Vibrations of Solid (Low T)

ions sitting at mechanical equilibrium at $T = 0$

At low $T \neq 0$, there are displacements from mean positions.

Writing the potential energy: $(T \neq 0)$

$$U = U_0 + \sum_{i\,;\,\alpha} \underbrace{\cancel{\frac{\partial U}{\partial \vec{r}_{i,\alpha}}}}_{0} d\vec{r}_{i,\alpha} + \sum_{i,j\,;\,\alpha,\beta} \frac{\partial^2 U}{\partial \vec{r}_{i,\alpha}\, \partial \vec{r}_{j,\beta}} d\vec{r}_{i,\alpha}\, d\vec{r}_{j,\alpha} + \underbrace{\cancel{O\left(d\vec{r}^{\,3}\right)}}_{0}$$

$i \to (1, N)$, $\alpha \to (1, 3)$

"Low T"

Close to mechanical equilibrium

$$\frac{\partial U}{\partial \vec{r}_{i,\alpha}} = -F_{i,\alpha} = 0$$

"Low T"

$$U = U_0 + \sum_{i,j\,;\,\alpha,\beta} \frac{\partial^2 U}{\partial \vec{r}_{i,\alpha}\, \partial \vec{r}_{j,\beta}} d\vec{r}_{i,\alpha}\, d\vec{r}_{j,\beta}$$

$$= U_0 + \sum_{i,j\,;\,\alpha,\beta} H^{i,j}_{\alpha,\beta}\, d\vec{r}_{i,\alpha}\, d\vec{r}_{j,\beta}$$

$H^{i,j}_{\alpha,\beta}$ $\equiv$ Matrix of second derivatives
"Hessian matrix"

Size $3N \times 3N$ for N particles in 3-d

Being symmetric in nature,
It is diagonizable. $\Rightarrow U H U^T = \Lambda$

$$= \begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \ddots & \\ & & & \lambda_{3N} \end{pmatrix}$$

λ_i's are normal modes of vibrations.

Hamiltonian due to these $3N$ oscillators!

$$\mathcal{H} = \sum_{\alpha=1}^{3N} \left(n_\alpha + \frac{1}{2}\right) \hbar \omega_\alpha$$

Zero point energy of α^{th} oscillator : $\frac{1}{2} \hbar \omega_\alpha$

n_α is the excitation of α^{th} oscillator.

Microstate : $\{n_i\}$ $i \in (1, 3N)$

$\nu_1 : (n_1, n_2, \dots n_{3N})$

$\nu_2 : (n_1', n_2', \dots n_{3N})$

$\vdots$

Large no. of micro-states

Partition function: $$Z = \sum_{\{n_i\}} e^{-\beta \mathcal{H}\{n_i\}}$$

$$= \sum_{\{n_i\}} e^{-\beta \sum_{\alpha=1}^{3N} (n_\alpha + 1/2) \hbar \omega_\alpha}$$

$$= \sum_{\{n_j\}} e^{-\beta(n_1+1/2)\hbar\omega_1} \cdot e^{-\beta(n_2+1/2)\hbar\omega_2} \cdots\cdots e^{-\beta(n_{3N}+1/2)\hbar\omega_{3N}}$$

$$= \prod_{j=1}^{3N} \sum_{n_j=0}^{\infty} e^{-\beta(n_j+1/2)\hbar\omega_j}$$

$$= \prod_{j=1}^{3N} e^{-\beta\hbar\omega_j/2} \sum_{n_j=0}^{\infty} e^{-\beta n_j \hbar\omega_j}$$

$$= \prod_{j=1}^{3N} e^{-\beta\hbar\omega_j/2} \left[\underbrace{1 + e^{-\beta\hbar\omega_j} + e^{-2\beta\hbar\omega_j} + \cdots}_{\text{Geometric series}} \right]$$

Geometric series

common ratio $= e^{-\beta\hbar\omega_j}$

$$= \frac{1}{1 - e^{-\beta\hbar\omega_j}}$$

$$= \prod_{j=1}^{3N} \frac{e^{-\beta\hbar\omega_j/2}}{1 - e^{-\beta\hbar\omega_j}}$$

$$Z = \prod_{j=1}^{3N} \frac{1}{e^{\beta\hbar\omega_j/2} - e^{-\beta\hbar\omega_j/2}} = \prod_{j=1}^{3N} \frac{1}{2\sinh(\beta\hbar\omega_j/2)}$$

Then,

$$\ln Z = -\sum_{j=1}^{3N} \ln\left[2\sinh\left(\beta\hbar\omega_j/2\right)\right] \quad \text{——— (1)}$$

We know that, $N \to \infty$, $V \to \infty$, $N/V \to$ finite

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

$$n_i \equiv (n_{i,x}, n_{i,y}, n_{i,z})$$

$\Delta k \longrightarrow 0$ as $L \longrightarrow \infty$

$$\because \quad k_{min} = \left[\left(\frac{2\pi}{L}\right)^2 + \left(\frac{2\pi}{L}\right)^2 + \left(\frac{2\pi}{L^2}\right)\right]^{1/2} \sim \frac{1}{L}$$

$$\omega \sim k \quad (\omega = ck)$$

In the thermodynamic limit,
modes are tightly spaced,

$$\ln Z = -\int_{\omega=0}^{\infty} \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] \underbrace{g(\omega)}_{\dim(1/\omega)}\, d\omega \quad \text{—— (2)}$$

$$\sum_{\omega} \longrightarrow \int d\omega\, g(\omega) \equiv \Omega_{\text{modes}}$$

$$g(\omega) \equiv \frac{d\Omega}{d\omega}$$

Einstein's proposal : $g(\omega) = 3N\,\delta(\omega - \omega_0)$ "All oscillators with same frequency"

Q. What is heat capacity in this model?

$$\ln Z = -\int_{\omega=0}^{\infty} 3N\,\delta(\omega-\omega_0)\ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] d\omega$$

$$= -3N \ln\left[2\sinh\left(\frac{\beta\hbar\omega_0}{2}\right)\right]$$

Compute $E = \langle H \rangle = \frac{-\partial}{\partial\beta}(\ln Z) = 3N\coth\left(\frac{\beta\hbar\omega_0}{2}\right)\cdot\frac{\hbar\omega_0}{2}$

$$E = \frac{3N\hbar\omega_0}{2} \cot h\left(\frac{\beta\hbar\omega_0}{2}\right)$$

Heat capacity $C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \frac{3N\hbar\omega_0}{2} \frac{\partial}{\partial T} \cot h\left(\frac{\beta\hbar\omega_0}{2}\right)$

Noting: $\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T} \Rightarrow \frac{\partial}{\partial T} = -\beta^2 k_B \frac{\partial}{\partial \beta}$

$$\therefore \quad C_V = \frac{3}{2} N\hbar\omega_0 (-\beta^2 k_B) \frac{\partial}{\partial \beta} \cot h\left(\frac{\beta\hbar\omega_0}{2}\right)$$

$$= -\frac{3}{2} \frac{N\hbar\omega_0}{k_B T^2} \left(\frac{\hbar\omega_0}{2}\right) \frac{\partial}{\partial\left(\frac{\hbar\omega_0\beta}{2}\right)} \cot h\left(\frac{\beta\hbar\omega_0}{2}\right)$$

$$= -3 N k_B \cdot \left(\frac{\hbar\omega_0}{2k_B T}\right)^2 \frac{\partial}{\partial\left(\frac{\hbar\omega_0}{2k_B T}\right)} \cot h\left(\frac{\hbar\omega_0}{2k_B T}\right)$$

... Substitute for $\frac{\hbar\omega_0\beta}{2} = x$ ...

$$= -3 N k_B x^2 \frac{\partial}{\partial x} \cot h x$$

Use the fact, $\frac{\partial}{\partial x} \cot hx = \frac{-1}{\sin h^2 x} = \frac{\partial}{\partial x}\left(\frac{e^x + e^{-x}}{e^x - e^{-x}}\right)$

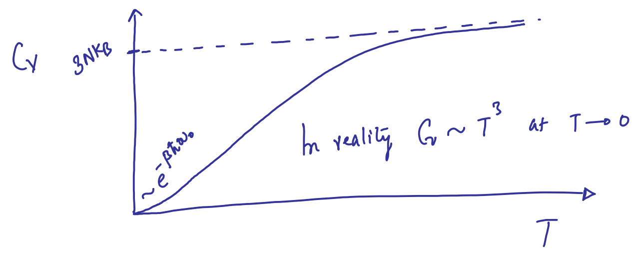
$$C_V = \frac{3 N k_B x^2}{\sin h^2 x} = \frac{3 N k_B x^2 \cdot 4}{(e^x - e^{-x})^2}$$

$$= 12 N k_B x^2 \frac{1}{e^{-2x}(e^{2x}-1)^2}$$

$$= \frac{12 N k_B x^2 e^{2x}}{(e^{2x}-1)^2}$$

Substituting for $x = \hbar\omega_0\beta/2$

$$C_V = 3 N k_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 e^{\hbar\omega_0\beta} \Big/ \left(e^{\hbar\omega_0\beta} - 1\right)^2$$



At high T ($T \longrightarrow \infty$, $\beta \longrightarrow 0$)

$$\frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{(e^{\hbar\omega_0\beta}-1)^2} \sim \frac{\cancel{(\hbar\omega_0\beta)^2}\, e^{\hbar\omega_0\beta}}{(\cancel{1}+\cancel{\hbar\omega_0\beta}+O(\beta^2)\ldots-\cancel{1})^2} \sim 1$$

$$\underline{\underline{C_V \sim 3Nk_B}}$$

At low T ($T \longrightarrow 0$, $\beta \longrightarrow \infty$)

$$\frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{(e^{\hbar\omega_0\beta}-1)^2} \sim \frac{(\hbar\omega_0\beta)^2 e^{\hbar\omega_0\beta}}{e^{2\hbar\omega_0\beta}} \sim (\hbar\omega_0\beta)^2 e^{-\hbar\omega_0\beta}$$

$$\sim e^{-\hbar\omega_0\beta} \xrightarrow[\substack{T\to 0\\ \beta\to\infty}]{}$$

$$\lim_{\beta\to\infty} f(\beta) = \lim_{\beta\to\infty} \frac{\beta^2}{e^{\hbar\omega_0\beta}} \quad \frac{\infty}{\infty} \xrightarrow{\text{L'opital}} \frac{2}{(\hbar\omega_0)^2 e^{\beta\hbar\omega_0}} \longrightarrow 0$$