

Quantum correspondence - Phonons

At a finite temperature, there will be a non-zero number of phonons given by the Bose occupation factor

$$n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

The energy expectation of the phonons at wavevector k

$$E_k = \hbar\omega(k) \left(n_B(\beta\hbar\omega(k)) + \frac{1}{2} \right)$$

The total energy is -

$$U_{total} = \sum_k \hbar\omega(k) \left(n_B(\beta\hbar\omega(k)) + \frac{1}{2} \right) \quad \sum_k \rightarrow \sum_{\substack{p=-N/2 \\ k=(2\pi p)/(Na)}}^{p=N/2-1}$$

Quantum correspondence - Phonons

For a large system, we can convert the sum to an integral

$$\sum_k \rightarrow \frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk$$

The total number of modes in the system $\frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk = N$

The total energy

$$U_{total} = \frac{N}{2\pi} \int_{-\pi/a}^{\pi/a} dk \hbar\omega(k) \left(n_B(\beta\hbar\omega(k)) + \frac{1}{2} \right)$$

Specific heat can be calculated as dU/dT

Einstein took a constant ω which is independent of k

Debye had taken $\omega = vk$ which is linear in k

The difference between the Einstein, Debye and the microscopic-harmonic model is what we use for the dispersion relation

Crystal Momentum

The wavevector of a phonon is defined only modulo the reciprocal lattice vector

k is the same as $k + G_m$ where $G_m = 2\pi m/a$

Thinking of the phonon as a particle having energy $\hbar\omega$ and momentum $\hbar k$ or $\hbar(k + G_m)$!

We thus define a concept known as crystal momentum which is the momentum modulo the reciprocal lattice - or we agree that we always use k within the first BZ

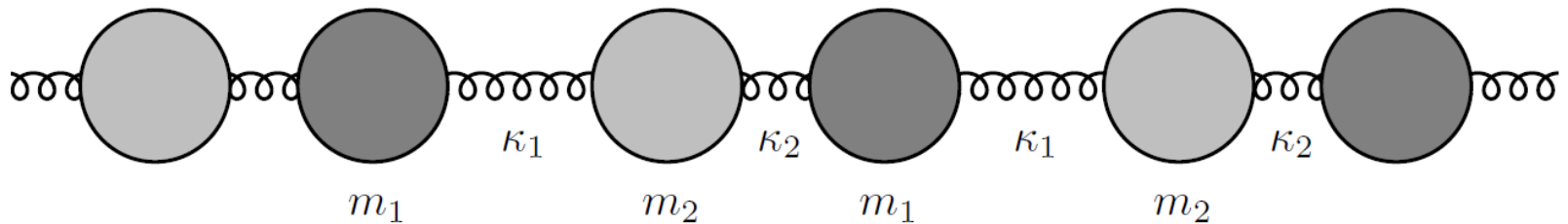
In collision of phonons the crystal momentum is conserved. Conserved quantities are results of symmetry (Noether's theorem). Conservation of momentum is possible if there is complete translational symmetry

In crystal space is invariant under translation by a , giving momentum that is conserved modulo $\frac{2\pi}{a}$

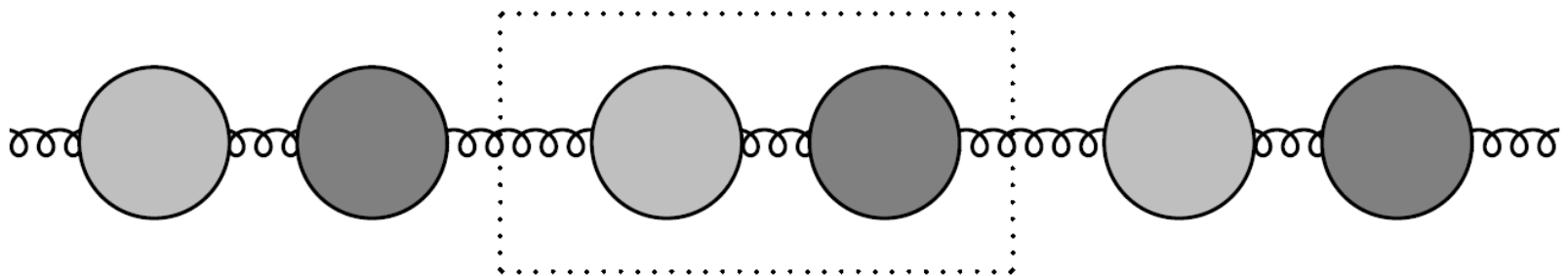
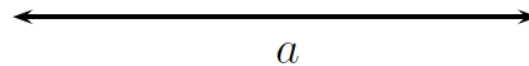
Vibrations of a 1D di-atomic chain

We often come across materials where the atoms are not same (like NaCl, CsCl where we have two types of atoms)

We would now generalize to a 1D solid with two types of atoms



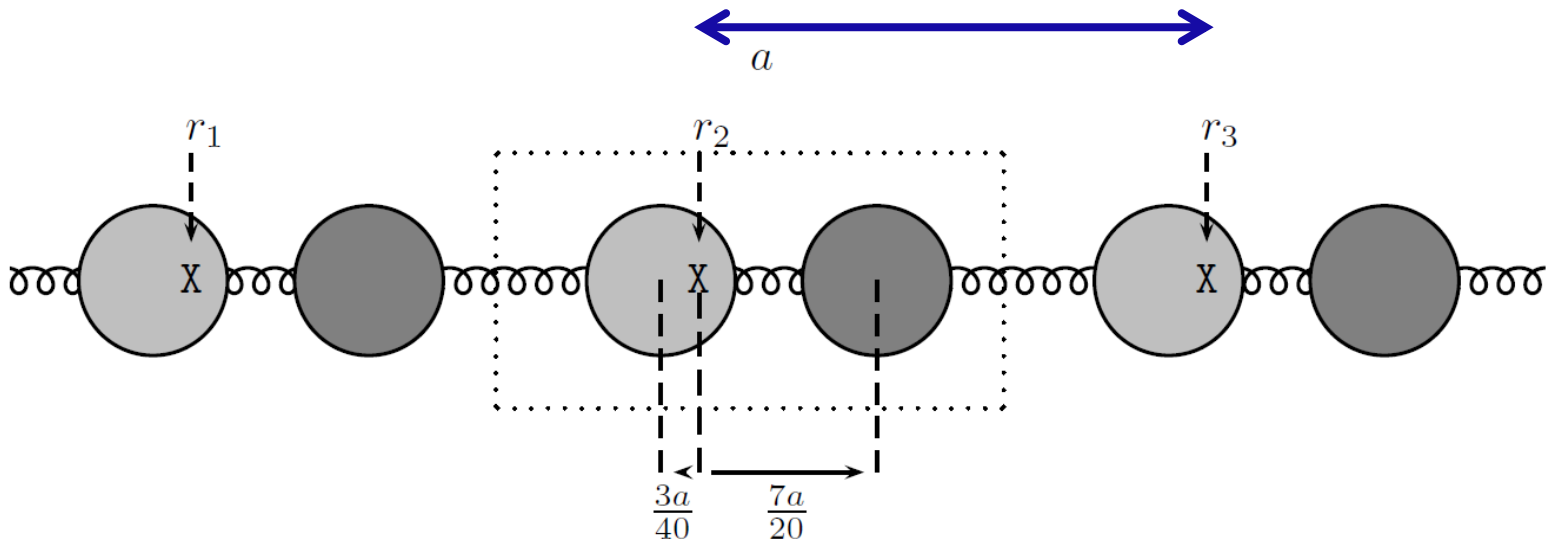
Identifying the unit-cell or the repeated motif (one possibility!)



Vibrations of a 1D di-atomic chain

Reference points X form a 1D lattice with lattice constant a

The reference point in the n^{th} unit cell $r_n = an$



Light Gray atom - Centered at position $\frac{3a}{40}$ to left of the reference

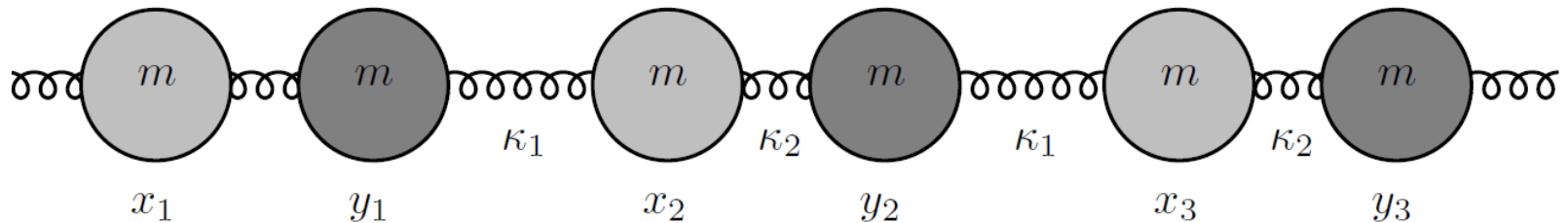
$$x_n^{eq} = an - 3a/40$$

Dark Gray atom - Centered at position $\frac{7a}{40}$ to right of the reference

$$y_n^{eq} = an + 7a/20$$

Normal modes of diatomic chain

Consider the atomic masses to be the same but with different spring constants



Newton's equation of motion for the deviations of the position of the masses from their equilibrium positions

$$m \ddot{\delta x_n} = \kappa_2(\delta y_n - \delta x_n) + \kappa_1(\delta y_{n-1} - \delta x_n)$$

$$m \ddot{\delta y_n} = \kappa_1(\delta x_{n+1} - \delta y_n) + \kappa_2(\delta x_n - \delta y_n)$$

Normal modes of diatomic chain

Analogous to the case of mono-atomic chain, we take these quantities as waves

$$\delta x_n = A_x e^{i\omega t - ikna}$$

$$\delta y_n = A_y e^{i\omega t - ikna}$$

Supposing there are N unit cells, then allowed values for k will be in units of $2\pi/(Na) = 2\pi/L$ and $-\pi/a \leq k < \pi/a$

The allowed number of k states is N , which is the no. of unit cells and not the number of atoms which is $2N$

Debye used that there should be one possible excitation mode per degree of freedom

Two degrees of freedom per unit cell !

Resolution - We will see two possible oscillation modes for each k

Normal modes of diatomic chain

The equations of motion -

$$-\omega^2 m A_x e^{i\omega t - i k n a} = \kappa_2 A_y e^{i\omega t - i k n a} + \kappa_1 A_y e^{i\omega t - i k (n-1) a} - (\kappa_1 + \kappa_2) A_x e^{i\omega t - i k n a}$$

$$-\omega^2 m A_y e^{i\omega t - i k n a} = \kappa_1 A_x e^{i\omega t - i k (n+1) a} + \kappa_2 A_x e^{i\omega t - i k n a} - (\kappa_1 + \kappa_2) A_y e^{i\omega t - i k n a}$$

The equations simplify

$$\begin{aligned} -\omega^2 m A_x &= \kappa_2 A_y + \kappa_1 A_y e^{i k a} - (\kappa_1 + \kappa_2) A_x \\ -\omega^2 m A_y &= \kappa_1 A_x e^{-i k a} + \kappa_2 A_x - (\kappa_1 + \kappa_2) A_y \end{aligned}$$

Normal modes of diatomic chain

These can be written as an eigen-value equation

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (\kappa_1 + \kappa_2) & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

Finding zeros of the secular determinant

$$0 = \begin{vmatrix} (\kappa_1 + \kappa_2) - m\omega^2 & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) - m\omega^2 \end{vmatrix}$$

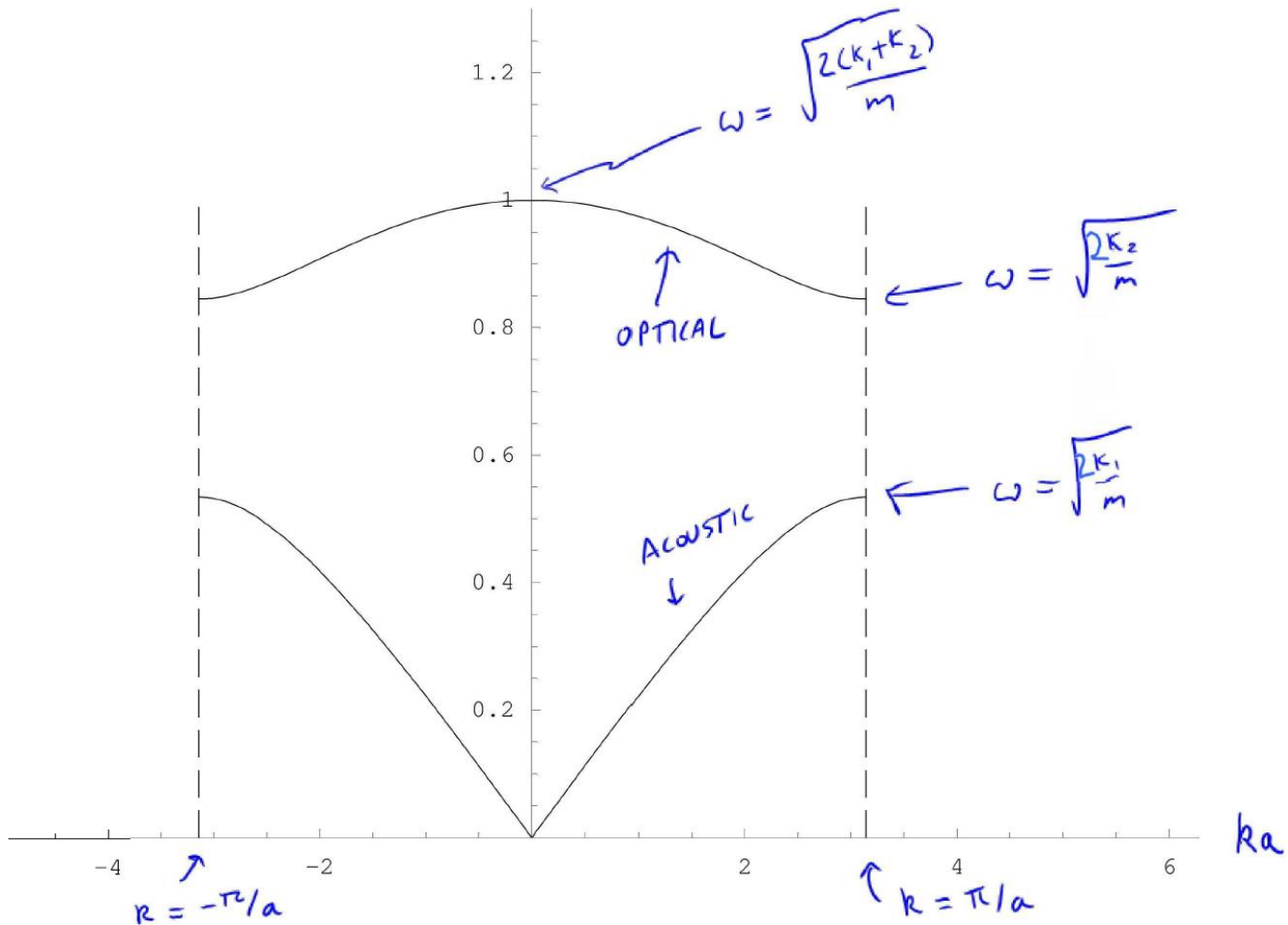
$$m\omega^2 = (\kappa_1 + \kappa_2) \pm \sqrt{(\kappa_1 + \kappa_2 e^{ika})(\kappa_1 + \kappa_2 e^{-ika})}$$

$$\omega_{\pm} = \sqrt{\frac{\kappa_1 + \kappa_2}{m}} \pm \frac{1}{m} \sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}$$

Normal modes of diatomic chain

For each k two normal modes - two branches of dispersion relation

For N allowed values of k total modes are $2N$ - equal to total DOF



Normal modes of diatomic chain

There is a long-wavelength low-energy branch of excitations (corresponding to ω_-).

This is the sound or acoustic mode

On expanding for small k we get
$$v_{sound} = \frac{d\omega_-}{dk} = \sqrt{\frac{a^2 \kappa_1 \kappa_2}{2m(\kappa_1 + \kappa_2)}}$$

The higher energy branch of excitations - Optical mode

The optical mode goes to frequency $\sqrt{2(\kappa_1 + \kappa_2)/m}$ at $k = 0$

When photon interacts with phonon - Conservation of E and momentum should hold. For photons $\omega = ck$ is a very large number. Phonons have max. energy, so photons can only be absorbed for very small k

Acoustic phonons for small k have energy $vk \ll ck$ so that E and momentum cannot be conserved

Optical phonons have energy $\omega_{optical}$ which is finite for small k
Thus only optical phonons can interact with photons

Examining the Normal modes as $k \rightarrow 0$

The eigenvalue equation -

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (\kappa_1 + \kappa_2) & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

In the limit $k \rightarrow 0$, this simplifies

$$\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \frac{\kappa_1 + \kappa_2}{m} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

Also we recollect definitions of A_x and A_y

$$\delta x_n = A_x e^{i\omega t - ikna}$$

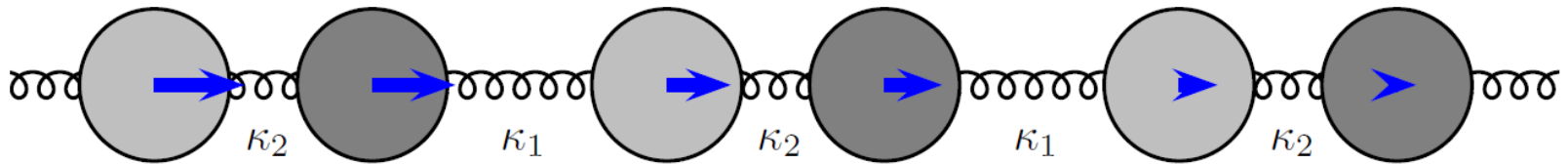
$$\delta y_n = A_y e^{i\omega t - ikna}$$

Examining the Normal modes as $k \rightarrow 0$

Corresponding to the acoustic mode, we have the eigenmode -

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

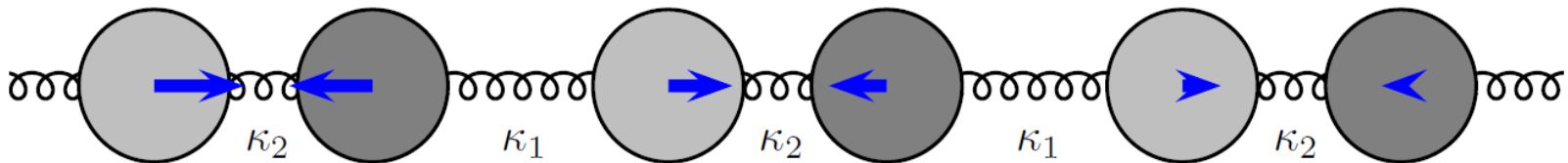
The two masses in the unit cell move together



The optical mode at $k = 0$, which has energy $\omega^2 = \frac{2(\kappa_1 + \kappa_2)}{m}$

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

The two masses in the unit cell move in opposite directions



Phonons in three-dimensional solids

For a three-dimensional solid with macroscopic side-length L , lattice spacing a and N unit cells in each direction

$$L = aN$$

$$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{aN} (n_x, n_y, n_z) = \left(\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L}, \frac{n_z 2\pi}{L} \right)$$

Total number of modes per allowed value of k
 $3 \times$ (No. of atoms per unit cell)

Wave type ansatz also solves the equations of motion for three dimensional solids

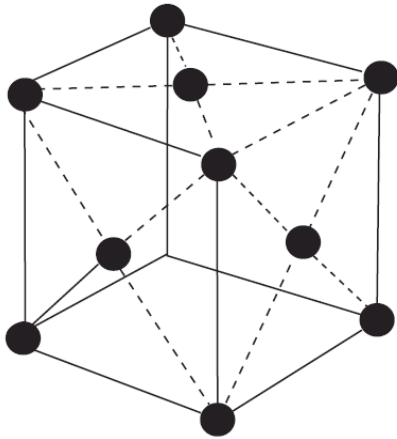
Ex.: For a 3D solid with two atoms per unit cell -
There will be three acoustic branches, one with longitudinal polarization and two with transverse polarization.
There will also be three optical branches

For a 3D solid with one atom per unit cell - Only 3 acoustic modes

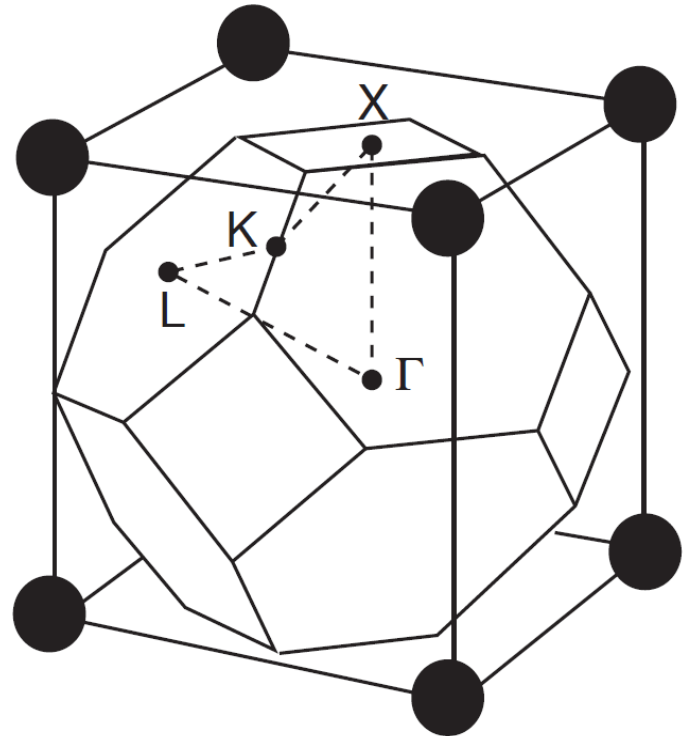
Phonons in three-dimensional solids

Considering an example of Aluminium

real
space

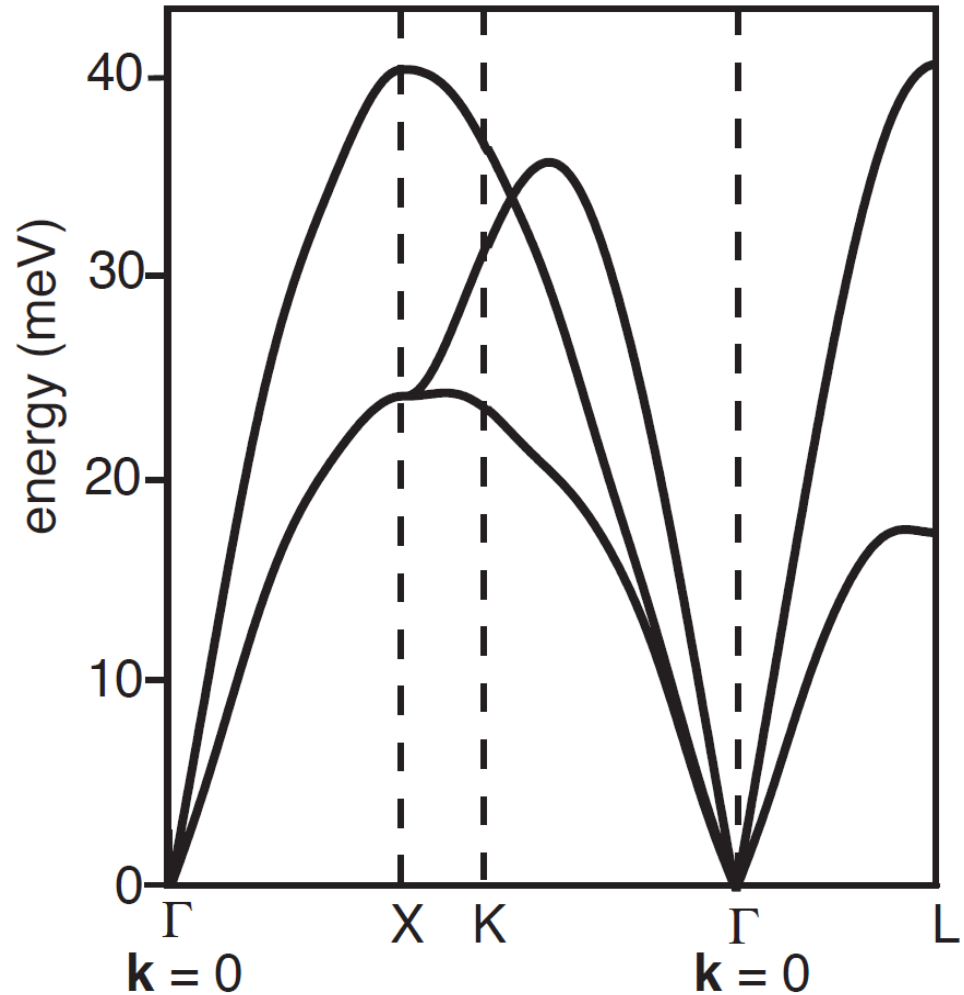
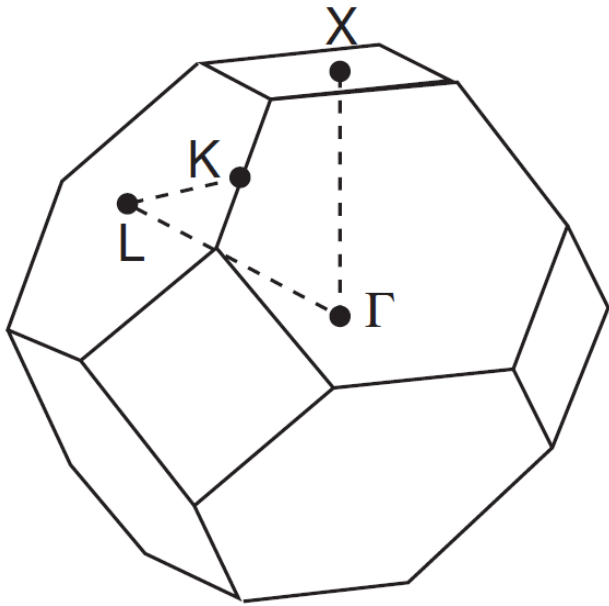


reciprocal
space



Phonons in three-dimensional solids

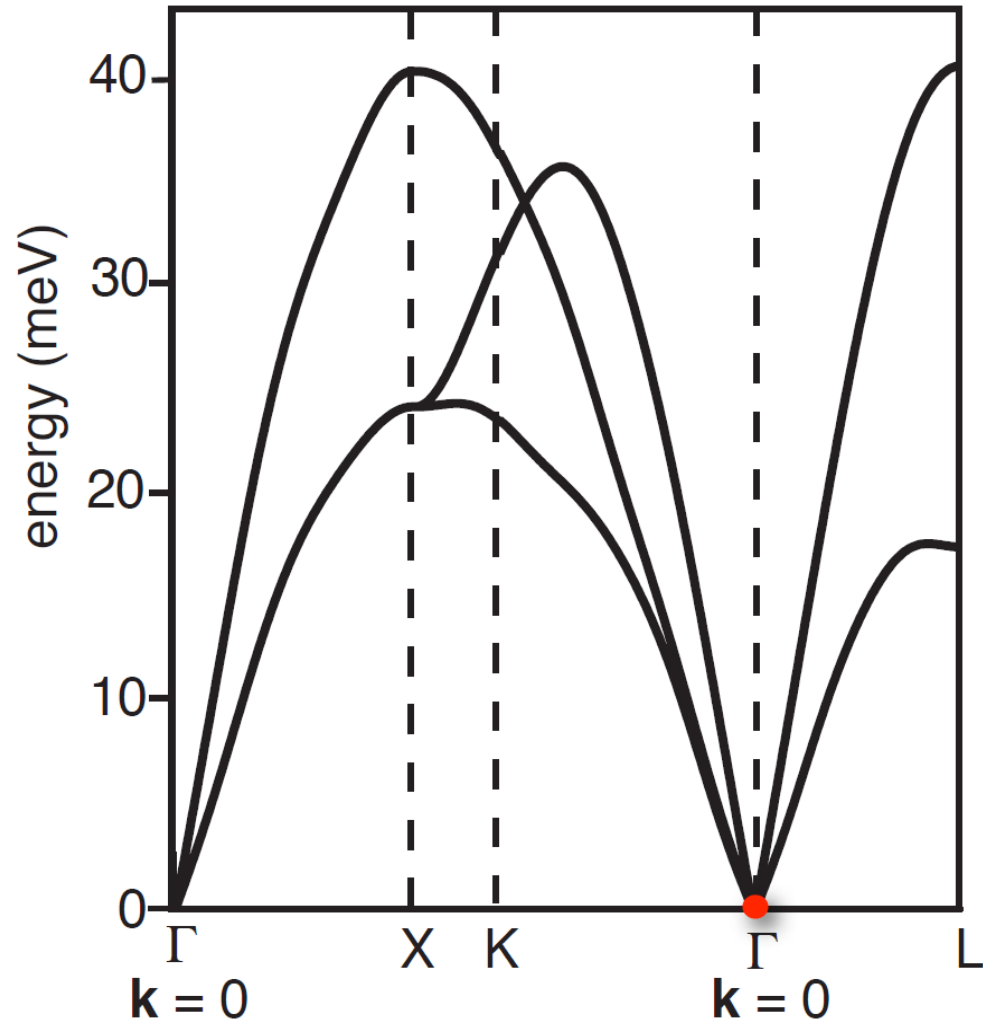
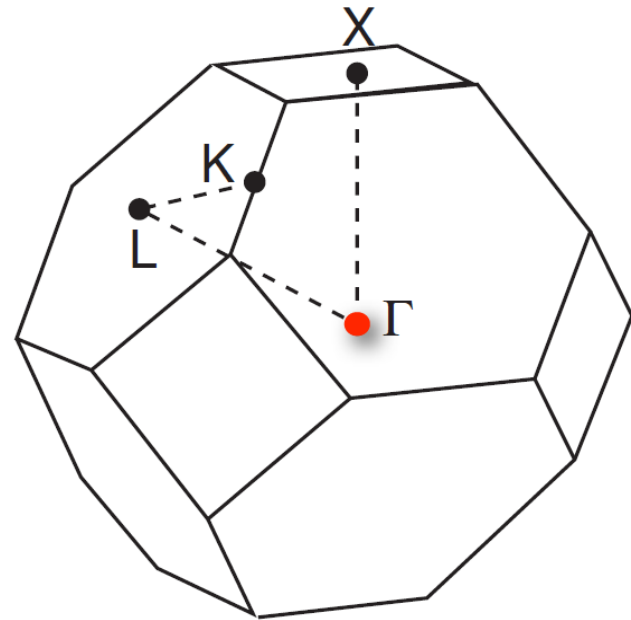
Considering an example of Aluminium



Results from Neutron diffraction

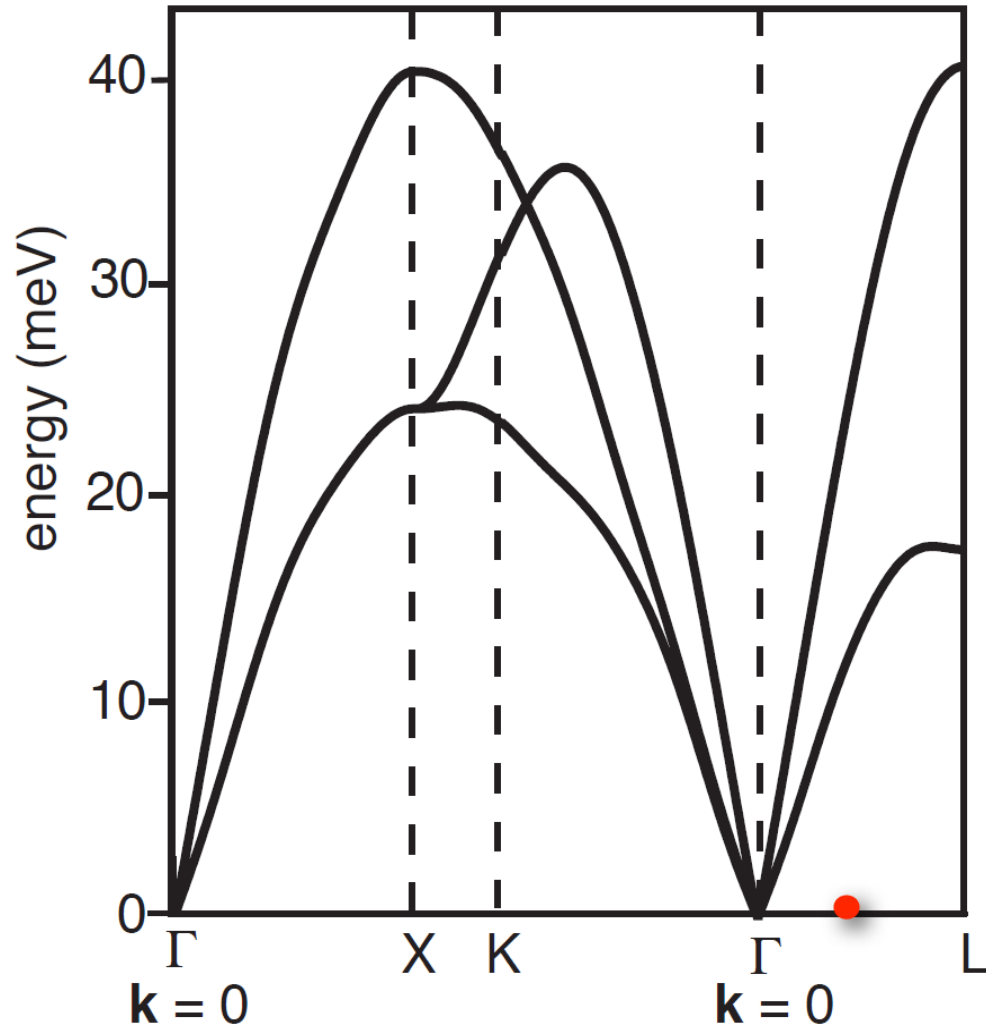
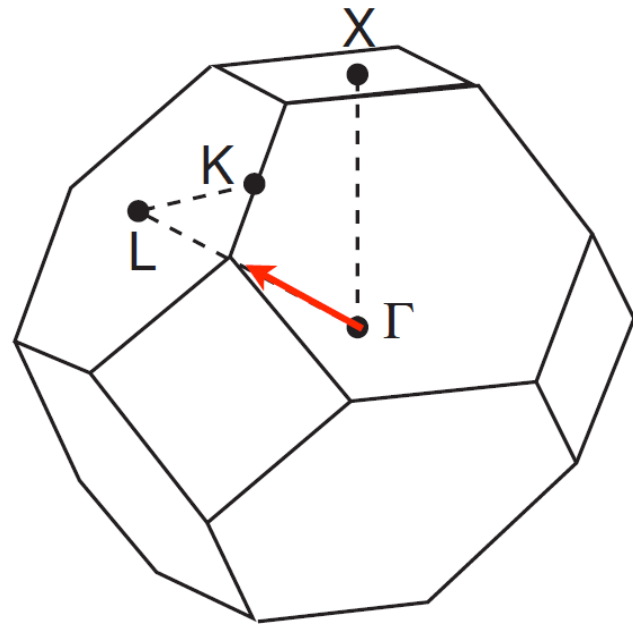
Phonons in three-dimensional solids

Considering an example of Aluminium



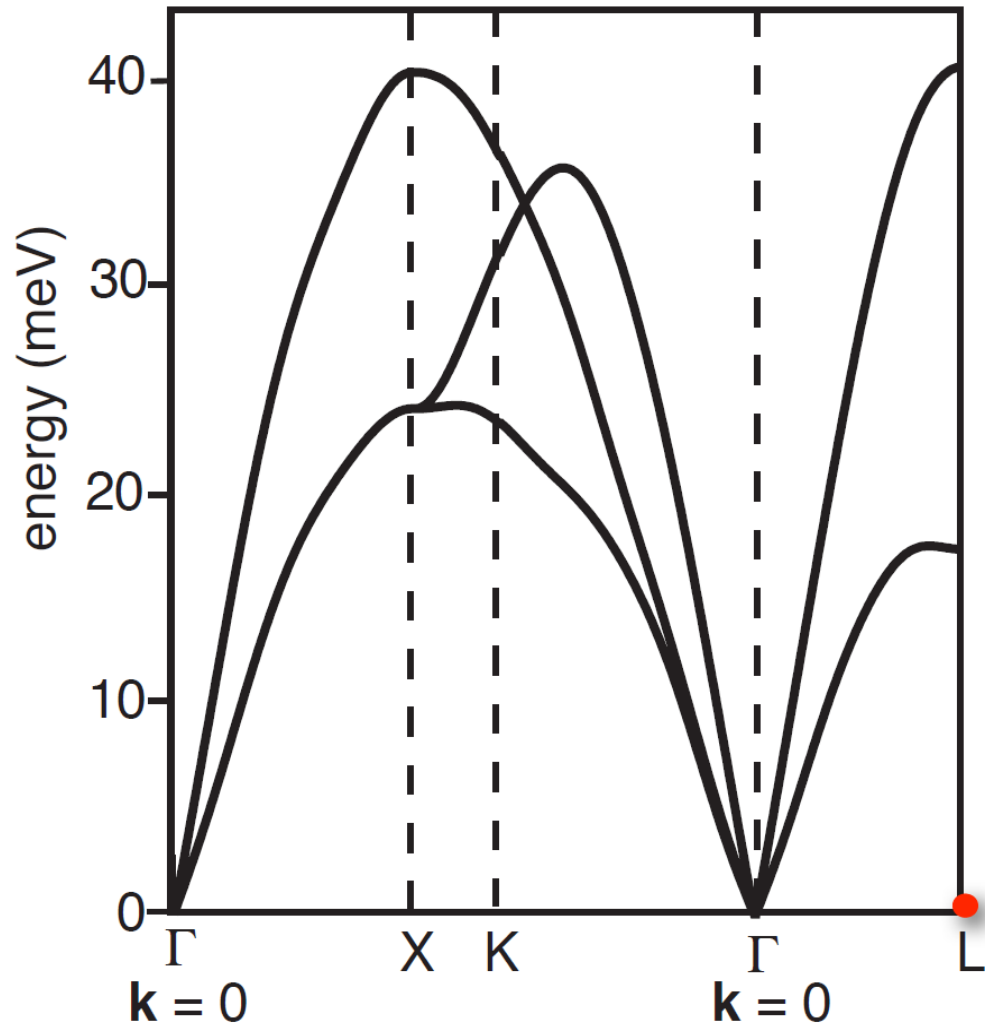
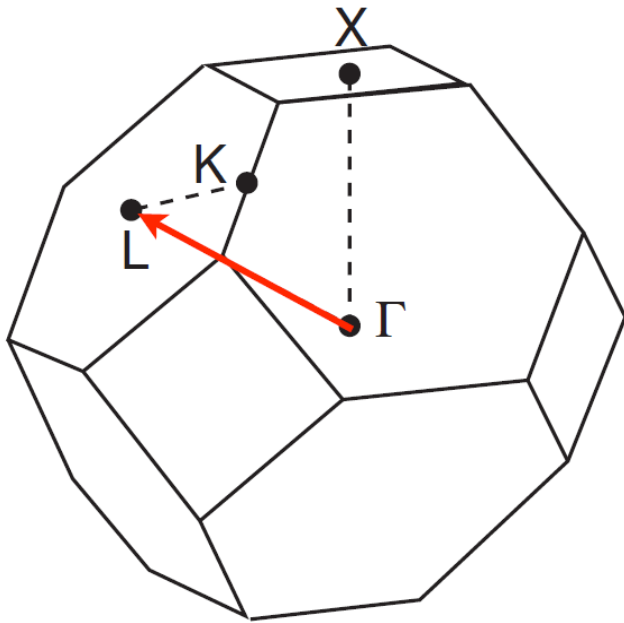
Phonons in three-dimensional solids

Considering an example of Aluminium



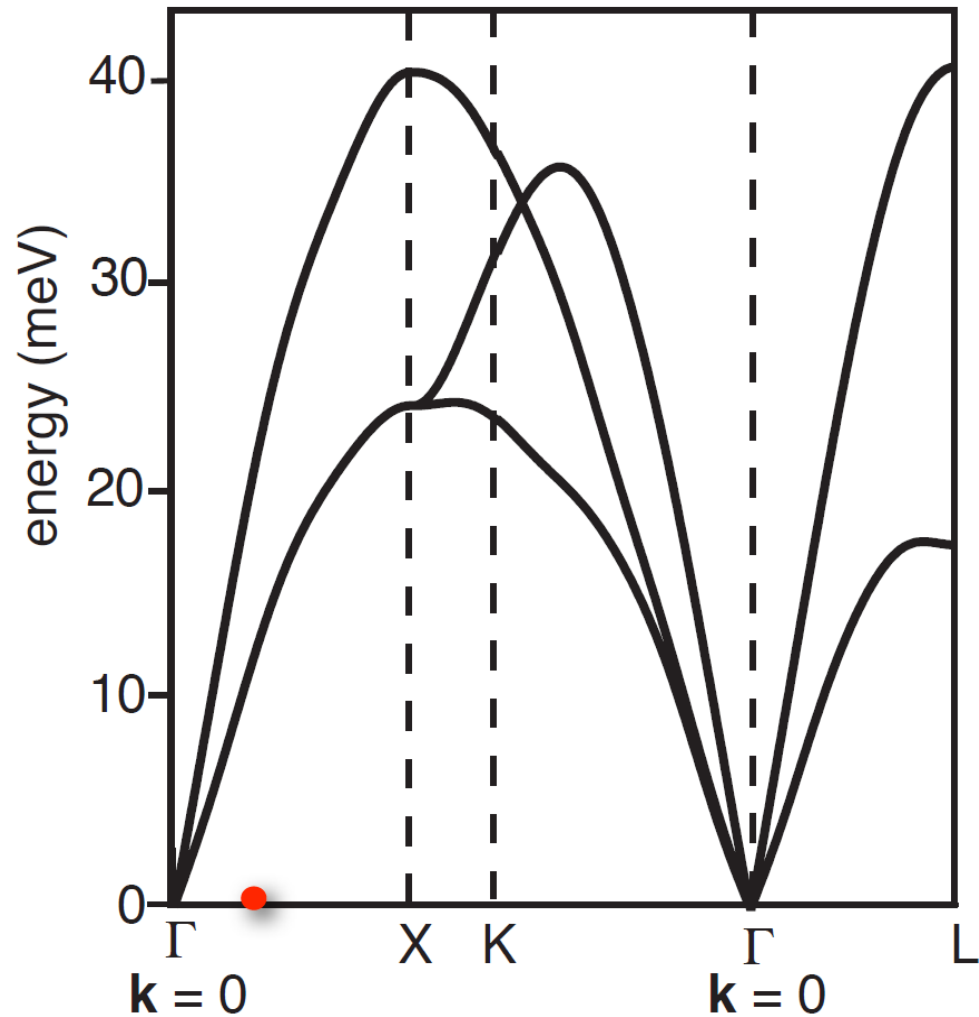
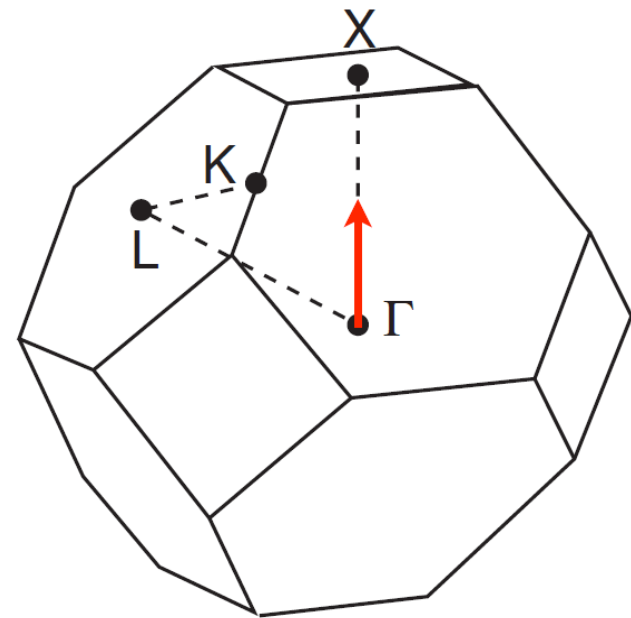
Phonons in three-dimensional solids

Considering an example of Aluminium



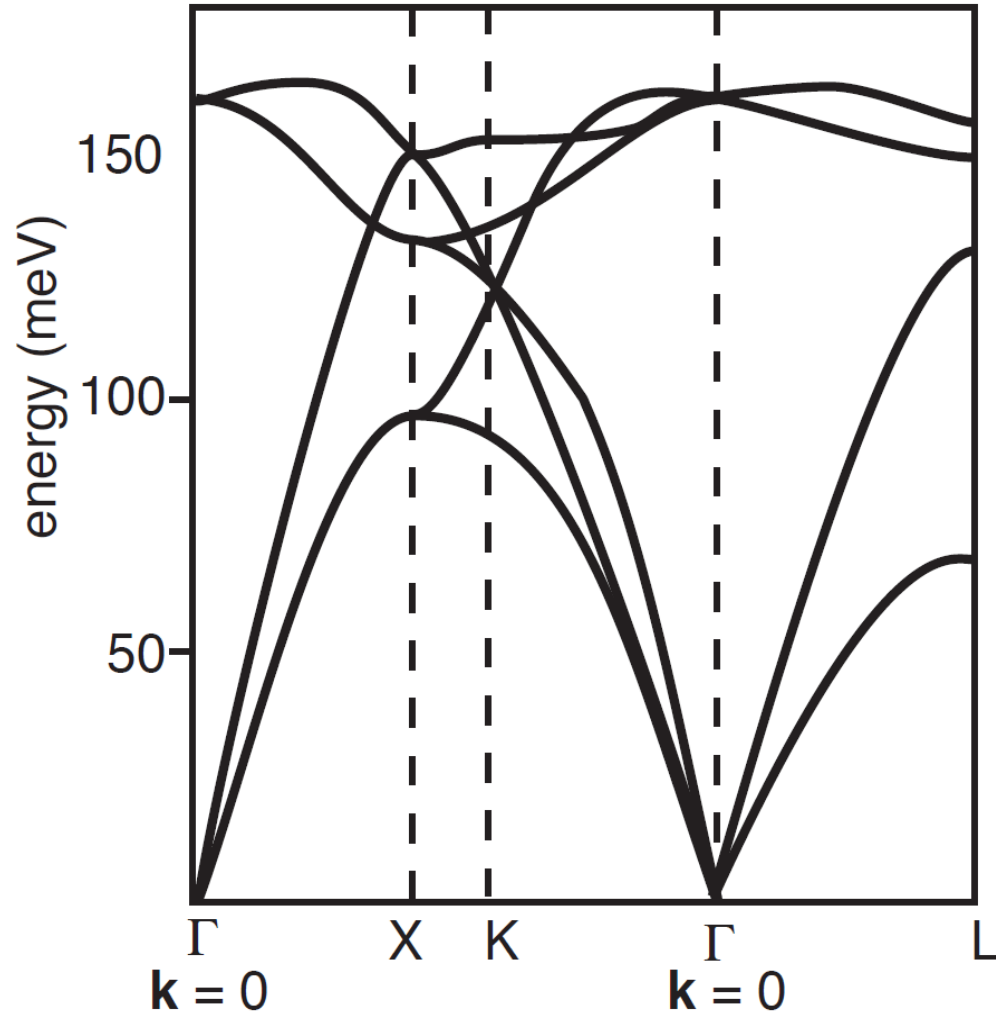
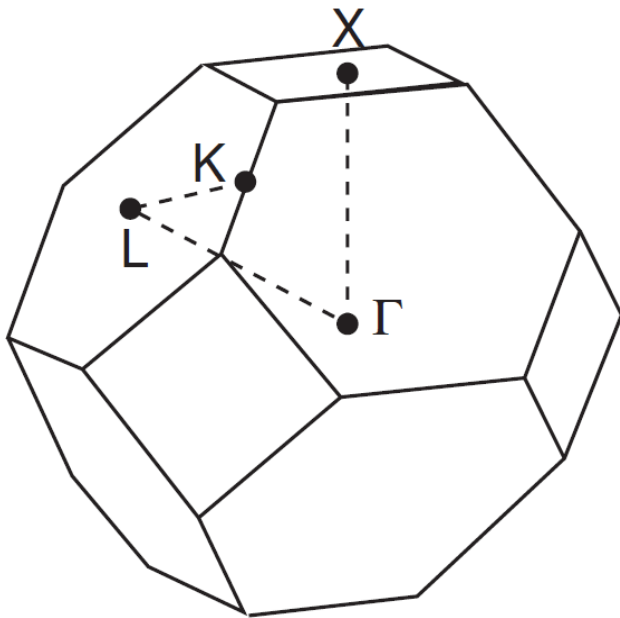
Phonons in three-dimensional solids

Considering an example of Aluminium



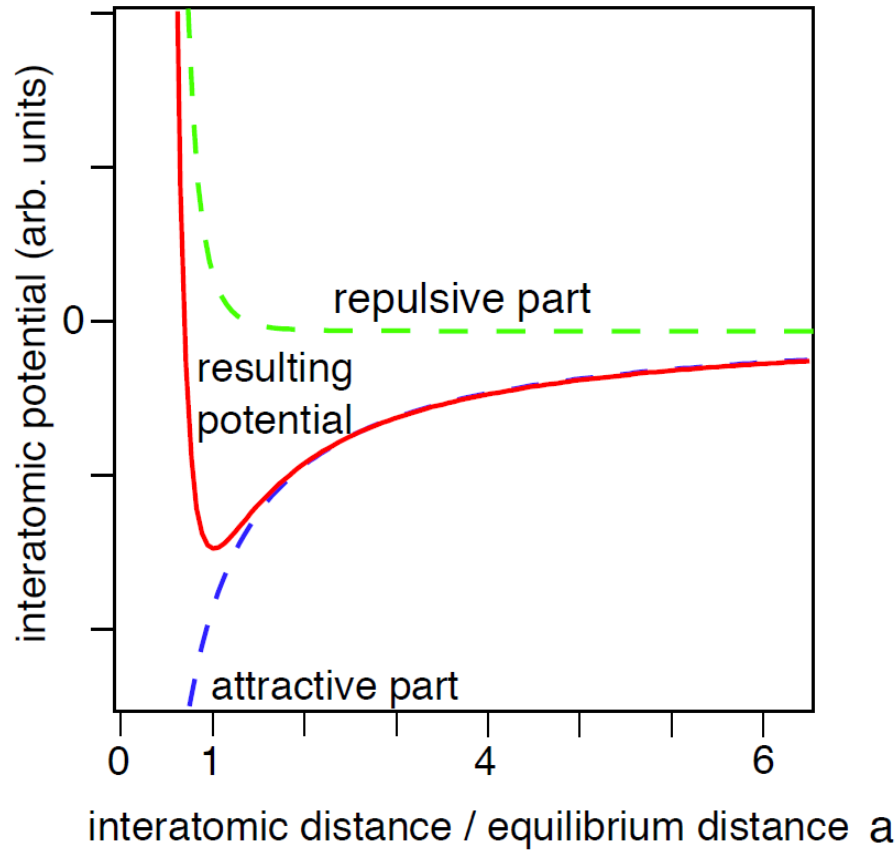
Phonons in three-dimensional solids

Considering an example of Diamond- 2 atoms per unit cell



Both acoustic and optical phonon dispersions

Thermal Expansion is due to Anharmonicity

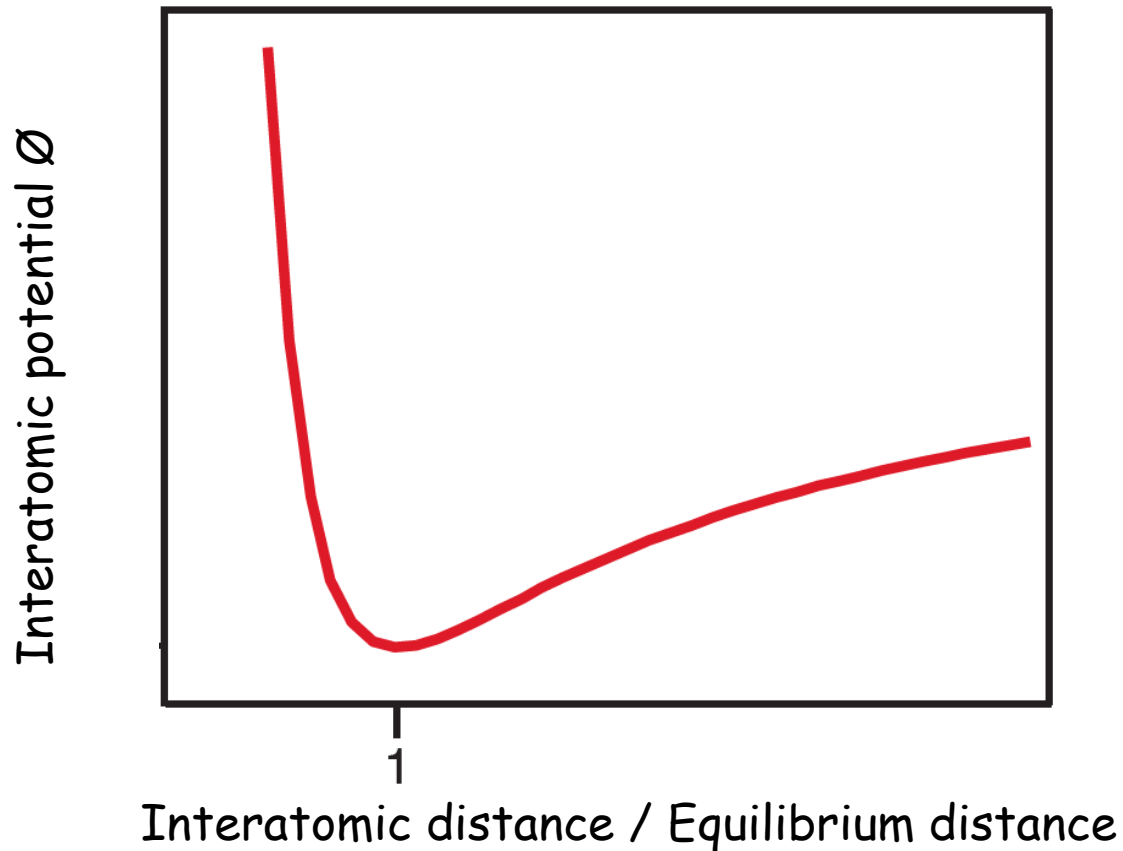


Taylor expanding the potential around the minimum position -

$$V(x) \approx V(x_{eq}) + \frac{\kappa}{2}(x - x_{eq})^2 + \boxed{\frac{\kappa_3}{3!}(x - x_{eq})^3} + \dots$$

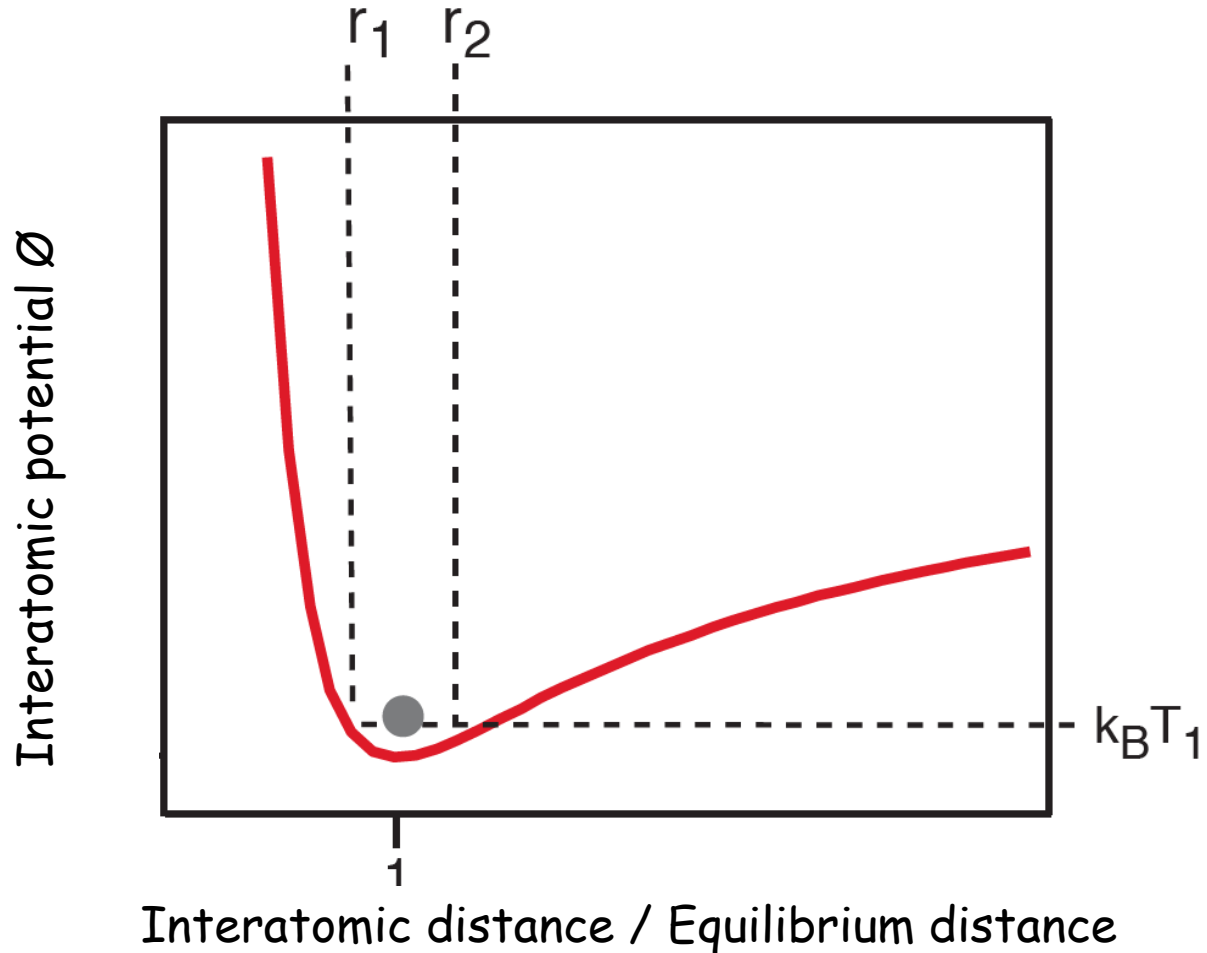
First anharmonic term

Thermal Expansion on the atomic scale



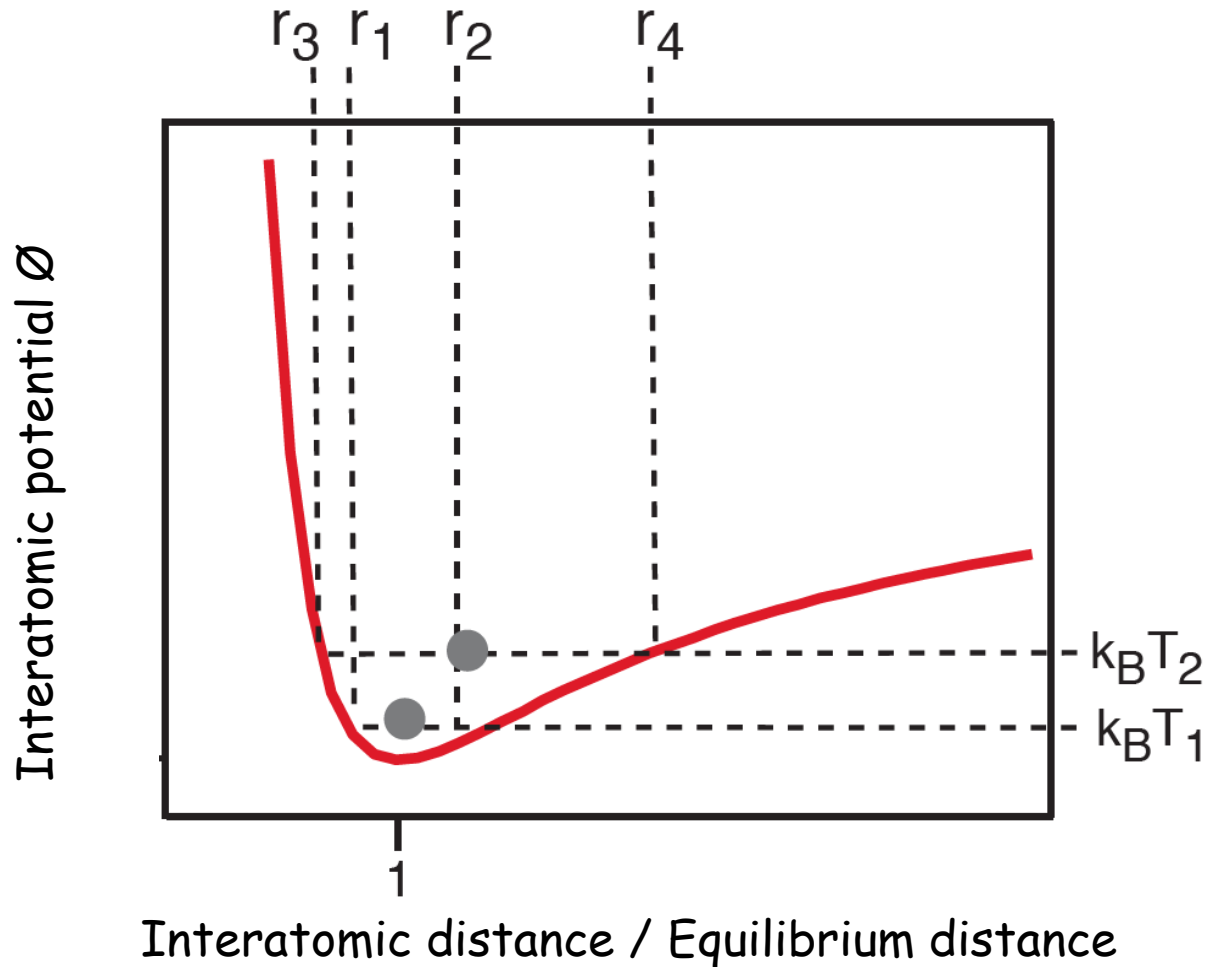
Consider a generic interatomic potential classically

Thermal Expansion on the atomic scale



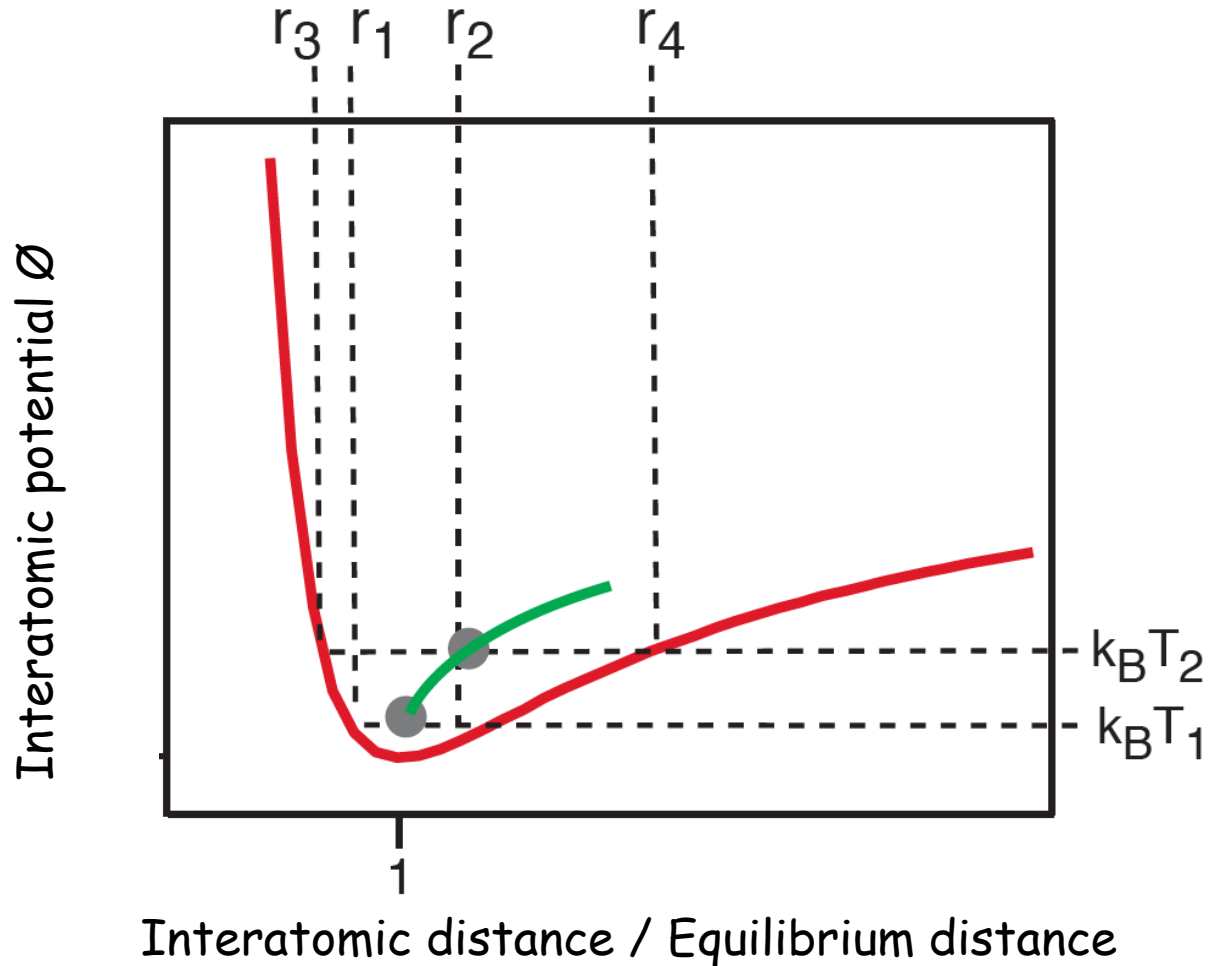
At temperature T_1 , the atom vibrates between position r_1 and r_2

Thermal Expansion on the atomic scale



At higher temperature T_2 , the atom vibrates between r_3 and r_4

Thermal Expansion on the atomic scale



Raising temperature increases the average inter-atomic distance

Thermal Expansion

All materials undergo expansion with increase in temperature



Invar is a Ni-Fe alloy with the lowest coefficient of thermal expansion of all metallic compounds

Charles Edouard Guillaume received Nobel prize in 1920 for this discovery

