Reciprocal Lattice

In crystallography, the reciprocal lattice of a Bravais lattice is the set of all vectors **K** such that

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$ for all lattice point position vectors **R**.

This reciprocal lattice is itself a Bravais lattice.

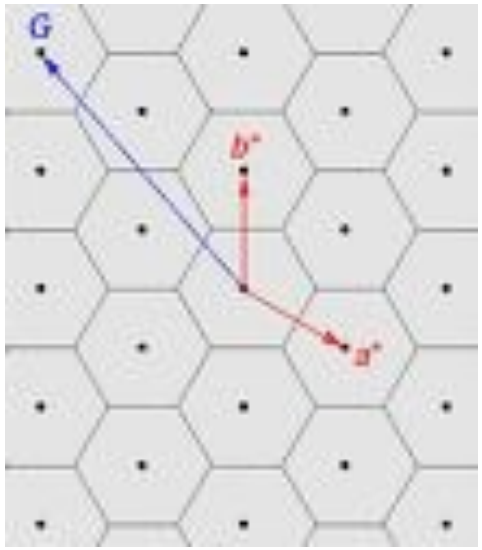
For an infinite three dimensional lattice, defined by $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, its reciprocal lattice can be determined by

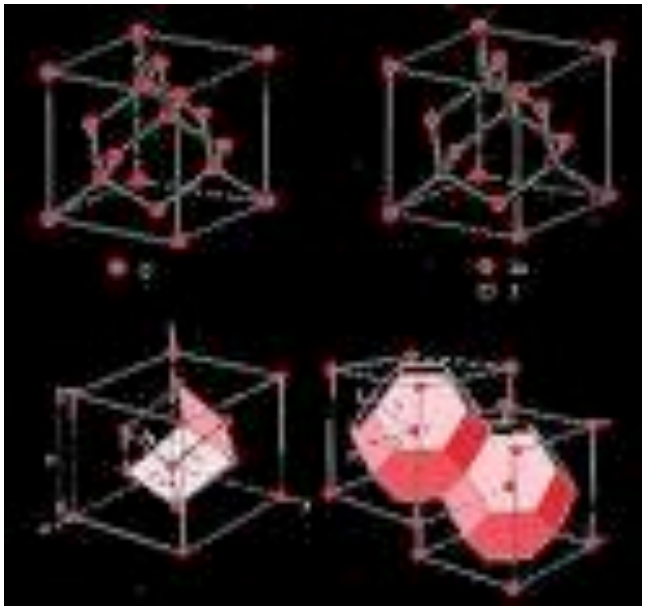
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$ ($\delta_{ij} = 1$, i=j; $\delta_{ij} = 0$, i≠j)



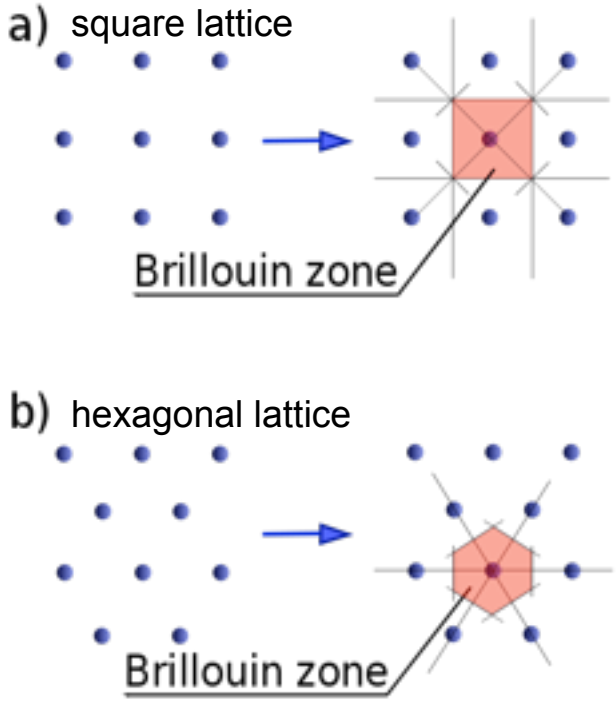


Reciprocal lattice of FCC is BCC

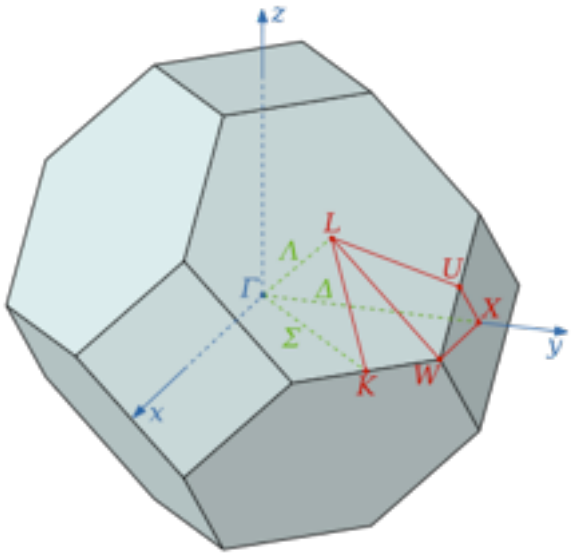
Reciprocal lattice of BCC is FCC

Brillouin zone

The first **Brillouin zone** is a uniquely defined **primitive cell** in **reciprocal space**.



First Brillouin zone of FCC lattice showing symmetry labels for high symmetry lines and points



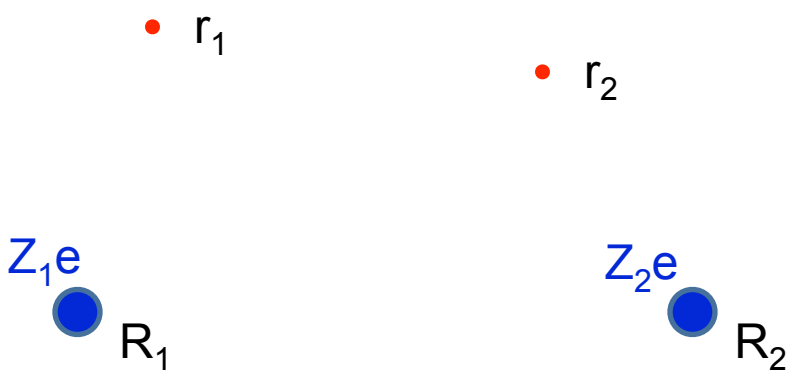
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face

Lattice Dynamics

A complete, non-relativistic, description of a system of N atoms having the positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_K, \ldots, \mathbf{R}_N)$ with n electrons located at $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_K, \ldots, \mathbf{r}_n)$ is provided by the time-dependent Schrödinger equation

$$\mathcal{H}\Xi(\mathbf{r}, \mathbf{R}; t) = i\hbar \frac{\partial}{\partial t}\Xi(\mathbf{r}, \mathbf{R}; t) \quad , \tag{1}$$

$$\mathcal{H}(\mathbf{r}, \mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r}, \mathbf{R}) + \mathcal{V}(\mathbf{r}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\mathrm{el}}(\mathbf{r}, \mathbf{R})$$



$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\rm el}(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}_{\rm el}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{r}) + \mathcal{V}(\mathbf{R}) + \mathcal{V}(\mathbf{r},\mathbf{R}) + \mathcal{V}(\mathbf{r})$$

$$\mathcal{T}(\mathbf{R}) = -\frac{\hbar^2}{2}\sum_{K=1}^{N}\frac{\boldsymbol{\nabla}_K^2}{M_K}$$

$$\mathcal{T}(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\sum_{k=1}^{n}\boldsymbol{\nabla}_k^2$$

$$\mathcal{V}(\mathbf{R}) = \frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N-1}\sum_{L>K}^{N}\frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|}$$

$$\mathcal{V}(\mathbf{r},\mathbf{R}) = -\frac{e^2}{4\pi\epsilon_0}\sum_{K=1}^{N}\sum_{k=1}^{n}\frac{Z_K}{|\mathbf{r}_k - \mathbf{R}_K|}$$

$$\mathcal{V}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0}\sum_{k=1}^{n-1}\sum_{l>k}^{n}\frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}$$

$$\mathcal{H}_{\rm el}(\mathbf{r},\mathbf{R})\phi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}_{\rm el}(\mathbf{r},\mathbf{R})\phi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}(\mathbf{r},\mathbf{R}) = \mathcal{T}(\mathbf{R}) + \mathcal{H}_{\rm el}(\mathbf{r},\mathbf{R})$$

$$\mathcal{H}\Xi(\mathbf{r},\mathbf{R};t) = i\hbar\frac{\partial}{\partial t}\Xi(\mathbf{r},\mathbf{R};t)$$

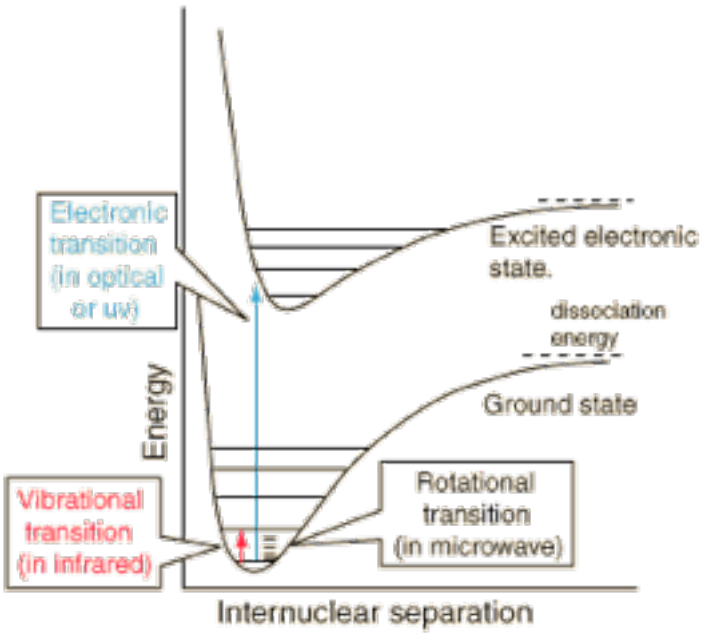
$$\left[\mathcal{T}(\mathbf{R}) + E_i(\mathbf{R})\right]\chi_i = i\hbar\frac{\partial}{\partial t}\chi_i$$

$$\Xi(\mathbf{r},\mathbf{R};t) \approx \phi_i(\mathbf{r},\mathbf{R})\chi_i(\mathbf{R},t)$$

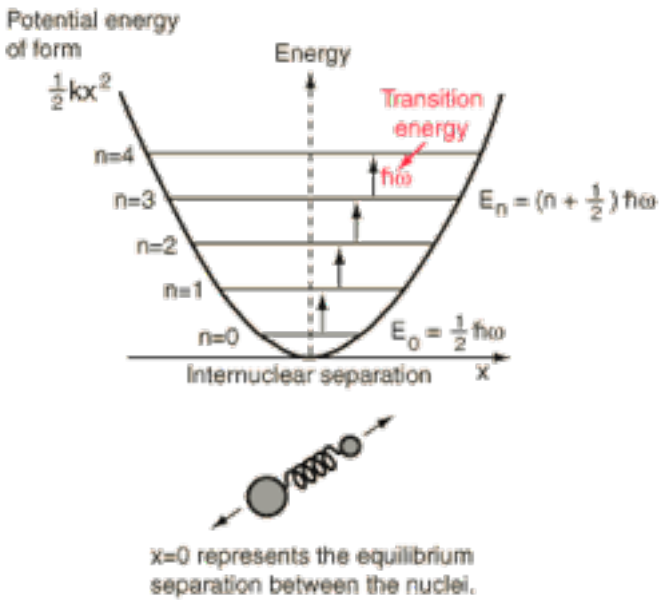
Born-Oppenheimer Approximation

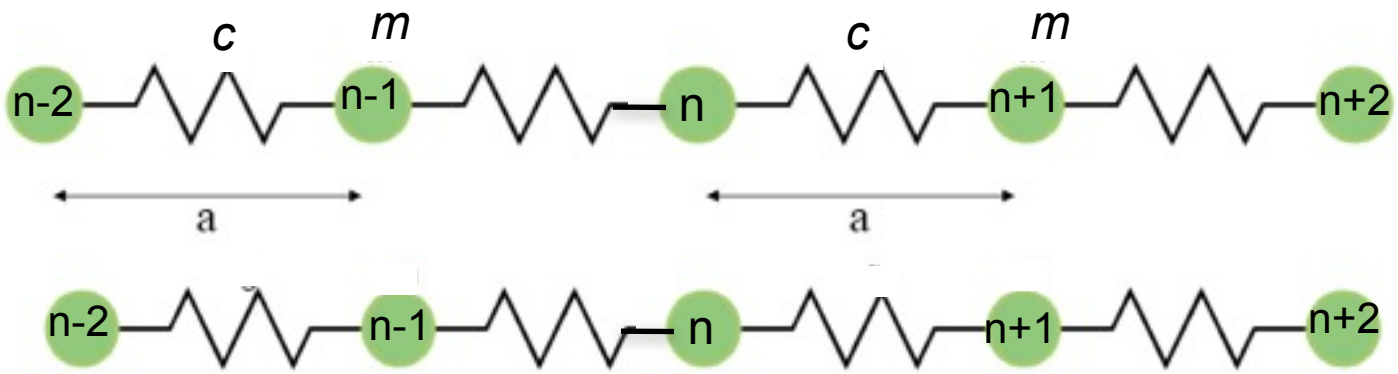
Born-Oppenheimer Approximation

$$\Psi_{\text{molecule}}(\vec{r}_i, \vec{R}_j) = \Psi_{\text{electrons}}(\vec{r}_i, \vec{R}_j)\Psi_{\text{nuclei}}(\vec{R}_j)$$



$$V(r) = \tfrac{1}{2}\, k\, (r-r_0)^2$$





$$F_n = c(u_{n+1} - u_n) + c(u_{n-1} - u_n)$$

$$m(d^2u_n/dt^2) = c(u_{n+1} + u_{n-1} - 2u_n)$$

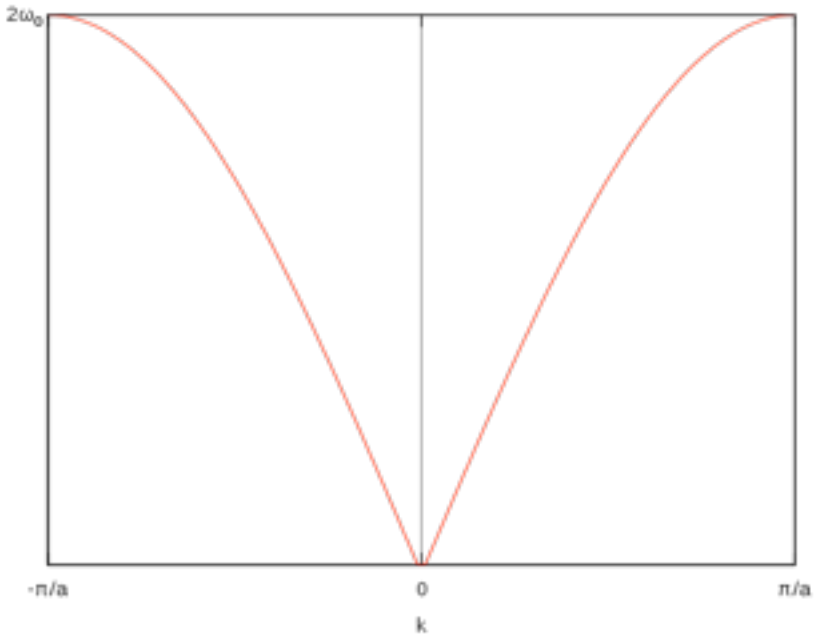
$u_n = u\, e^{inKa}\, e^{-i\omega t}$ ➡ $-m\omega^2 u_n = c(u_{n+1} + u_{n-1} - 2u_n)$

➡ $-m\omega^2 = c(e^{+iKa} + e^{-iKa} - 2)$

➡ $\omega^2 = (2c/m)(1 - \cos Ka)$

Dispersion relation for 1D acoustic phonons

$$\omega(K) = (2c/m)^{1/2}(1 - \cos Ka)^{1/2} = 2(c/m)^{1/2}|\sin(Ka/2)|$$

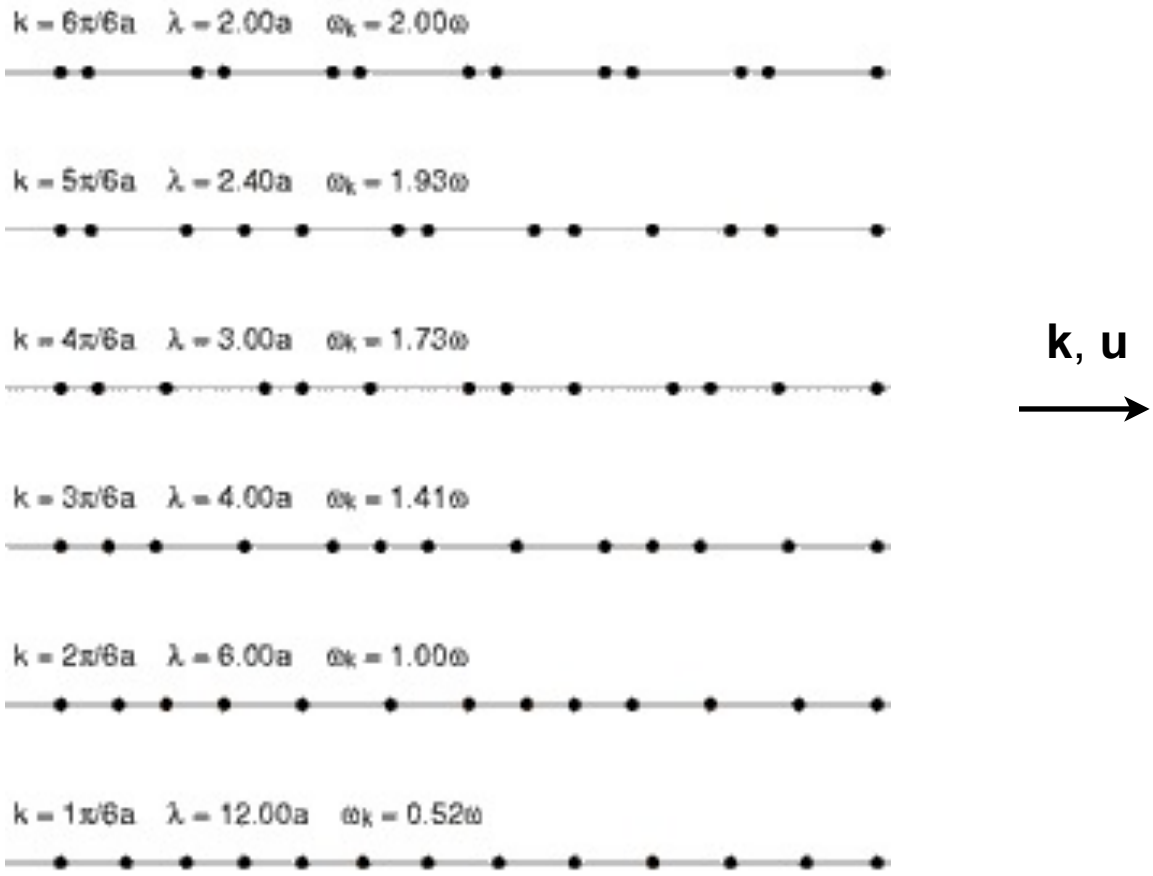


Phase velocity: $v_p = \omega/K$

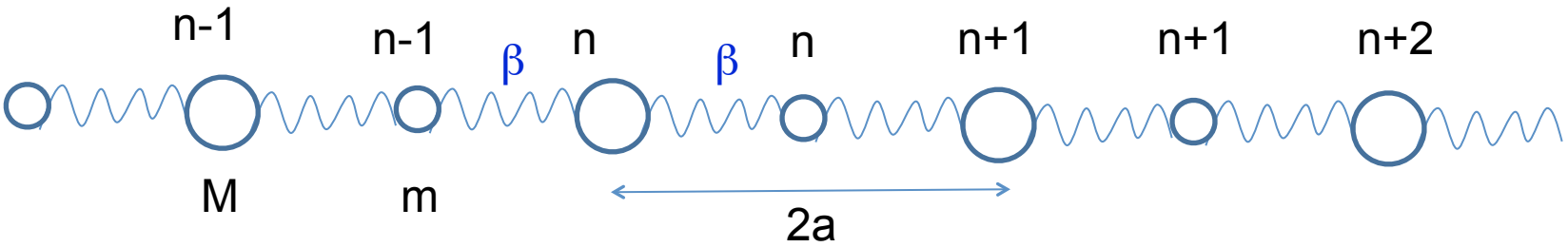
Group velocity: $v_g = \partial\omega/\partial K = a(c/m)^{1/2}\cos(Ka/2)$

For small K: $v_g = v_p$

Longitudinal Phonon



Diatomic linear chain



$$M(d^2u_n/dt^2) = \beta(s_{n+1} + s_{n-1} - 2u_n)$$

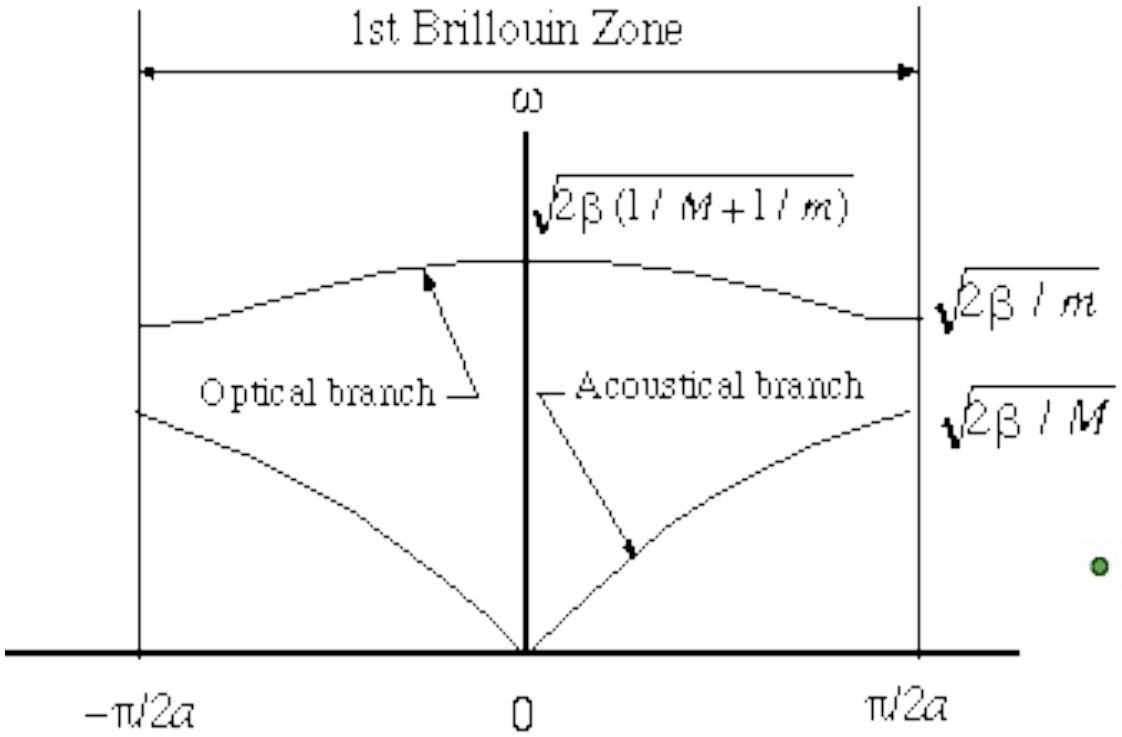
$$m(d^2s_n/dt^2) = \beta(u_{n+1} + u_{n-1} - 2s_n)$$

$u_n = u\, e^{i2nKa}\, e^{-i\omega t}$ and $s_n = s\, e^{i2nKa}\, e^{-i\omega t}$

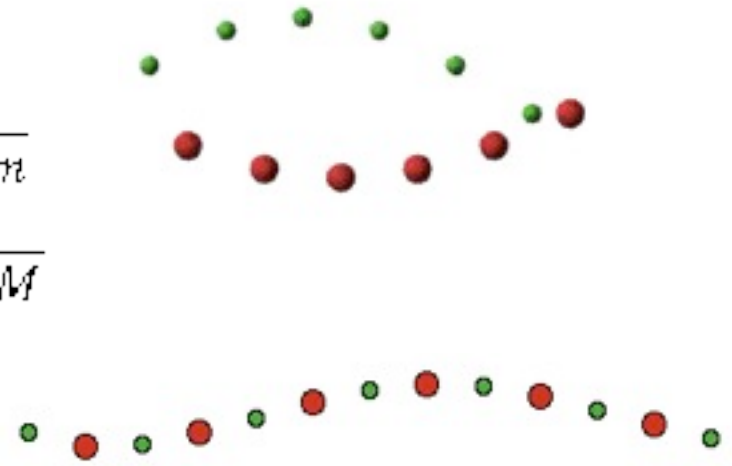
$$\Rightarrow \begin{cases} -M\omega^2 u = \beta s(1 + e^{-i2Ka}) - 2\beta u \\ -m\omega^2 s = \beta u(1 + e^{i2Ka}) - 2\beta s \end{cases}$$

$$\Rightarrow \quad \omega^2 = \beta\left(\frac{1}{m} + \frac{1}{M}\right) \pm \beta\sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{Mm}}$$

$$\omega^2 = \beta\left(\frac{1}{m}+\frac{1}{M}\right) \pm \beta\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin^2 ka}{Mm}}$$



Transverse optical mode



Transverse acoustical mode

Scattering by phonons

Phonon is the quantum unit of a crystal vibration.

Incident beam with momentum k interacts with a crystal and comes out with momentum k'.

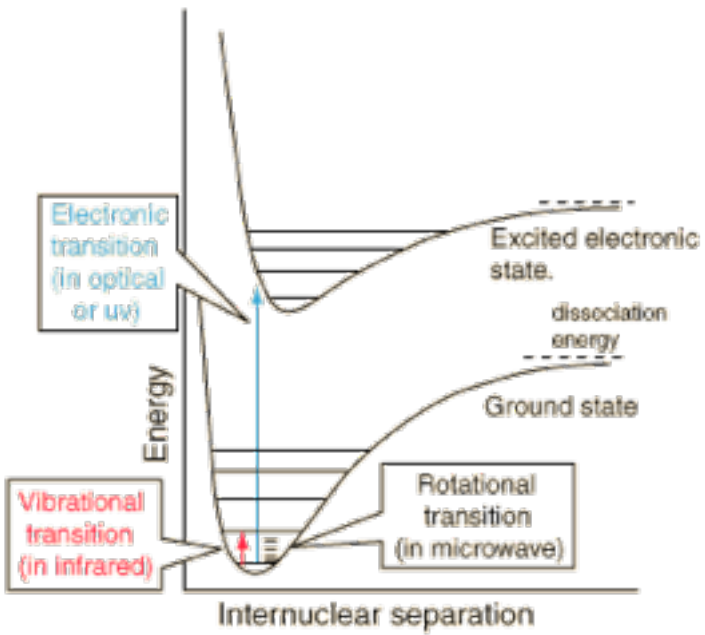
$$k + G = k' \pm K$$

G is a vector in reciprocal lattice.

K lies in the *first brillouin zone*. For 1D, $|K| \leq \pi/a$.

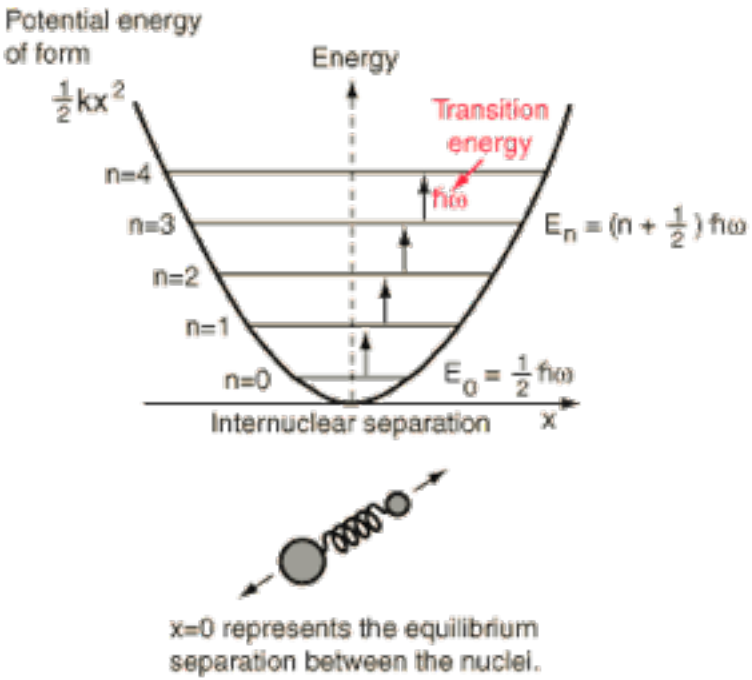
Electronic Spectroscopy

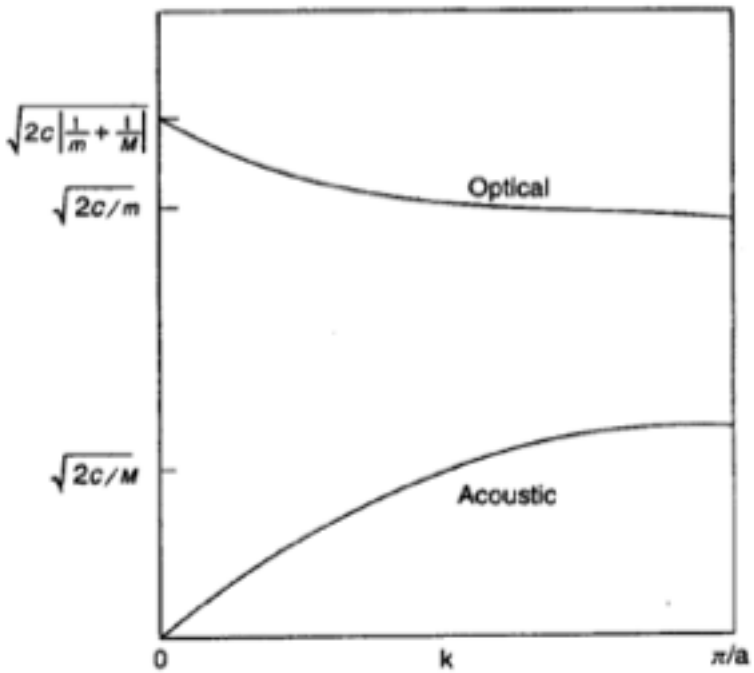
1. Photons in, photons out – PL
2. Photons in, electrons out – UPS, XPS
3. Electrons in, electrons out – EELS



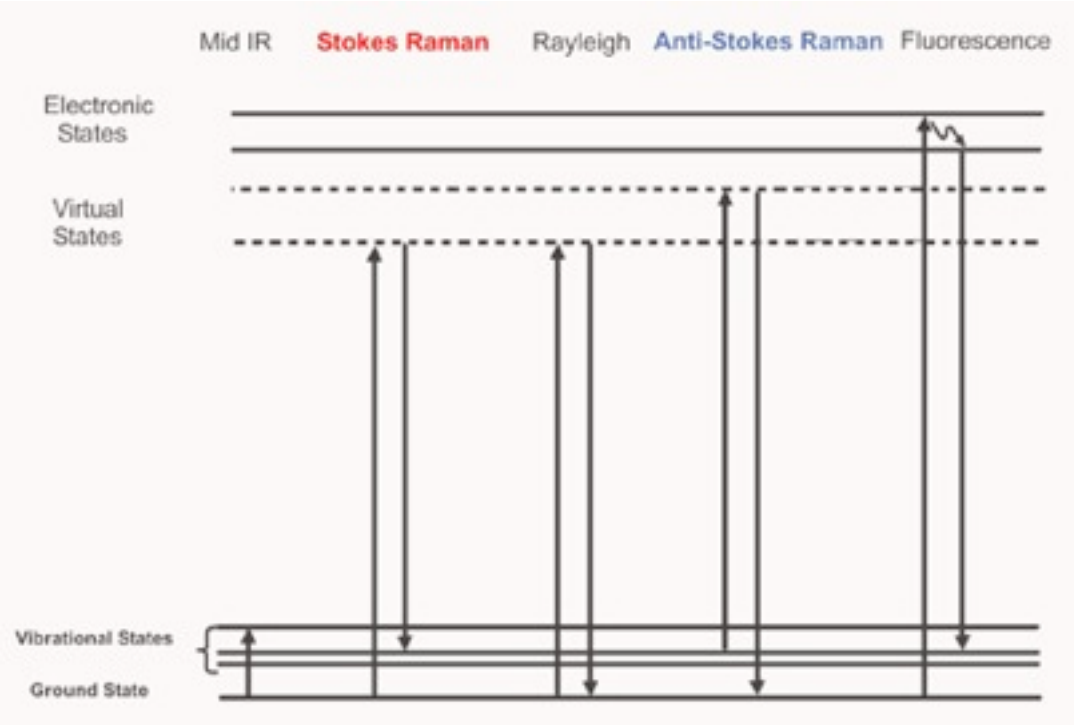
Vibrational Spectroscopy

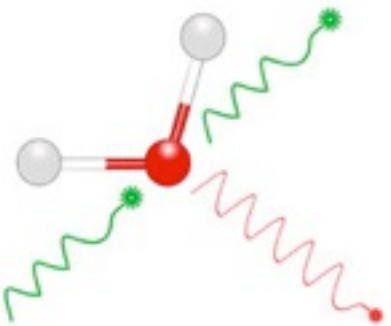
1. Photons in, photons out – IR, Raman
2. Electrons in, electrons out – EELS

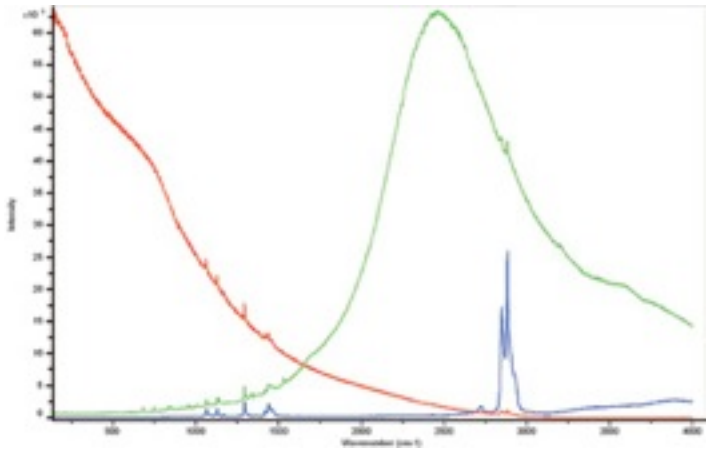




The Theory of Raman Spectroscopy







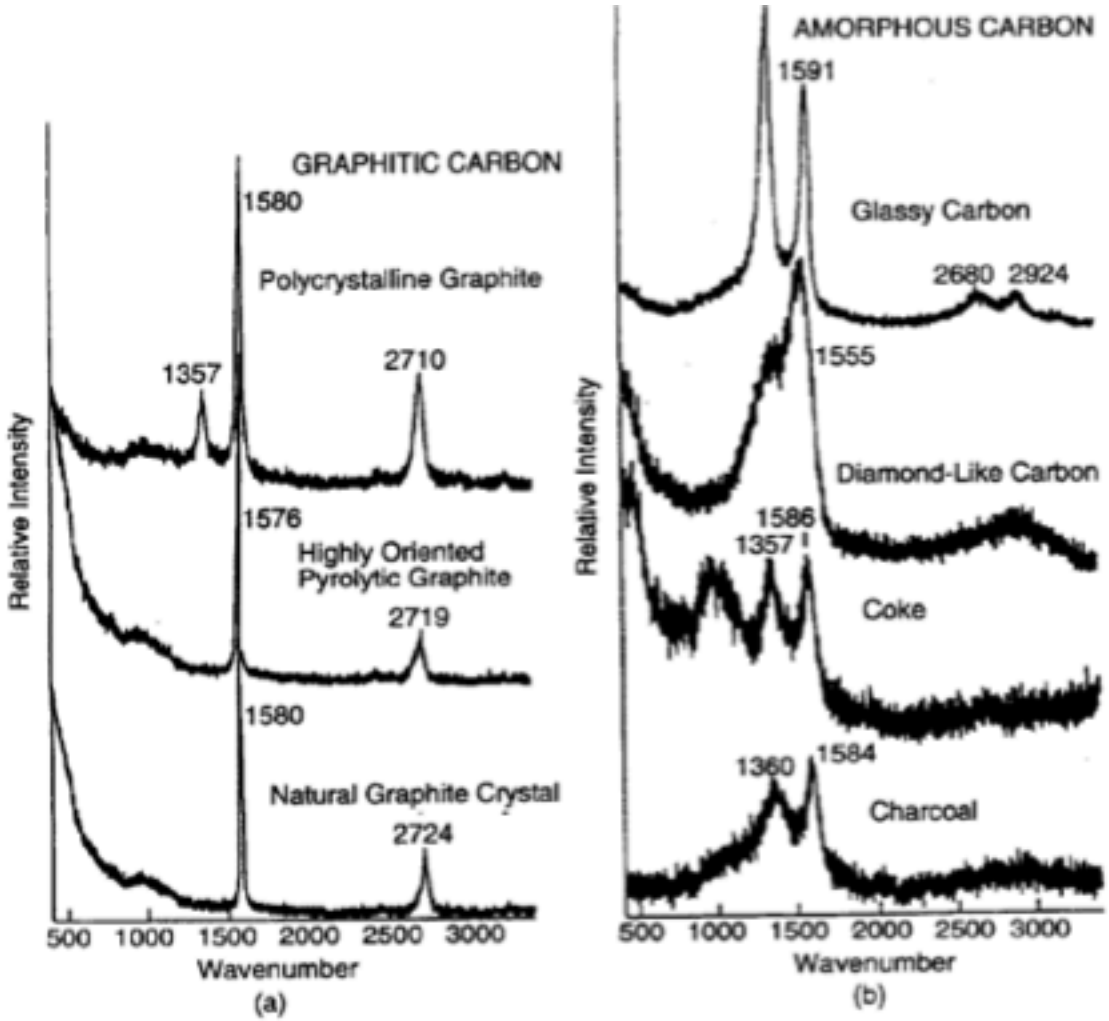


Figure 8.19. Raman spectra of (a) crystalline graphites and (b) noncrystalline, mainly graphitic, carbons. The *D* band appears near 1355 cm^{-1} and the *G* band, near 1580 cm^{-1}. [From D. S. Knight and W. B. White, *J. Mater. Sci.* **4**, 385 (1989).]

Density of Phonon States

The phonon density of states gives the number of modes per unit frequency per unit volume of real space.

For 1D: $D(\omega) = (1/L)(dN/d\omega) = (1/L)(dN/dK)(dK/d\omega) = (1/(\pi v_g))$

For 2D: $D(\omega) = (1/L^2)(dN/d\omega) = (K/(2\pi v_g))$

For 3D: $D(\omega) = (1/L^3)(dN/d\omega) = (K^2/(2\pi^2 v_g))$

Phonon heat capacity

Heat capacity at constant volume

$$C_v = (\partial U/\partial T)_v$$

Debye Model

$$\omega = vK$$

$$D(\omega) = (1/L^3)(dN/d\omega) = (K^2/(2\pi^2 v_g)) = (\omega^2/(2\pi^2 v^3))$$

$$U = \int D(\omega)<n(\omega)>\hbar\omega \, d\omega$$

$$N = \int_{\omega_D} D(\omega) \, d\omega$$

$$C_v = (\partial U/\partial T)_v = 2.4\pi^4 N k_B (T/\theta)^3$$

Homework#12 (Dec. 6, 2010):

Consider a longitudinal wave

$$u_s = u \cos(\omega t - sKa)$$

which propagates in a monoatomic linear lattice of atoms of mass M, spacing a, and nearest neighbor interaction C.

(a) Write down the expression for the total energy of the wave.

(b) By substitution of u_s in the above expression, what is the time-average total energy per atom?