)
s = integer-spin particle

Surface Phonons

skip 2008



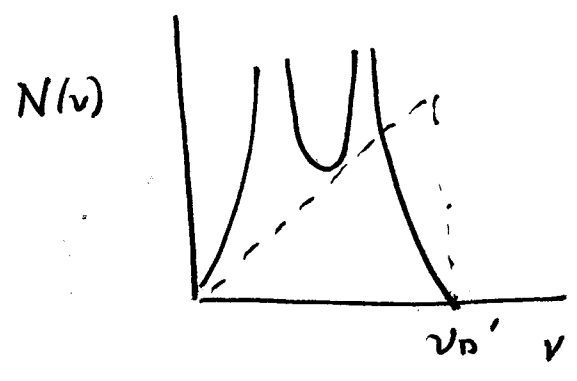
surface phonons also exist, ω and ω_0 adiabatic.

$$\omega'_0 < \omega_0$$

$$N(\omega) d\omega = \frac{2\pi A}{v^2} \omega d\omega$$

$$\omega'_0 = \omega \left(\frac{2N}{\pi A} \right)^{1/2}$$

But reality is different: according to Montroll, for a square lattice the density of states function shows two strong bands.



LEED (Low Energy Electron Diffraction)

Both X-rays + electrons of the right energy range have wave lengths corresponding with spacings in crystals. Their penetration power differs: X-rays can go through solids whereas electrons have smaller penetration depths.

X-Ray Diffraction (bulk) (geometrical, not dynamic)

The actual equations for X-ray scattering can be reduced to reflection off successive planes:



$2d \sin \theta = n \lambda$ for phases of R_1 + R_2 to match up and allow constructive interference

(cubic)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

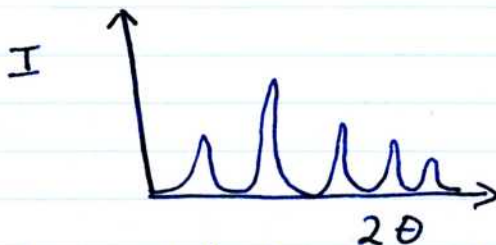
Laue Method: "white" X-ray source with fixed angle

$$\sin \theta = \frac{n \lambda}{2d}$$

Bragg Method: monochromatic X-ray source + rotate crystal

$$= \frac{n \lambda}{2} \frac{\sqrt{h^2 + k^2 + l^2}}{a}$$

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$



Positions of peaks determined by n, h, k, l, a - cell dimension

Intensities determined by type of cell + basis

b) LEED

$$\lambda = \lambda_{DB} = \frac{h}{P} \quad E = P^2 / 2m_e$$

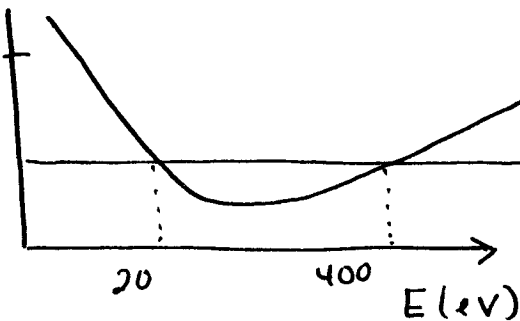
$$\lambda = \frac{h}{(2Em_e)^{1/2}} = \left(\frac{150.6}{E(\text{eV})} \right)^{1/2} \lambda - \text{\AA} \text{ngstroms}$$

$$E = 10 \text{ eV} \Rightarrow \lambda \cong 4 \text{ \AA}$$

$$E = 500 \text{ eV} \Rightarrow \lambda \cong 0.6 \text{ \AA}$$

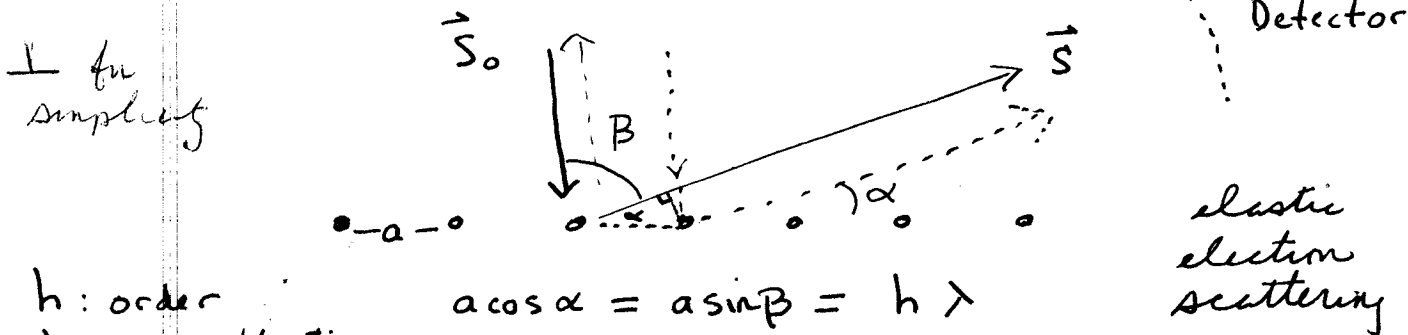
Penetrating Power: 100 \AA
Mean Free Path 10 \AA

(before losing energy)



In small MFP region: a) low penetration depth (≤ 3 layers)
b) surface diffraction $\lambda \sim a$.
(elastic scattering from surface) from surface periodicity.

First, consider a 1-D surface lattice:



h : order
 $h=0$ reflection

$$a \cos \alpha = a \sin \beta = h \lambda$$

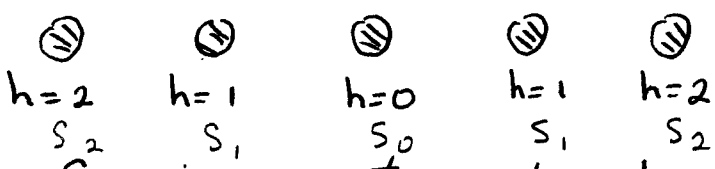
small β $\sin \beta \sim \beta = \frac{h \lambda}{a}$

$$h=0 \quad \beta=0$$

$$h=1 \quad \beta = \frac{\lambda}{a} \quad [2 \text{ directions}]$$

"2nd order" $h=2 \quad \beta = \frac{2\lambda}{a}$

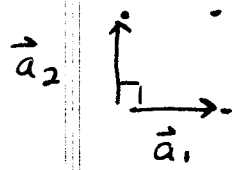
Spots on detector ("reflexes")



Spacings proportional to $\frac{1}{a} \equiv a^*$ and λ

small $a \rightarrow$ large a^* $\beta = h \lambda a^*$
 large $a \rightarrow$ small a^*

Now consider a 2D surface lattice:

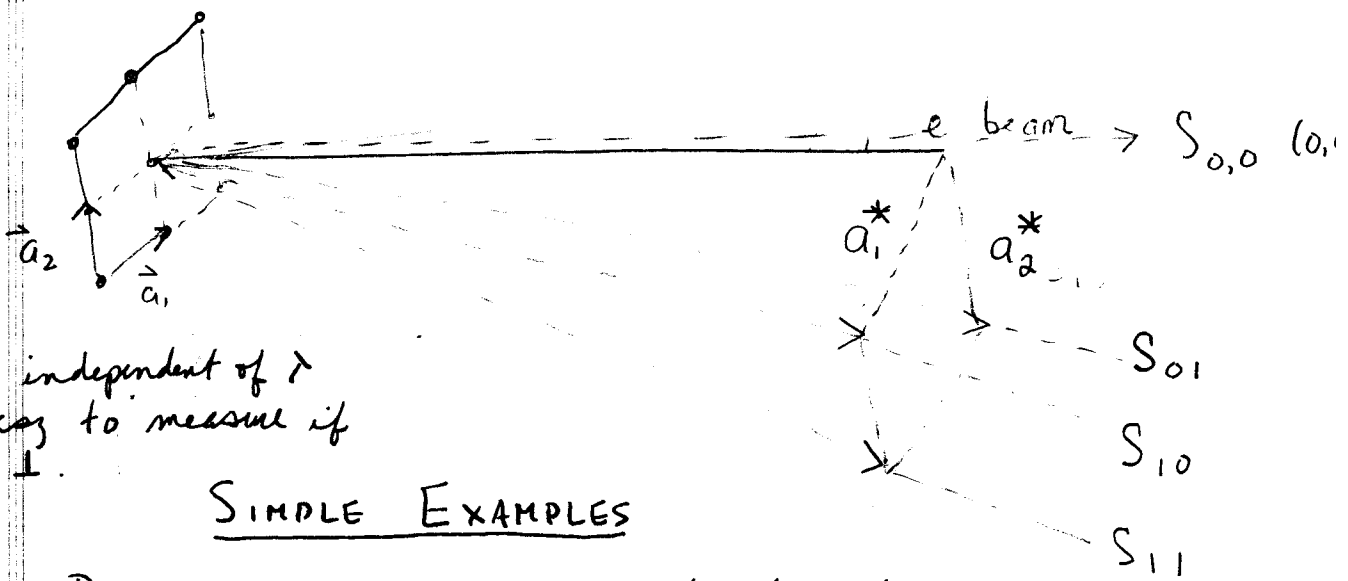


For each dimension of periodicity, there is a diffraction equation:

$$a_1 \cos \alpha_1 = a_1 \sin \beta_1 = h_1 \lambda$$

$$a_2 \cos \alpha_2 = a_2 \sin \beta_2 = h_2 \lambda$$

$$\beta_1 = \frac{h_1 \lambda}{a_1} \quad \beta_2 = \frac{h_2 \lambda}{a_2} \quad \text{or} \quad \beta_1 = h_1 \lambda a_1^* \quad \beta_2 = h_2 \lambda a_2^*$$



(0,0) independent of λ
 so easy to measure if not \perp .

SIMPLE EXAMPLES

(a) Primitive cubic: no reconstruction of 100 ($\lambda \equiv 1$)

