Bose-Einstein distribution

Oscillator (normal mode) with frequency ω

has energy levels $\varepsilon_n = (n+\frac{1}{2})\hbar\omega$

Maxwell-Bolzmann:

Probability for energy ε_n: $P_n = A \cdot e^{-\varepsilon_n/k_BT}$

Normalization: $\sum_{n=0}^{\infty} P_n = 1$

$$\Rightarrow \quad P_n = \frac{e^{-\varepsilon_n/k_BT}}{\sum_n e^{-\varepsilon_n/k_BT}}$$

$$\text{Average} \quad \langle n \rangle = \sum_{n=0}^{\infty} n \cdot P_n = \frac{\sum_{n=0}^{\infty} n \cdot e^{-\varepsilon_n/k_BT}}{\sum_{n=0}^{\infty} e^{-\varepsilon_n/k_BT}}$$

$$e^{-\varepsilon_n/k_BT} = e^{-(n+\frac{1}{2})\hbar\omega/k_BT} = e^{-\frac{1}{2}\hbar\omega/k_BT} \cdot e^{-n\cdot\frac{\hbar\omega}{k_BT}}$$

$$\Rightarrow \quad \langle n \rangle = \frac{\sum_{n=0}^{\infty} n \cdot e^{-n\cdot\frac{\hbar\omega}{k_BT}}}{\sum_{n=0}^{\infty} e^{-n\cdot\frac{\hbar\omega}{k_BT}}} = \frac{\sum_{n=0}^{\infty} n\cdot x^n}{\sum_{n=0}^{\infty} x^n} \quad \text{where } x = e^{-\hbar\omega/k_BT}$$

$$\boxed{\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}}$$

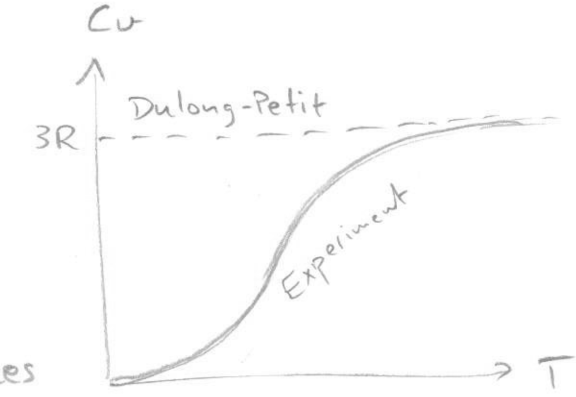
$$\boxed{\sum_{n=0}^{\infty} n\cdot x^n} = x \cdot \frac{d}{dx}\sum_{n=0}^{\infty} x^n = x\cdot\frac{d}{dx}\left(\frac{1}{1-x}\right) = \boxed{\frac{x}{(1-x)^2}}$$

$$\Rightarrow \quad \langle n \rangle = \frac{x}{1-x} = \frac{1}{\frac{1}{x}-1} = \boxed{\frac{1}{e^{\hbar\omega/k_BT}-1}} \quad \text{Bose-Einstein distrib.}$$

f_{BE}

Specific heat

Classical problem ...



$$U = \underbrace{\tfrac{1}{2} k_B T}_{\text{energy per degree of freedom}} \cdot \underbrace{6N}_{\text{6 degrees of freedom in crystal}}$$

Why low-T behavior?

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 3 k_B \cdot N = 3R/\text{mol}$$

Dulong-Petit

$C_p \approx C_v$ in solids/liquids

Quantum mechanics : $\langle n \rangle = f_{BE} = \dfrac{1}{e^{\hbar\omega/k_BT} - 1}$

$\Rightarrow$ Energy of state $\langle n \rangle \cdot \hbar\omega$

Total energy $U = \sum\limits_{K} \sum\limits_{\text{pol.}} \sum\limits_{\text{branches}} \hbar\omega(K) \cdot f_{BE}(\hbar\omega, T)$

Introduce density of states $D(\omega)$

$$U = \int_0^\infty \hbar\omega \cdot f_{BE} \cdot D(\omega)\, d\omega \quad ; \quad C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

In general : $D(\omega)$ not easy

use × numerical calc

or × models $\rightarrow$ Einstein model

$\rightarrow$ Debye model

High-T specific heat

$$U = \sum_{K} \sum_{s} \hbar\omega_s(K) \cdot \underbrace{f_{BE}(\omega_s(K), T)}_{\langle n \rangle} =$$

$$= \sum \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

$$\frac{\hbar\omega}{k_BT} << 1 \implies e^{\hbar\omega/k_BT} \approx 1 + \frac{\hbar\omega}{k_BT}$$

$$\implies \sum (\cdots) \longrightarrow \sum \frac{\hbar\omega}{\left(1+\frac{\hbar\omega}{k_BT}\right) - 1} = \sum k_BT$$

$\sum_{K} \sum_{s}$ = sum over $3 N_{ions}$ terms

K: N_{cell} K-points

s: $3p$ branches (p: ions/cell, 3: pol. directions)

$N_{ions} = N_{cell} \cdot p$

$$\implies U = 3 N_{ions} \cdot k_BT$$

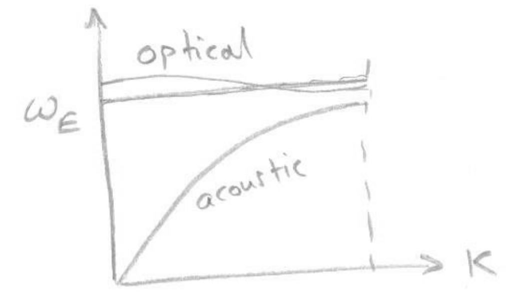
$$u = \frac{U}{V} = 3 n k_BT$$

$$c_v = \frac{\partial u}{\partial T} = 3 n k_B \qquad \text{Dulong-Petit value}$$

Einstein model

Assumption : All oscillators have the same frequency $\omega = \omega_E$

$\Rightarrow$ resemble optical branch



$$\Rightarrow \quad \varepsilon_n = n \cdot \hbar\omega$$

$$U = \int_0^\infty \hbar\omega \cdot \frac{1}{e^{\hbar\omega/k_BT} - 1} D(\omega)\, d\omega$$

$$D(\omega) = 3N \cdot \delta(\omega - \omega_E)$$

Dirac delta function $\quad \int_0^\infty \delta(x)\, dx = 1$

$$\Rightarrow \quad U = 3N \cdot \hbar\omega_E \cdot \frac{1}{e^{\hbar\omega_E/k_BT} - 1}$$

$$C_v = \frac{dU}{dT} = 3N\hbar\omega_E \cdot \frac{e^{\hbar\omega_E/k_BT} \cdot \frac{\hbar\omega_E}{k_BT^2}}{\left(e^{\hbar\omega_E/k_BT} - 1\right)^2}$$

$$C_v = 3N \cdot \left(\frac{\hbar\omega_E}{k_BT}\right)^2 \cdot \frac{\exp(\hbar\omega_E/k_BT)}{\left[\exp(\hbar\omega_E/k_BT) - 1\right]^2}$$

$$C_v(T \to 0) \to 0$$

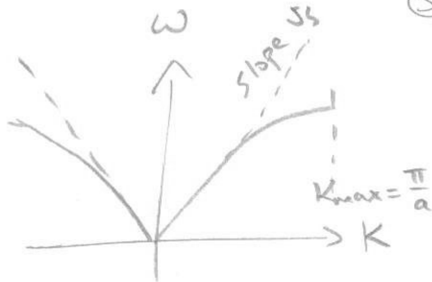
Define Θ_E : $\hbar\omega_E = k_B\Theta_E \quad \Rightarrow \quad C_v = 3N \cdot \left(\frac{\Theta_E}{T}\right)^2 \cdot \frac{\cdots}{\cdots}$

Model gives $C_v \to 0$ but not good absolute accuracy for C_v

Debye model

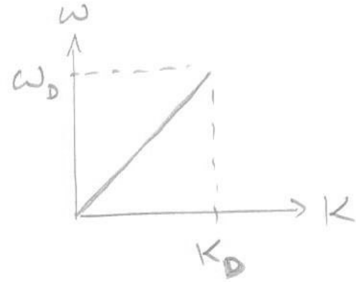
Assumptions

i) $\omega = v_s \cdot |K|$ — sound velocity



ii) Introduce ω_D:

$$3N = \int_0^{\omega_D} D(\omega)\, d\omega$$



$$\omega_D = v_s \cdot K_D$$

$$D(\omega)\, d\omega = D(K)\, dK \quad ; \quad 3N = \int_0^{K_D} D(K)\, dK$$

General

$$D(K)\, dK = \underbrace{3}_{\text{pol. directions}} \cdot \underbrace{\left(\frac{L}{2\pi}\right)^3}_{} \cdot \underbrace{4\pi K^2 dK}_{K\text{-volume}}$$

K-volume per K-point : $\left(\frac{2\pi}{L}\right)^3$

$\Longrightarrow$ number of K-points per K-volume $= \left(\frac{L}{2\pi}\right)^3$

$$D(K) = 3 \cdot \frac{V}{2\pi^2} \cdot K^2$$

$$g(K) = \frac{D(K)}{V} = \frac{3}{2\pi^2} K^2$$

$$g(\omega) = g(K) \cdot \underbrace{\frac{dK}{d\omega}}_{\frac{1}{v_s}} = \frac{3}{2\pi^2} \frac{\omega^2}{v_s^3}$$

$$\boxed{g(\omega) = \frac{3}{2\pi^2} \frac{\omega^2}{v_s^3}}$$

$$3 \cdot \frac{N}{V} = \int_0^{\omega_D} \frac{3}{2\pi^2} \frac{\omega^2}{v_s^3}\, d\omega = \frac{1}{2\pi^2} \cdot \frac{1}{v_s^3} \cdot \omega_D^3 = \frac{1}{2\pi^2} K_D^3$$

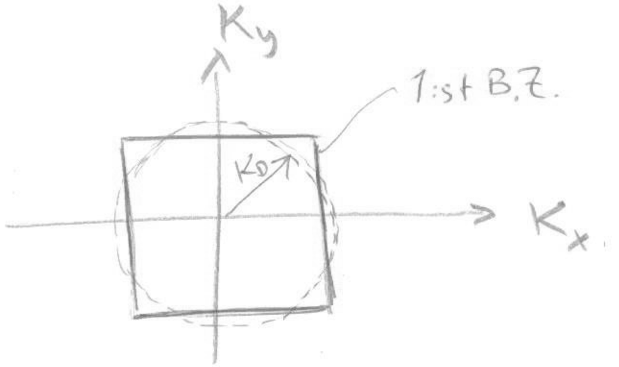
$$\Longrightarrow \boxed{K_D = (6\pi^2 n)^{1/3}}$$

Specific heat with Debye model

$$U = \int_0^{\omega_D} \hbar\omega \cdot \underbrace{f_{BE}(T,\omega)}_{\langle n \rangle} \cdot D(\omega)\, d\omega$$

Debye: cut-off at ω_D

integral instead of integrating over 1:st B.Z.



Sphere of radius K_D same volume as 1:st B.Z.

$$\frac{4}{3}\pi K_D^3 \cdot \left(\frac{L}{2\pi}\right)^3 = N$$

i.e. $\frac{4}{3}\pi K_D^3 = \left(\frac{2\pi}{a}\right)^3$

$\Longrightarrow$ easier integral

$$U = \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1} \cdot \underbrace{\frac{3V}{2\pi^2}\frac{\omega^2}{v_s^3}}_{D(\omega)}\, d\omega$$

$$u = \frac{U}{V} = \frac{3}{2\pi^2 v_s^3} \cdot \frac{1}{\hbar^3} \int_0^{\hbar\omega_D} \frac{(\hbar\omega)^3}{e^{\hbar\omega/k_BT}-1}\, d(\hbar\omega)$$

$$c_V = \frac{du}{dT} = \frac{3}{2\pi^2 v_s^3} \cdot \frac{1}{\hbar^3} \cdot \int_0^{\hbar\omega_D} \frac{(\hbar\omega)^3 \cdot e^{\hbar\omega/k_BT} \cdot \left(\frac{\hbar\omega}{k_BT^2}\right)}{\left(e^{\hbar\omega/k_BT}-1\right)^2}\, d(\hbar\omega)$$

$$= \left\{ \text{put } x = \frac{\hbar\omega}{k_BT} \right\} = \frac{3}{2\pi^2 v_s^3} \cdot \frac{1}{\hbar^3} \int_0^{x_D} \frac{x^3 (k_BT)^3 \cdot e^x \cdot \frac{x}{T} \cdot k_BT \cdot dx}{(e^x-1)^2}$$

$d(\hbar\omega) = k_BT\, dx$

$$= \frac{3k_B}{2\pi^2 v_s^3} \cdot \left(\frac{k_BT}{\hbar}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\, dx$$

Define θ_D : $\hbar\omega_D = k_B\theta_D$

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T}$$

$$C_v = \frac{3k_B}{2\pi^2 v_s^3}\cdot\left(\omega_D\cdot\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx$$

but $\left(\frac{\omega_D}{v_s}\right)^3 = k_D^3 = 6\pi^2 n$

$$\Longrightarrow \boxed{C_v = 9nk_B\cdot\left(\frac{T}{\theta_D}\right)^3\cdot\int_0^{\theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\,dx}$$

High T: $T \gg \theta_D$ $\quad e^x \approx 1+x$

$$\frac{x^4e^x}{(e^x-1)^2} \approx \frac{x^4\cdot 1}{x^2} = x^2 \qquad \int_0^{\theta_D/T} x^2\,dx = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

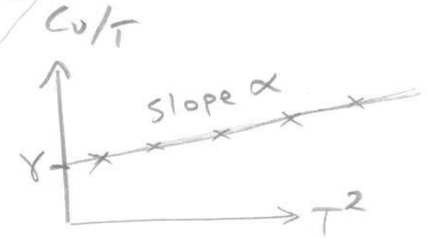
$\Longrightarrow C_v = 3nk_B$ Dulong-Petit value

Low T: $T \ll \theta_D \Longrightarrow \int_0^{\infty}\frac{x^4e^x}{(e^x-1)^2}\,dx = \frac{4}{15}\pi^4$

$$\boxed{C_v = \underbrace{234}_{\frac{12\pi^4}{5}}\cdot nk_B\cdot\left(\frac{T}{\theta_D}\right)^3}$$ Debye's T^3-law

gives $D(\varepsilon_F)$ $\qquad$ gives θ_D

Metals : $C_v = \underbrace{\gamma T}_{\text{el. contrib.}} + \underbrace{\alpha T^3}_{\text{phonons}}$



Heat conductivity in crystals

Earlier: $K = \frac{1}{3} C_v l v$

Valid also for phonons if C_v, v, l phonon properties

Low T ($T \ll \Theta_D$):

$C_v \sim T^3$

$v = v_s = \text{const.}$

$l = \{\text{increases with decreasing } T\} \rightarrow d = \text{sample dim.}$

$\Longrightarrow K \sim T^3$

High T ($T \gg \Theta_D$):

$$\left.\begin{aligned} C_v &= 3 n k_B = \text{const.} \\ v &= v_s = \text{const} \\ l &\sim \frac{1}{T} \end{aligned}\right\} K \sim \frac{1}{T}$$