

Class 16: (04.03.2021)

Systems of interacting particles

Lattice vibrations and Normal modes

Solid \rightarrow made of N atoms

Each atom can be described by its mass and position coordinates

To describe the displacements from the equilibrium we introduce the variable

$$\xi_{i\alpha} = x_{i\alpha} - x_{i\alpha}^{(0)} \xleftarrow{\text{Eq. 1}} ; \quad \alpha = 1, 2, 3$$

The kinetic energy of vibration of the solid

ith atom
 m_i

γ_i

$$(x_{i1}, x_{i2}, x_{i3})$$

Like (x_i, y_i, z_i)

\dot{x}_{id} \rightarrow α component of vel. of ith atom

$$K = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 m_i \dot{\xi}_{i\alpha}^2 = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 m_i \dot{x}_{i\alpha}^2$$

"Potential energy" $V(x_{11}, x_{12}, \dots, x_{N3})$

Potential energy in eqⁿ position can be expressed as a Taylor series (since the displacements are small)

$$V = V_0 + \sum_{i\alpha} \left(\frac{\partial V}{\partial x_{i\alpha}} \right)_0 \xi_{i\alpha} + \frac{1}{2} \sum_{i\alpha, j\beta} \left(\frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\beta}} \right)_0 \xi_{i\alpha} \xi_{j\beta} + \dots$$

↓
"0"
i or j from 1 to N
 α, β from 1 to 3

Evaluated at the equilibrium positions $x_{i\alpha} = x_{i\alpha}^{(0)}$

$$V = V_0 + \frac{1}{2} \sum_{i\alpha, j\beta} A_{i\alpha, j\beta} \xi_{i\alpha} \xi_{j\beta}$$

$$H = \frac{1}{2} \sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + V_0 + \frac{1}{2} \sum_{i\alpha, j\beta} A_{i\alpha, j\beta} \xi_{i\alpha} \xi_{j\beta}$$

Hamiltonian

interacting

"Complicated Hamiltonian"

Change of variables \rightarrow eliminates the cross terms in the potential energy

"Classical Mechanics"

$$\{q_i\}_{i=1}^{3N} \rightarrow q_r \quad (\text{generalized co-ordinate})$$

$$\{q_i\}_{i=1}^{3N} = \sum_{r=1}^{3N} B_{i, r} q_r$$

A proper choice of coefficients gives the following Hamiltonian

$$H = V_0 + \frac{1}{2} \sum_{r=1}^{3N} \dot{q}_r^2 + \frac{1}{2} \sum_{r=1}^{3N} \omega_r^2 q_r^2$$

$\omega_r \rightarrow$ positive constants

$q_r \rightarrow$ normal co-ordinates

$$H_r = \frac{1}{2} (\dot{q}_r^2 + \omega_r^2 q_r^2) \xrightarrow{QM} E_r = (n_r + \frac{1}{2}) \hbar \omega_r$$

$$E_{n_1, \dots, n_{3N}} = V_0 + \sum_{r=1}^{3N} (n_r + \frac{1}{2}) \hbar \omega_r$$

independent of quantum no.

$$\sum_{r=1}^{3N} n_r \hbar \omega_r$$

$$V_0 + \frac{1}{2} \sum_{r=1}^{3N} \hbar \omega_r$$

$\eta \rightarrow$ binding energy per atom in the solid at absolute zero

zero point energy

partition function:

$$Q = \sum_{n_1, n_2, \dots, n_{3N}} e^{-\beta E_{n_1, n_2, \dots}}$$
$$E_{n_1, n_2, \dots} = -N\eta + \sum_{r=1}^{3N} \hbar \omega_r$$

$$Q = e^{\beta N\eta} \sum_{n_1, n_2, \dots, n_{3N}} e^{-\beta(\eta_1\omega_1 + \eta_2\omega_2 + \dots + \eta_{3N}\omega_{3N})}$$

$$= e^{\beta N\eta} \left(\sum_{n_1=0}^{\infty} e^{-\beta \eta_1 \omega_1} \right) \left(\sum_{n_2=0}^{\infty} e^{-\beta \eta_2 \omega_2} \right) \dots \left(\sum_{n_{3N}=0}^{\infty} e^{-\beta \eta_{3N} \omega_{3N}} \right)$$

$$Q = e^{\beta N\eta} \left(\frac{1}{1 - e^{-\beta \eta_1 \omega_1}} \right) \left(\frac{1}{1 - e^{-\beta \eta_2 \omega_2}} \right) \dots \left(\frac{1}{1 - e^{-\beta \eta_{3N} \omega_{3N}}} \right)$$

$$\ln Q = \beta N\eta - \sum_{r=1}^{3N} \ln(1 - e^{-\beta \eta_r \omega_r})$$

If normal mode frequencies are closely spaced (ω_r)

$$\ln Q = \beta N \eta - \int_0^\infty \ln(1 - e^{-\beta \hbar \omega}) \sigma(\omega) d\omega$$

A knowledge is required
 the no. of normal
 modes with angular
 frequency in the range
 bet'n ω and $\omega + d\omega$

$$\langle E \rangle = - \frac{\partial \ln Q}{\partial \beta} = - N \eta + \int_0^\infty \frac{(0 + \hbar \omega e^{-\beta \hbar \omega})}{(1 - e^{-\beta \hbar \omega})} \sigma(\omega) d\omega$$

$$\langle E \rangle = - N \eta + \int_0^\infty \frac{\hbar \omega}{(e^{\beta \hbar \omega} - 1)} \sigma(\omega) d\omega$$

$$\langle E \rangle = -N\eta + \int_0^{\infty} \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \sigma(\omega) d\omega$$

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = -\frac{1}{k_B T^2} \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_V = -k_B \beta^2 \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_V$$

$$= -k_B \beta^2 \left[\int_0^{\infty} \frac{(\hbar\omega)(0 - \hbar\omega e^{\beta\hbar\omega})}{(e^{\beta\hbar\omega} - 1)^2} d\omega \right]$$

$$C_V = k_B \int_0^{\infty} \frac{(\beta\hbar\omega)^2 \sigma(\omega) e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} d\omega$$

$$\begin{aligned} \frac{d}{dx} \left(\frac{f(x)}{g(x)} \right) &= \frac{f'(x)g(x) - g'(x)f(x)}{g(x)^2} \end{aligned}$$

$$C_V = k_B \int_0^{\infty} \sigma(\omega) d\omega$$

$C_V = k_B 3N = 3Nk_B$

if T is large
 β is small

↑ "Dulong-Petit's result"

$$C_V = k_B \int_0^{\infty} \frac{(\beta\hbar\omega)^2 \sigma(\omega) (1 + \beta\hbar\omega + \dots)}{(1 + \beta\hbar\omega + \dots - 1)^2} d\omega$$

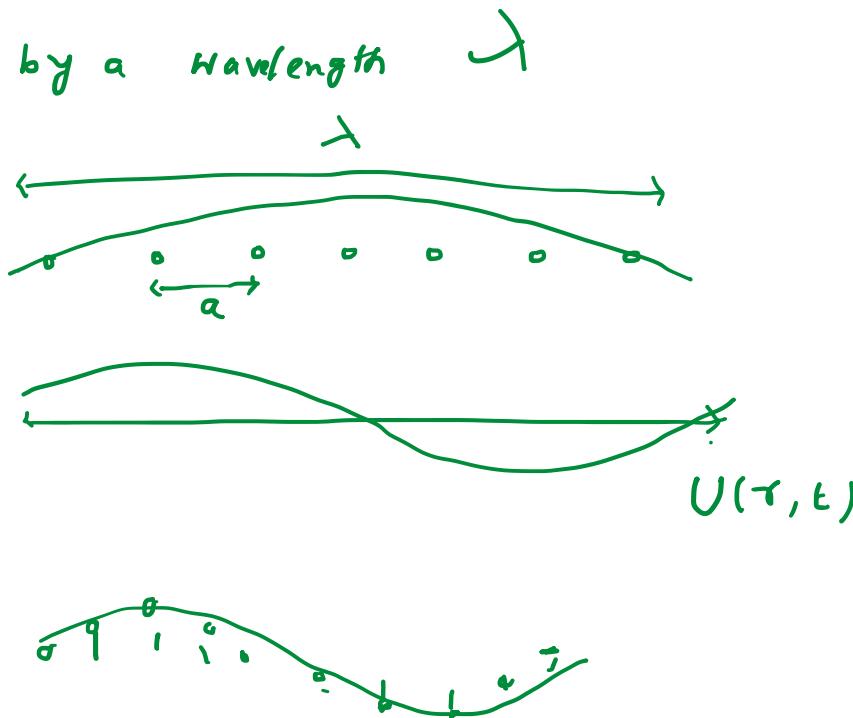
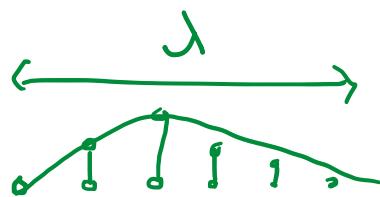
"Debye"

Solid \equiv Neglecting the discreteness of the atoms
and treating the latter as if it were
a continuous isotropic elastic medium

" a " \rightarrow mean interatomic separation in solid ($\sim 1\text{ \AA}$)

Elastic medium is characterised by a wavelength λ

$$\lambda \gg a$$



$$\lambda \approx a$$

Discreteness becomes important



$$\omega = c_s k$$

\leftarrow velocity of 'wave vector'
sound

$$\sigma_c(\omega) d\omega = 3 \frac{V}{(2\pi)^3} (4\pi k^r dk) = 3 \frac{V}{(2\pi c_s^3)} \omega^r d\omega = \sigma(\omega) d\omega$$

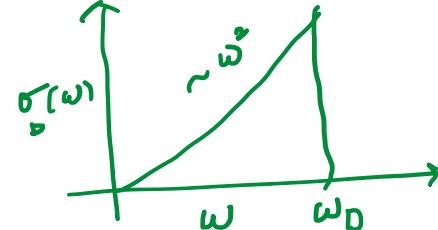
three possible polarizations

2 - transverse
1 - longitudinal

Debye approximation

$$\left. \begin{aligned} \sigma_D(\omega) &= \sigma_c(\omega) \\ &= 0 \end{aligned} \right\}$$

$$\begin{cases} \omega < \omega_D \\ \omega > \omega_D \end{cases}$$



Debye frequency spectrum

$$\int_0^\infty \sigma_D(\omega) d\omega = \int_0^\infty \sigma_c(\omega) d\omega = 3N$$

$$\left(\frac{3V}{2\pi^r c_s^3} \right) \int_0^{\omega_D} \omega^r d\omega = 3N$$

$$\Rightarrow \left(\frac{3V}{2\pi^r c_s^3} \right) \frac{\omega_D^3}{3} = 3N$$

"Debye frequency"

$$\omega_D = \left(6\pi^r \frac{N}{V} \right)^{\frac{1}{3}} c_s$$

$c_s = 5 \times 10^5 \text{ cm/s}$

$$\left(\frac{V}{N} \right)^{\frac{1}{3}} = a$$

$= 10^{-8} \text{ cm}$

$\omega_D \sim 10^{14} \text{ sec}^{-1}$ "Infrared"

Different for different solids

$$C_V = k_B \int_{\omega_D}^{\infty} \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} (\beta \hbar \omega)^2 \left(\frac{3V}{2\pi^2 c_s^3} \right) \omega^2 d\omega$$

$$= k_B \int_0^{\beta \hbar \omega_D} \frac{e^x}{(e^x - 1)^2} x^2 \left(\frac{3V}{2\pi^2 c_s^3} \right) \frac{1}{(\beta \hbar)^3} x^2 dx$$

$$C_V = k_B \frac{3V}{2\pi^2 (c_s \rho \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{e^x x^4}{(e^x - 1)^2} dx$$

$$C_V = k_B \frac{3 \cdot 4 \pi^2 N \left(\frac{c_s}{\omega_D} \right)^3}{2\pi^2 (c_s \rho \hbar)^3} \int_0^{\beta \hbar \omega_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$C_V = (3Nk_B) f_D \left(\frac{\Theta_D}{T} \right)$$

"Dulong-Petit" result

$$\Theta_D = \frac{k \omega_D}{k_B}$$

$$x = \beta \hbar \omega$$

$$\omega = \frac{x}{\beta \hbar}$$

$$d\omega = \frac{dx}{\beta \hbar}$$

(F. Reif
Fundamentals
of Statistical
and Thermal
Physics)

$$V = \frac{3N (2\pi^2 c_s^3)}{\omega_D^3}$$

$$T \rightarrow \infty$$

$$= \frac{3}{(\beta \hbar \omega_D)^3} \int_0^{\beta \hbar \omega_D} \frac{x^4 (1 + x + \dots)}{(1 + x + \dots)^2} dx$$

$$= \frac{3}{(\beta \hbar \omega_D)^3} \int_0^{\beta \hbar \omega_D} x^4 dx$$

$$= 1$$

$$f_D(\beta \hbar \omega_D)$$

$$= (3Nk_B) \frac{3}{(\beta \hbar \omega_D)^3} \int_0^{\beta \hbar \omega_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$x = \beta \hbar \omega$$

At high temperature? $T \gg 1$

$$C_V = 3Nk_B$$

$$f_D(y) \underset{y \rightarrow \infty}{=} 1$$