Debye theory of heat capacity C_V : (At low T)

Q: Why we need this model?

A: Einstein model predicted $C_V \sim e^{-\beta\hbar\omega}$ (At low T) "$C_V \sim T^3$ from experiment"

$C_V \sim 3Nk_B$ (At high T) "OK"

Reason: Einstein's assumption $g(\omega) = 3N\,\delta(\omega - \omega_0)$

$\Longrightarrow$ Source of problem!

Debye's DOS : $g(\omega) = \frac{9N}{\omega_D^3}\,\omega^2$, $\omega < \omega_D$ $\qquad \omega = c|\vec{k}|$

$\qquad\qquad = 0$, $\omega > \omega_D$

Start with Partition function:

Recalling.... $$-\ln Z = \int_{\omega=0}^{\infty} g(\omega) \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] d\omega$$

$$= \int_{\omega=0}^{\omega=\omega_D} \frac{9N\omega^2}{\omega_D^3} \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] d\omega$$

$$-\ln Z = \frac{9N}{\omega_D^3}\int_{\omega=0}^{\omega_D} \omega^2 \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] d\omega \quad \text{—— (1)}$$

$$E = \frac{\partial}{\partial\beta}(-\ln Z)$$ "Bridge connecting S.M $\longleftrightarrow$ Therm."

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = -\beta^2 k_B \left.\frac{\partial E}{\partial \beta}\right|_V \qquad \because \frac{\partial}{\partial\beta} \equiv -k_B T^2 \frac{\partial}{\partial T}$$

$$C_V = -\beta^2 k_B \frac{\partial^2}{\partial\beta^2}(-\ln Z)$$

$$C_V = -\beta^2 k_B \frac{9N}{\omega_D^3} \frac{\partial}{\partial \beta} \int_{\omega=0}^{\omega_D} \omega^2 \cot h \left(\frac{\beta \hbar \omega}{2}\right) \left(\frac{\hbar \omega}{2}\right) d\omega$$

$$= +\beta^2 k_B \frac{9N}{\omega_D^3} \int_{\omega=0}^{\omega_D} \omega^2 \cdot \left(\frac{\hbar\omega}{2}\right)^2 \frac{1}{\left[\sin h \left(\frac{\beta\hbar\omega}{2}\right)\right]^2} \, d\omega \quad \ldots\ldots \frac{d}{dx} \cot hx = \frac{-1}{(\sin hx)^2}$$

$$= \frac{9Nk_B}{4\omega_D^3} \int_{\omega=0}^{\omega_D} \frac{\omega^2 (\beta\hbar\omega)^2}{\left(\sin h \left(\frac{\beta\hbar\omega}{2}\right)\right)^2} d\omega$$

$$= \frac{9}{4} \frac{Nk_B}{\omega_D^3 (\hbar\beta)^2} \int_{\omega=0}^{\omega_D} \frac{(\beta\hbar\omega)^4 \, d\omega}{\left(\sin h \left(\frac{\beta\hbar\omega}{2}\right)\right)^2}$$

$\ldots\ldots\ldots$ substituting $\beta\hbar\omega = x \ldots\ldots$

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

$$= \frac{9}{4} \frac{Nk_B}{\omega_D^3 (\hbar\beta)^3} \int_{x=0}^{x=\beta\hbar\omega_D} \frac{x^4}{\left(\sin h \frac{x}{2}\right)^2} dx$$

$\ldots\ldots \hbar\omega_D = k_B T_D \ldots\ldots$ Debye Temperature

$$= \frac{9}{\cancel{4}} \cdot Nk_B \cdot \left(\frac{T}{T_D}\right)^3 \int_{x=0}^{x=T_D/T} \frac{x^4}{(e^{x/2} - e^{-x/2})^2} \cancel{4} \, dx \quad \ldots\ldots \sin hx = \frac{e^x - e^{-x}}{2}$$

$$= 9 Nk_B \left(\frac{T}{T_D}\right)^3 \int_{x=0}^{T_D/T} \frac{x^4}{(e^{x/2} - e^{-x/2})^2} dx$$

$$= 9 Nk_B \left(\frac{T}{T_D}\right)^3 \int_{x=0}^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

At low T ($T_0/T \to \infty$)

Integral becomes $\to \displaystyle\int_0^\infty \frac{x^4 e^x}{(e^x-1)^2}\,dx = 4!\,\frac{\pi^4}{90} = 24\,\frac{\pi^4}{90}$

$$C_v \approx \cancel{9}\, N k_B \left(\frac{T}{T_D}\right)^3 \frac{\overset{12}{\cancel{24}}\,\pi^4}{\cancel{90}\,\cancel{10}\,5}$$

$$\approx \frac{12}{5}\pi^4 N k_B \left(\frac{T}{T_D}\right)^3$$

$\sim T^3$ ... as seen in experiments

At high T: $(\beta \to 0)$

Recalling:
$$-\ln Z = \frac{9N}{\omega_D^3}\int_{\omega=0}^{\omega_D} \omega^2 \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right] d\omega$$

$$E = \frac{\partial}{\partial\beta}(-\ln Z) = \frac{9N}{\omega_D^3}\int_{\omega=0}^{\omega_0} \omega^2 \left(\frac{e^{\frac{\beta\hbar\omega}{2}} + e^{-\frac{\beta\hbar\omega}{2}}}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}\right) \frac{\hbar\omega}{2}\, d\omega$$

$$= \frac{9N}{\omega_0^3}\cdot\frac{\hbar}{2}\int_{\omega=0}^{\omega_0} \omega^3 \left(\frac{e^{\beta\hbar\omega/2} + e^{-\beta\hbar\omega/2}}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}\right) d\omega$$

At high T : $(\beta \to 0)$

$$E \approx \frac{9N}{\omega_0^3}\frac{\hbar}{2}\int_{\omega=0}^{\omega_D} \omega^3 \left(\frac{2}{\beta\hbar\omega}\right) d\omega \;\ldots O(\cancel{\beta^2})$$

$$E \approx \frac{9N}{\omega_D^3}\cdot k_B T \int_{\omega=0}^{\omega_D} \omega^2\, d\omega$$

$$E \approx 3Nk_BT$$

Hence $C_V = \left.\frac{\partial E}{\partial T}\right|_V = 3Nk_B \qquad (T \to \infty)$ $\quad \beta \to 0$