The specific heat of Solids: Phonons

Phonons: harmonic oscillators

$$\mathcal{E}_{ph} = \sum_{modes} \left[\frac{1}{2}\hbar\omega_{mode} + \frac{\hbar\omega_{mode}}{e^{\beta\hbar\omega_{mode}}-1} \right]$$

Einstein: replace ω_{mode} by ω_E.

$$C_V = \left.\frac{\partial \mathcal{E}_{ph}}{\partial T}\right)_{N,V} = + \frac{\hbar\omega_E}{k_B T^2} \sum_{modes} \frac{\hbar\omega_E\, e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E}-1)^2}$$

$$x_E = \frac{\hbar\omega_E}{k_B T} = \frac{T_E}{T}$$

$$= k_B \frac{x_E^2 e^{x_E}}{(\underbrace{e^{x_E}}_{1+x_E}-1)^2} \sum_{modes}$$

Number of modes: $3N$ (acoustical) $\rightarrow C_V = 3Nk_B K\left(\frac{T_E}{T}\right)$

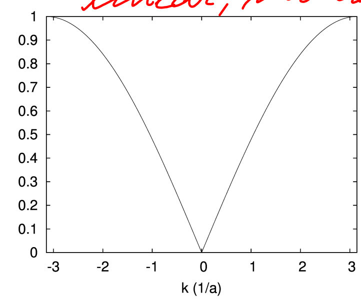
$x_E \ll 1 \rightarrow K(x_E) = 1. \longrightarrow$ Dulong Petit.

$x_E \gg 1 \longrightarrow K(x_E) \rightarrow \left(\frac{T_E}{T}\right)^2 e^{-T_E/T}$

Debye: include phonon spectrum

Phonon spectrum of a linear, monatomic chain.

$\omega_{\underline{k}} \leftarrow$



$\omega_{\underline{k}} = c_s |\underline{k}| \qquad \omega_{\underline{k}}$ small.

$$\mathcal{E} = \sum_{modes} \frac{\epsilon_{mode}}{e^{\beta\epsilon_{mode}}-1} = 3\sum_{\underline{k}} \frac{\hbar\omega_{\underline{k}}}{e^{\hbar\omega_{\underline{k}}/k_B T}-1} \;; \quad C_V = \left.\frac{\partial\mathcal{E}}{\partial T}\right)_N$$

$$3N = 3\sum_{\underline{k}} = \frac{3V}{(2\pi)^3}\int_0^{k_D} 4\pi k^2\, dk = \frac{3V}{(2\pi)^3}\,\frac{4\pi}{3}k_D^3 = \frac{3V}{2\pi^2}\,\frac{\omega_D^3}{3c_s^3} \to \frac{V}{2\pi c_s^2} = \frac{3N}{\omega_D^3}$$

$$(\omega_D = c_s k_D) \qquad \omega_D^3 = 6\pi n c_s^2 \,;\; n = N/V$$

From now on: $\displaystyle\sum_{modes} \dots = \frac{3V}{2\pi^2 c_s^3}\int_0^{\omega_D}\omega^2\, d\omega \dots$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D}\omega^2\, d\omega \dots$$

$$\to \mathcal{E} = \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3\, d\omega}{e^{\beta\hbar\omega}-1} \;; \qquad C_V = \left.\frac{\partial\mathcal{E}}{\partial T}\right)_{N,V}$$

$$\to C_V = \frac{9N}{\omega_D^3}\,\frac{\hbar^2}{k_B T^2}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}\, d\omega}{(e^{\beta\hbar\omega}-1)^2} \qquad x = \beta\hbar\omega \quad x_D = \beta\hbar\omega_D$$

$$= \frac{9Nk_B}{\omega_D^3}(\beta\hbar)^2\int_0^{x_D}\frac{x^4 e^x\, dx}{(e^x-1)^2}\,\frac{1}{(\beta\hbar)^5} =$$

$$= \frac{9Nk_B}{(\beta\hbar\omega_D)^3}\int_0^{x_D}\frac{x^4 e^x\, dx}{(e^x-1)^2} = \frac{9Nk_B}{x_D^3}\int_0^{x_D}\frac{x^4 e^x\, dx}{(e^x-1)^2}$$

Define $\displaystyle D(x_D) = \frac{3}{x_D^3}\int_0^{x_D}\frac{x^4 e^x\, dx}{(e^x-1)^2}$

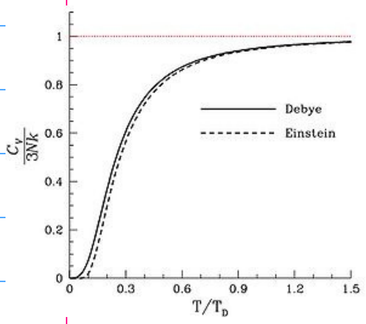
$$\to C_V(T) = \underbrace{3Nk_B}_{D-P}\, D(x_D).$$

T high $\to x_D$ small $\to \displaystyle D(x_D) \simeq \frac{3}{x_D^3}\int_0^{x_D}\frac{x^4\, dx}{(x)^2} = \frac{3}{x_D^3}\,\frac{1}{3}x_D^3 = 1.$

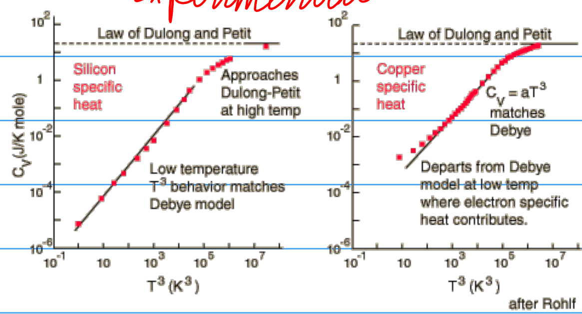
T low $\to x_D$ high:

So $\displaystyle C_V(T) \to 3Nk_B\,\frac{3}{x_D^3}\,\overbrace{\int_0^{\infty}\frac{x^4 e^x\, dx}{(e^x-1)^2}}^{4\pi^4/15} \qquad x_D = \frac{T_D}{T}$

$C_V(T) \sim T^3$ small T.



Experimental



'Modern Physics from A-Z', Wiley 1994