

## Vibrations of a Solid

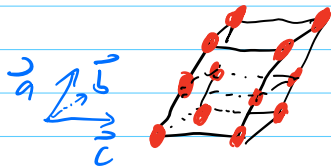
At low temperatures, the state of minimum free energy is often a solid, which is usually a periodic arrangement of atoms forming a lattice.

Equilibrium positions of atoms in a simple crystal:

$$\vec{q}^*(l, m, n) = [l \vec{a} + m \vec{b} + n \vec{c}] \equiv \vec{r}$$

$$l, m, n \in \mathbb{Z}$$

$\vec{a}, \vec{b}, \vec{c}$  lattice basis vectors



Small deformations:  $\vec{q}_{\vec{r}} = \vec{r} + \vec{u}(\vec{r})$

$$\text{potential energy: } V = V^* + \frac{1}{2} \sum_{\substack{\vec{r}, \vec{r}' \\ \alpha, \beta}} \frac{\partial^2 V}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} u_{\alpha}(\vec{r}) u_{\beta}(\vec{r}')$$

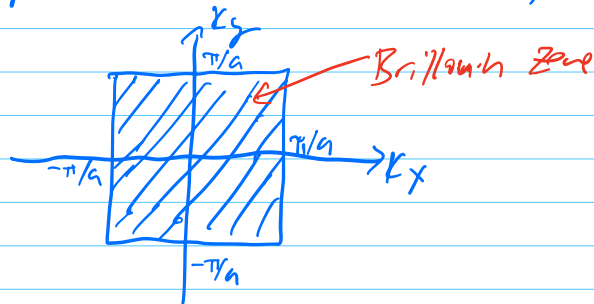
$$\text{Translational symmetry} \rightarrow \frac{\partial^2 V}{\partial q_{\vec{r}, \alpha} \partial q_{\vec{r}', \beta}} = K_{\alpha\beta}(\vec{r} - \vec{r}')$$

$$\text{Fourier basis: } u_{\alpha}(\vec{r}) = \sum_{\vec{k}} \frac{e^{i\vec{k} \cdot \vec{r}}}{\sqrt{N}} \tilde{u}_{\alpha}(\vec{k})$$

← inside Brillouin zone

Brillouin zone - contains all independent wavevectors

Example: Cubic lattice of spacing  $a$



Any wavevector outside the Brillouin zone carries no new information:

$$\left(k_x + \frac{2\pi m}{a}\right) \cdot (na) = k_x \cdot na + 2m n \pi$$

$$e^{i\left(k_x + \frac{2\pi m}{a}\right)(na)} = e^{i k_x na} e^{i 2m n \pi}$$
$$= e^{i k_x na}$$

Can shift any wavevector outside the Brillouin zone into the Brillouin zone by adding multiples of  $\frac{2\pi}{a}$  to  $k_x, k_y, k_z$ .

In terms of Fourier modes:

$$V = V^* + \frac{1}{2N} \sum_{\substack{\vec{r}, \vec{r}' \\ \vec{k}, \vec{k}' \\ \alpha, \beta}} V_{\alpha\beta}(\vec{r} - \vec{r}') e^{i\vec{k} \cdot \vec{r}} \tilde{u}_{\alpha}(\vec{k}) e^{i\vec{k}' \cdot \vec{r}'} \tilde{u}_{\beta}(\vec{k}')$$

Center of Mass coordinate  $\vec{R} = \frac{\vec{r} + \vec{r}'}{2}$   $\left. \begin{array}{l} \vec{r} = \vec{R} + \frac{\vec{p}}{2} \\ \vec{r}' = \vec{R} - \frac{\vec{p}}{2} \end{array} \right\}$

Relative coordinate  $\vec{p} = \vec{r} - \vec{r}'$

$$V = V^* + \frac{1}{2N} \sum_{\substack{\vec{k}, \vec{k}' \\ \alpha, \beta}} \left( \sum_{\vec{R}} e^{i(\vec{k} + \vec{k}') \cdot \vec{R}} \right)$$

$$\times \left( \sum_{\vec{p}} \chi_{\alpha\beta}(\vec{p}) e^{i(\vec{k} - \vec{k}') \cdot \vec{p}/2} \tilde{u}_{\alpha}(\vec{k}) \tilde{u}_{\beta}(\vec{k}') \right)$$

Since  $\sum_{n=0}^{N-1} e^{i(k+k')(n+m)a} = N \delta_{k+k', 0}$  if  $k = -k'$ ,  $\sum_{n=0}^{N-1} 1 = N$ .

$$\sum_{\vec{R}} e^{i(\vec{k} + \vec{k}') \cdot \vec{R}} = N \delta_{\vec{k} + \vec{k}', \vec{0}}$$

Then,

$$V = V^* + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} \left( \sum_{\vec{p}} \chi_{\alpha\beta}(\vec{p}) e^{i\vec{k} \cdot \vec{p}} \right) \tilde{u}_{\alpha}(\vec{k}) \tilde{u}_{\beta}(\vec{k}')$$

$$= V^* + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} \tilde{\chi}_{\alpha\beta}(\vec{k}) \tilde{u}_{\alpha}(\vec{k}) \tilde{u}_{\beta}(-\vec{k})$$

$$= V^* + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} \tilde{\chi}_{\alpha\beta}(\vec{k}) \tilde{u}_{\alpha}(\vec{k}) \tilde{u}_{\beta}(\vec{k})^*$$

$$\tilde{u}_{\beta}(-\vec{k}) = \sum_{\vec{r}} \frac{e^{-i(\vec{k}) \cdot \vec{r}}}{\sqrt{N}} u_{\beta}(\vec{r}) = \sum_{\vec{r}} \frac{e^{+i\vec{k} \cdot \vec{r}}}{\sqrt{N}} u_{\beta}(\vec{r}) = \tilde{u}_{\beta}(\vec{k})^*$$

At this order the potential involves a sum over  $\vec{k}$  with no mixing between different  $\vec{k}$

⇒ Only need to diagonalize  $3 \times 3$  matrix  $K_{\alpha\beta}(\vec{k})$ ,  
for each  $\vec{k}$ ,  
not a  $3N \times 3N$  matrix of second derivatives.

For simplicity (not general), assume  $K_{\alpha\beta}(\vec{k}) = \delta_{\alpha\beta} K(\vec{k})$

Kinetic energy:

$$\sum_{i=1}^N \frac{m}{2} \dot{\vec{r}}_i^2 = \sum_{\vec{k}} \frac{m}{2} \dot{\tilde{u}}_{\alpha}(\vec{k}) \dot{\tilde{u}}_{\alpha}(\vec{k})^{\dagger}$$

$$= \sum_{\vec{k}, \alpha} \frac{1}{2m} \tilde{p}_{\alpha}(\vec{k}) \tilde{p}_{\alpha}(\vec{k})^{\dagger}$$

$$\text{where } \tilde{p}_{\alpha}(\vec{k}) = \frac{\partial \mathcal{L}}{\partial \tilde{u}_{\alpha}(\vec{k})} = m \dot{\tilde{u}}_{\alpha}(\vec{k})$$

$$\mathcal{H} = \mathcal{V}^{\dagger} + \sum_{\vec{k}, \alpha} \left[ \frac{1}{2m} |\tilde{p}_{\alpha}(\vec{k})|^2 + \frac{K(\vec{k})}{2} |\tilde{u}_{\alpha}(\vec{k})|^2 \right]$$

→  $3N$  independent harmonic oscillators with

$$\omega_{\alpha}(\vec{k}) = \sqrt{\frac{K(\vec{k})}{m}}$$

→ Classically, heat capacity  $\approx 3k_B$  per atom.

Quantum:  $\mathcal{H}^* = V^* + \sum_{\vec{k}, \alpha} \hbar \omega_{\alpha}(\vec{k}) (n_{\vec{k}, \alpha} + 1/2)$

partition Function:

$$Z = \sum_{\{n_{\vec{k}, \alpha}\}} e^{-\beta \mathcal{H}^*} = e^{-\beta E_0} \prod_{\vec{k}, \alpha} \sum_{n_{\vec{k}, \alpha}} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n_{\vec{k}, \alpha}}$$

$$Z = e^{-\beta E_0} \prod_{\vec{k}, \alpha} \left[ \frac{1}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}} \right]$$

$$E_0 = V^* + \sum_{\vec{k}, \alpha} \frac{1}{2} \hbar \omega_{\alpha}(\vec{k})$$

Internal Energy:

$$\begin{aligned} E(T) = \langle \mathcal{H}^* \rangle &= - \frac{\partial}{\partial \beta} \ln Z \\ &= E_0 + \sum_{\vec{k}, \alpha} \hbar \omega_{\alpha}(\vec{k}) \langle n_{\alpha}(\vec{k}) \rangle \end{aligned}$$

Average Occupation numbers:

$$\langle n_{\alpha}(\vec{k}) \rangle = \frac{\sum_{n=0}^{\infty} n e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n}}{\sum_{n=0}^{\infty} e^{-\beta \hbar \omega_{\alpha}(\vec{k}) n}} = \frac{e^{-\beta \hbar \omega_{\alpha}(\vec{k})}}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}}$$

$$E(T) = E_0 + \sum_{\vec{k}, \alpha} \hbar \omega_{\alpha}(\vec{k}) \frac{e^{-\beta \hbar \omega_{\alpha}(\vec{k})}}{1 - e^{-\beta \hbar \omega_{\alpha}(\vec{k})}}$$

## Debye Model

lowest energy modes have smallest  $k \equiv |\vec{k}|$ ,  
and longest  $\lambda = 2\pi/k$ .

$\vec{k} = \vec{0}$  modes — pure translations of lattice.  
— have zero stiffness

$$\lim_{\vec{k} \rightarrow \vec{0}} \tilde{K}(\vec{k}) = 0.$$

$$\text{Assume } \tilde{K}(\vec{k}) = B \vec{k}^2 + \mathcal{O}(k^4).$$

(Odd terms vanish because  $K(\vec{r} - \vec{r}') = K(\vec{r}' - \vec{r})$ )

$$\rightarrow \tilde{K}(\vec{k}) = \tilde{K}(-\vec{k})$$

$$\text{Frequencies } \omega(\vec{k}) = \sqrt{\frac{\tilde{K}(\vec{k})}{m}} = v k \quad \text{Phonon dispersion relation}$$

$$\text{with } v = \sqrt{\frac{B}{m}} \quad \text{speed of sound in crystal}$$

Normally  $K_{\alpha\beta}$  is not proportional to  $\delta_{\alpha\beta}$

but for simplicity here we assume isotropy.

(In reality, long, ~~transverse~~ phonon polarizations have different dispersion relations, even in isotropic crystals.)

The contribution of these long-wavelength vibrational modes to the internal energy is

$$\langle E_{\text{vibrational}} \rangle = E_0 + \sum_{\vec{k}} \frac{\hbar \nu_{\vec{k}}}{e^{\beta \hbar \nu_{\vec{k}}} - 1}$$

Assume periodic boundary conditions in a box of size  $L_x \times L_y \times L_z$ .

$$\vec{k} = \left( \frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right)$$

Large size limit  $\rightarrow$  # nodes in  $d^3 k$  is

$$dN = \frac{d k_x}{2\pi/L_x} \frac{d k_y}{2\pi/L_y} \frac{d k_z}{2\pi/L_z}$$

$$\approx \frac{V}{(2\pi)^3} d^3 k = \rho d^3 k$$

$\rho$  Density of states.

$$\lim_{V \rightarrow \infty} \sum_{\vec{k}} f(\vec{k}) = \int d^3 k \rho(\vec{k}) f(\vec{k})$$

for any integrable function  $f(\vec{k})$ .

$$\text{Now, } E = E_0 + 3V \int_{\text{Brillouin Zone}} \frac{d^3 k}{(2\pi)^3} \frac{\hbar \nu_{\vec{k}}}{e^{\beta \hbar \nu_{\vec{k}}} - 1}$$

Assume same sound velocity for each polarization.

The internal energy and consequently the heat capacity depends on the shape of the Brillouin zone.

low-temperatures compared to the Debye temp,

$$T_D = \frac{\hbar v k_{\max}}{k_B} \approx \frac{\hbar v}{k_B} \frac{\pi}{a}$$

\* lattice spacing

$T \ll T_D \rightarrow \exp(\beta \hbar v k) \gg 1$  near edge of Brillouin zone

$\rightarrow$  integral is dominated from region of small  $k$ ,  
can extend limit of integration to infinity.

spherical symmetry

$T \ll T_D$ : let  $x = \beta \hbar v k$ ,  $d^3 k = 4\pi x^2 \frac{dx}{(\beta \hbar v k)^3}$

$$E(T) \approx E_0 + \frac{3V}{8\pi^3} \left( \frac{k_B T}{\hbar v} \right)^3 4\pi k_B T \int_0^\infty \frac{dx x^3}{e^x - 1}$$

$$\frac{\pi^4}{15} \approx 6.5$$

$$E(T) \approx E_0 + \frac{\pi^2}{10} V \left( \frac{k_B T}{\hbar v} \right)^3 \cdot k_B T$$



Heat Capacity:

$$C = \frac{dE}{dT} = k_B V \cdot \frac{2\pi^2}{5} \left( \frac{k_B T}{\hbar v} \right)^3$$

$$\propto N k_B (T/T_D)^3$$

The  $T^3$  dependence of the heat capacity is observed in experiment at low  $T$ .

Physical interpretation:

For  $T \ll T_D$ , only low-frequency phonons can be excited,  $\hbar \omega(E) \ll k_B T$ .

$$|\mathbf{E}| < k^*(T) \approx \frac{k_B T}{\hbar v}$$

$$\# \text{ of modes excited} \sim V (k^*)^d \sim V \left( \frac{k_B T}{\hbar v} \right)^d$$

Each mode contributes  $\frac{1}{2} k_B T$  to energy  $E$

$$\rightarrow E \sim V \left( \frac{k_B T}{\hbar v} \right)^d \cdot k_B T$$

$$C \sim V k_B \left( \frac{k_B T}{\hbar v} \right)^d \propto T^d \text{ for } T \ll T_D$$

Note: Even though we used the linear dispersion relation  $\omega = v_k$ , which is not valid near the edge of the Brillouin zone, the Debye model still has the correct high-T limit for the heat capacity:

$$E = E_0 + 3V \int_{\text{Brillouin zone}} \frac{d^3k}{(2\pi)^3} \frac{\hbar v_k}{e^{\hbar v_k / k_B T} - 1}$$

$$\xrightarrow{\hbar v_k \ll k_B T} E_0 + 3V \cdot k_B T \cdot \int_{\text{Brillouin zone}} \frac{d^3k}{(2\pi)^3}$$

$$\int_{\text{Brillouin zone}} \frac{d^3k}{(2\pi)^3} = \frac{N}{V}$$

$$E = E_0 + 3Nk_B T$$

$$\Rightarrow C = \frac{dE}{dT} \xrightarrow{T \gg T_D} 3Nk_B \quad \text{from } 3N \text{ modes.}$$

