

## §1. Lattice dynamics

### \* Heat capacity from lattice vibrations

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3D crystal,  $r$  atoms in a unit cell

$$H = \sum_{\vec{q}} \sum_{\nu=1 \dots 3r} \hbar \omega_{\vec{q}, \nu} \left( a_{\vec{q}, \nu}^+ a_{\vec{q}, \nu}^- + \frac{1}{2} \right)$$

Finite temperature  $T > 0$ :

$$\langle a_{\vec{q}, \nu}^+ a_{\vec{q}, \nu}^- \rangle_T = \frac{1}{e^{\beta \hbar \omega_{\vec{q}, \nu}} - 1}$$

Internal energy:

Bose-Einstein distribution!

$$\begin{aligned} U(T) &= \langle H \rangle_T = \sum_{\vec{q}, \nu} \hbar \omega_{\vec{q}, \nu} \left( \langle a_{\vec{q}, \nu}^+ a_{\vec{q}, \nu}^- \rangle_T + \frac{1}{2} \right) \\ &= \sum_{\vec{q}, \nu} \left( \frac{\hbar \omega_{\vec{q}, \nu}}{e^{\beta \hbar \omega_{\vec{q}, \nu}} - 1} + \frac{1}{2} \right) \end{aligned}$$

Heat capacity at constant volume:

$$\begin{aligned} C_V(T) &= \frac{\partial}{\partial T} U(T) \\ &= \frac{\partial}{\partial T} \sum_{\vec{q}, \nu} \frac{\hbar \omega_{\vec{q}, \nu}}{e^{\hbar \omega_{\vec{q}, \nu} / k_B T} - 1} \end{aligned}$$

## - Einstein model

$$\omega_{\vec{q},\nu} = \omega_e \quad (\text{no dependence on } \vec{q}, \nu)$$

→ averaged frequency

$$\Rightarrow C_V(T) = \frac{\partial}{\partial T} \sum_{\vec{q}, \nu} \frac{\hbar \omega_e}{e^{\hbar \omega_e / k_B T} - 1}$$

$$\downarrow \\ \begin{matrix} q=1, \dots, N \\ \nu=1, \dots, 3r \end{matrix} \quad (N_a = N r : \text{number of atoms})$$

$$= 3N_a \frac{\partial}{\partial T} \frac{\hbar \omega_e}{e^{\hbar \omega_e / k_B T} - 1}$$

$$= 3N_a \frac{-\hbar \omega_e}{(e^{\hbar \omega_e / k_B T} - 1)^2} \cdot e^{\hbar \omega_e / k_B T} \left( -\frac{\hbar \omega_e}{k_B T^2} \right)$$

$$= 3N_a k_B \left( \frac{\hbar \omega_e}{k_B T} \right)^2 \frac{e^{\hbar \omega_e / k_B T}}{(e^{\hbar \omega_e / k_B T} - 1)^2}$$

$$\rightarrow \left\{ \begin{array}{l} e^{-\hbar \omega_e / k_B T}, \quad k_B T \ll \hbar \omega_e \quad (\text{low temperature}) \\ 3N_a k_B, \quad k_B T \gg \hbar \omega_e \end{array} \right.$$

$$\downarrow \quad (\text{high temperature}) \quad \checkmark$$

Dulong-Petit law (classical limit)

Experiments:  $C_V \sim T^3$  at low temperature!

- Debye model

$$\omega_{\vec{q}, \nu} = \omega_{\vec{q}} = v_s |\vec{q}| \quad \nu = 1, 2, 3$$

→ acoustic phonon

Density-of-states:

Cut-off frequency  $\omega_D$

$$D(\omega) = \sum_{\vec{q}} \delta(\omega - \omega_{\vec{q}})$$

V: volume of the crystal

$$\begin{aligned} &= \frac{V}{(2\pi)^3} \int d\vec{q} \delta(\omega - \omega_{\vec{q}}) \\ &\quad \xrightarrow{\text{cut-off momentum } (\sim \frac{\pi}{a}, a: \text{lattice spacing})} \\ &= \frac{V}{(2\pi)^3} \int_0^{\omega_D} dq 4\pi q^2 \delta(\omega - v_s q) \rightarrow \delta(\omega - v_s q) = \frac{1}{v_s} \delta\left(\frac{\omega}{v_s} - q\right) \\ &= \frac{V}{(2\pi)^3} 4\pi \left(\frac{\omega}{v_s}\right)^2 \frac{1}{v_s} \quad \text{for } 0 \leq \omega \leq \omega_D \end{aligned}$$

$$\frac{4}{3}\pi q_D^3 \approx \frac{(2\pi)^3}{\Omega} \rightarrow \text{volume of unit cell}$$

↪ volume of the FBZ (rough estimate)

$$\Rightarrow V_s^3 = \frac{\Omega}{6\pi^2} \omega_D^3$$

$$\begin{aligned} \Rightarrow D(\omega) &= \frac{V}{(2\pi)^3} 4\pi \frac{\omega^2}{V_s^3} = \frac{V}{8\pi^3} 4\pi \cdot 6\pi^2 \frac{1}{\Omega} \frac{\omega^2}{\omega_D^3} \\ &= 3N \frac{\omega^2}{\omega_D^3} \end{aligned}$$

$D(\omega) \sim \omega^2$  at low energies.

This comes from linear dispersions!

$$\frac{V}{\Omega} = N \quad (\text{number of unit cells})$$

Debye temperature:

$$\hbar\omega_D = k_B T_D \Rightarrow T_D = \frac{\hbar\omega_D}{k_B} \simeq 10^2 \sim 10^3 \text{ K}$$

(Check "Debye temperature table")

$$\Rightarrow U_{\text{acoustic}}(T) = 3 \sum_{\vec{q}} \left( \frac{\hbar\omega_{\vec{q}}}{e^{\hbar\omega_{\vec{q}}/k_B T} - 1} + \frac{1}{2} \hbar\omega_{\vec{q}} \right)$$

$$= 3 \int dw \sum_{\vec{q}} \delta(w - \omega_{\vec{q}}) \left( \frac{1}{e^{\hbar w/k_B T} - 1} + \frac{1}{2} \hbar w \right)$$

$\underbrace{\hspace{10em}}$   
 $D(w)$

zero-point  
energy dropped below  
(no T dependence)

$$= 3 \int_0^{\omega_D} dw \ N \underbrace{\frac{3w^2}{\omega_D^3}}_{\sim} \frac{\hbar w}{e^{\hbar w/k_B T} - 1}$$

$\downarrow x = \frac{\hbar w}{k_B T}$

$$= \frac{9N\hbar}{\omega_D^3} \left( \frac{k_B T}{\hbar} \right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

$$\downarrow \omega_D = \frac{k_B T_D}{\hbar}$$

$$= \frac{9Nk_B T^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

$$= \begin{cases} 3Nk_B T, & T \gg T_D \\ \frac{3\pi^4}{5} N k_B \frac{T^4}{T_D^3}, & T \ll T_D \end{cases}$$

$\uparrow e^x - 1 \simeq x$   
 $\downarrow \int_0^{T_D/T} x^2 dx = \frac{1}{3} \left( \frac{T_D}{T} \right)^3$

$$\downarrow \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

$$C_{V,\text{acoustic}}(T) = \frac{\partial}{\partial T} U_{\text{acoustic}}(T)$$

$$= \begin{cases} 3Nk_B, & T \gg T_D \\ \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3, & T \ll T_D \end{cases}$$

Lattice vibration contribution:

$$C_V(T) \rightarrow AT^3 \quad \text{for } T \rightarrow 0 \quad \text{Debye's } T^3 \text{ law!}$$

agrees with experiments!

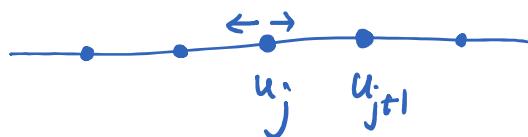
(quantum treatment of lattice vibrations necessary!)

Remark:  $AT^3$  holds in 3D.

In 1D & 2D, one has  $\underbrace{AT}_{\downarrow}$  and  $AT^2$  at low T.

due to different density-of-states

## \* Melting of Solids



$$V(\{u_j\}) = V_0 + \frac{1}{2} \sum_{i,j} D_{ij} u_i u_j + \dots$$

↓

beyond harmonic approximation

$u_i u_k$ ,  $u_i u_j u_k$ , ...

$\langle u_j^2 \rangle_T$ : quadratic displacement about the equilibrium position

large  $\langle u_j^2 \rangle_T$ : solid  $\rightarrow$  liquid  
 ↓  
 anharmonic terms important

Consider 3D crystal,  $N$  unit cells:

1D monoatomic chain

$$u_j = \frac{1}{\sqrt{N}} \sum_{\vec{q}} e^{i\vec{q} \cdot \vec{r}_j} \sqrt{\frac{\hbar}{2MNw_{\vec{q}}}} (a_{\vec{q}} + a_{-\vec{q}}^*)$$

3D crystal (consider  $z$  direction)  $\Leftarrow$  decoupled harmonic oscillators in  $x, y, z$  directions

$$u_n^z = \sum_{\vec{q}} \sqrt{\frac{\hbar}{2MNw_{\vec{q}}}} e^{i\vec{q} \cdot \vec{R}_n} (a_{\vec{q}} + a_{-\vec{q}}^*)$$

$\uparrow$   
unit cell

$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

assume  $w_{\vec{q},\nu} = w_{\vec{q}}$  for simplicity

Calculate  $\langle (u_n^z)^2 \rangle_T = \langle (u_{n=(0,0,0)}^z)^2 \rangle_T \equiv \langle u_z^2 \rangle_T$  :

$\downarrow$   
translation symmetry       $\downarrow$  short-hand notation

$$u_z^2 = \sum_{\vec{q}, \vec{q}'} \frac{\hbar}{2NM} \sqrt{\frac{1}{w_{\vec{q}} w_{\vec{q}'}}} (a_{\vec{q}} + a_{-\vec{q}}^+) (a_{\vec{q}'} + a_{-\vec{q}'}^+)$$

$$H = \sum_{\vec{q}, \nu} \hbar w_{\vec{q}} (a_{\vec{q}, \nu}^+ a_{\vec{q}, \nu} + \frac{1}{2})$$

boson number "conserved" (harmonic approximation)

$$\langle a_{\vec{q}} a_{\vec{q}'} \rangle_T = \langle a_{\vec{q}}^+ a_{\vec{q}'}^+ \rangle_T = 0$$

$$\langle a_{\vec{q}}^+ a_{\vec{q}'}^+ \rangle_T = \frac{1}{e^{\hbar w_{\vec{q}}/k_B T} - 1} \delta_{\vec{q}, \vec{q}'}$$

$$\Rightarrow \langle u_z^2 \rangle_T = \sum_{\vec{q}} \frac{\hbar}{2NM w_{\vec{q}}} \left( \underbrace{\langle a_{\vec{q}}^+ a_{\vec{q}}^+ \rangle_T}_{\approx 1} + \langle a_{\vec{q}}^+ a_{\vec{q}}^+ \rangle_T \right)$$

assumed

$$w_{\vec{q}} = w_{-\vec{q}}$$

$$= \sum_{\vec{q}} \frac{\hbar}{2NM w_{\vec{q}}} \left( 2 \langle a_{\vec{q}}^+ a_{\vec{q}}^+ \rangle_T + 1 \right)$$

$$= \sum_{\vec{q}} \frac{\hbar}{2NM w_{\vec{q}}} \left( \frac{2}{e^{\hbar w_{\vec{q}}/k_B T} - 1} + 1 \right)$$

Use the approach from the Debye model:

$$\langle u_z^2 \rangle = \sum_{\vec{q}} \frac{\hbar}{2NMw_{\vec{q}}} \left( \frac{2}{e^{\hbar w_{\vec{q}}/k_B T} - 1} + 1 \right)$$

insert  $\int_0^{w_D} dw \delta(w - w_{\vec{q}})$ ,

use Debye's model:

$$D(w) = \sum_{\vec{q}} \delta(w - w_{\vec{q}}) = 3N \frac{w^2}{w_D^3}$$

$$= \int_0^{w_D} dw D(w) \frac{\hbar}{2NMw} \left( \frac{1}{e^{\hbar w/k_B T} - 1} + 1 \right)$$

$$= \int_0^{w_D} dw \frac{3w}{w_D^3} \frac{\hbar}{2M} \left( \frac{2}{e^{\hbar w/k_B T} - 1} + 1 \right)$$

$$= \frac{3\hbar}{Mw_D^3} \left( \frac{k_B T}{\hbar} \right)^2 \int_0^{T_D/T} x \left( \frac{1}{e^x - 1} + \frac{1}{2} \right) dx \quad x = \frac{\hbar w}{k_B T}$$

$$w_D = \frac{k_B T_D}{\hbar}$$

$$= \frac{3\hbar^2 T^2}{M k_B T_D^3} \int_0^{T_D/T} x \left( \frac{1}{e^x - 1} + \frac{1}{2} \right) dx$$

$$\int_0^\infty \frac{x}{e^x - 1} dx = \frac{\pi^2}{6}$$

$$\int_0^{T_D/T} \frac{1}{2} x dx = \frac{1}{4} \left( \frac{T_D}{T} \right)^2$$

$$= \left\{ \begin{array}{l} \frac{3\hbar^2}{4M k_B T_D}, \quad T \ll T_D \\ \text{quantum zero-point motion!} \end{array} \right.$$

$$\left. \frac{3\hbar^2 T}{M k_B T_D^2}, \quad T \gg T_D \right. \rightarrow e^x - 1 \approx x$$

$$\int_0^{T_D/T} x \left( \frac{1}{x} + \frac{1}{2} \right) dx \approx \frac{T_D}{T}$$

qualitative criterion for melting : (Lindemann criterion)

$$f = \frac{\sqrt{\langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle}}{r_0} = \sqrt{\frac{9\pi^2 T}{M k_B T_D^2 r_0^2}} \quad \text{for } T \gg T_D$$

radius of the unit cell

critical value  $f_c = 0.2 \sim 0.3$