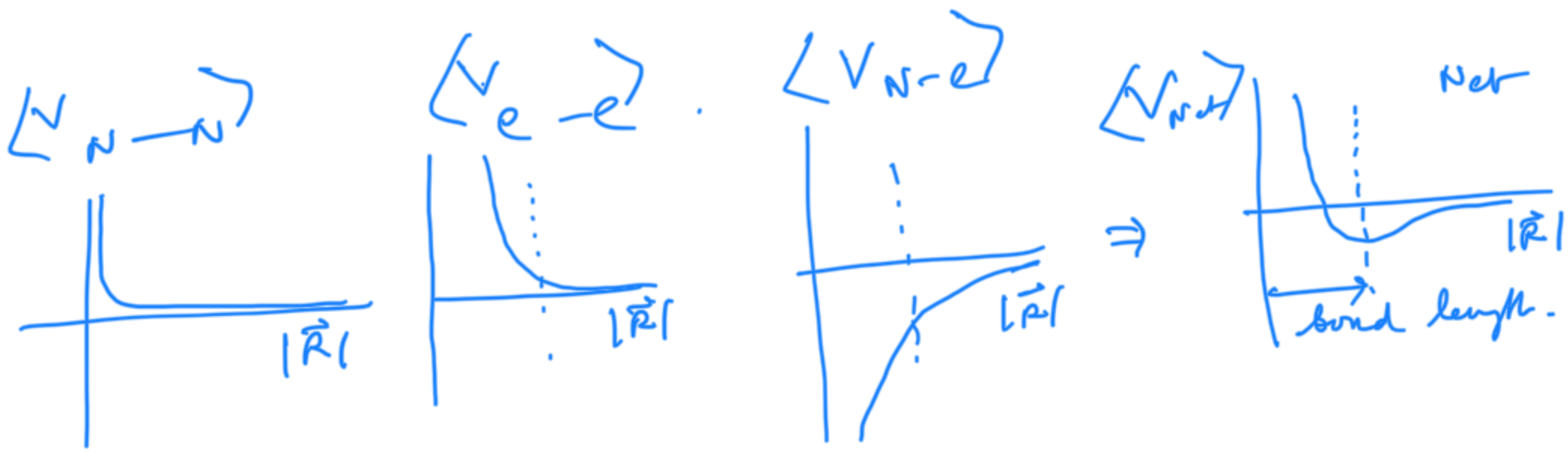
Intro to CMP : lecture 1 : Heat capacity of solids

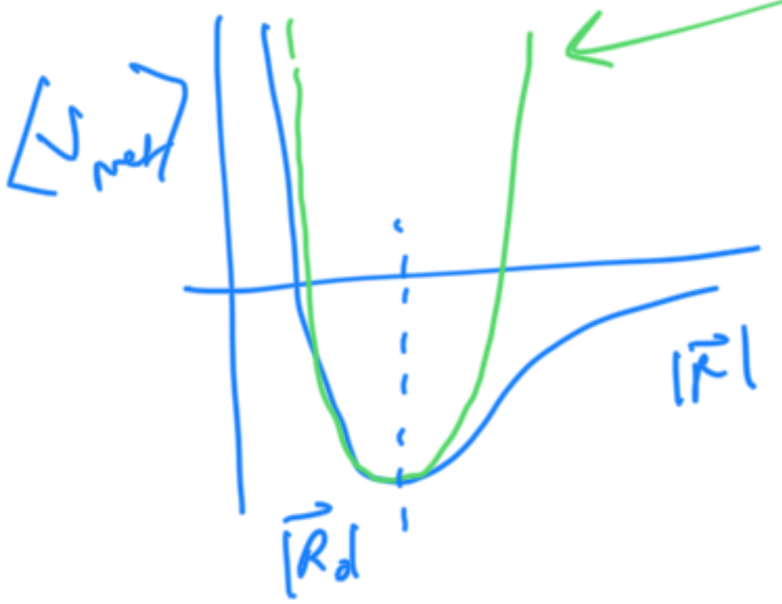
Diatomic

$\vec{R} = \vec{R}_A - \vec{R}_B$

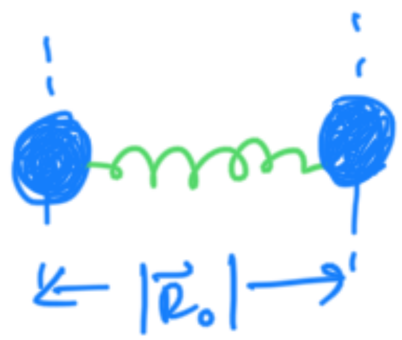
$$H = T_e + T_N + \underbrace{V_{N-N} + V_{N-e} + V_{e-e}}_{V_{Net}}$$



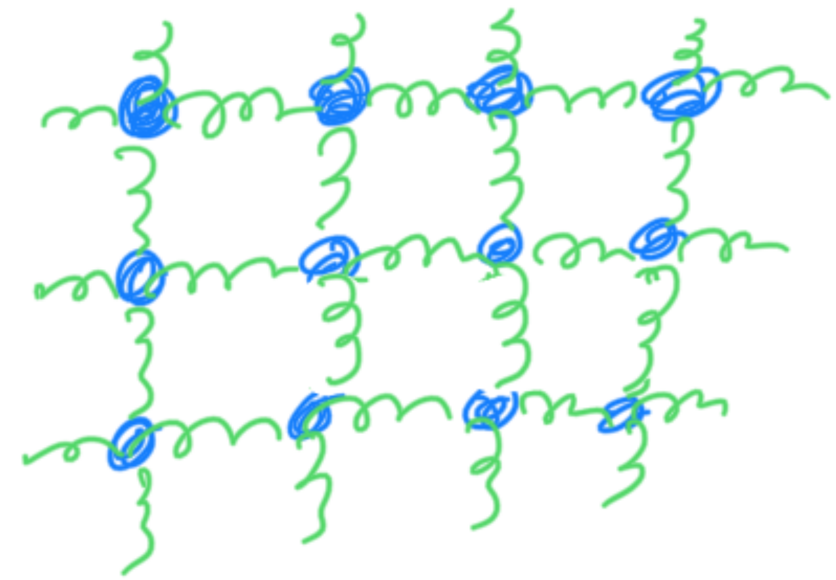
Simplest approach: Harmonic approximation!



$\Rightarrow$



$\Rightarrow$



Classical estimate of $\langle E \rangle = N[\langle KE \rangle + \langle PE \rangle] = N[\frac{3}{2}k_BT + \frac{3}{2}k_BT]$
$= N\, 3k_BT$

$\Rightarrow$ heat capacity : $C = 3k_B$ per atom
$= 3Nk_B = 3R$ per mole.

$\rightarrow$ Dulong Petit' Law. $\rightarrow$ Good at room temp. but deviates as low T.

First attempt to solve (by Einstein, 1907) :

Brings in Q Mech: $E_n = \hbar\omega\,(n + \frac{1}{2})$; $\omega \rightarrow$ Einstein freq. (To be found)

$$\Rightarrow Z_{1D} = \sum_{n \geq 0} e^{-\beta\hbar\omega(n+\frac{1}{2})} \qquad \beta = \frac{1}{k_BT}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

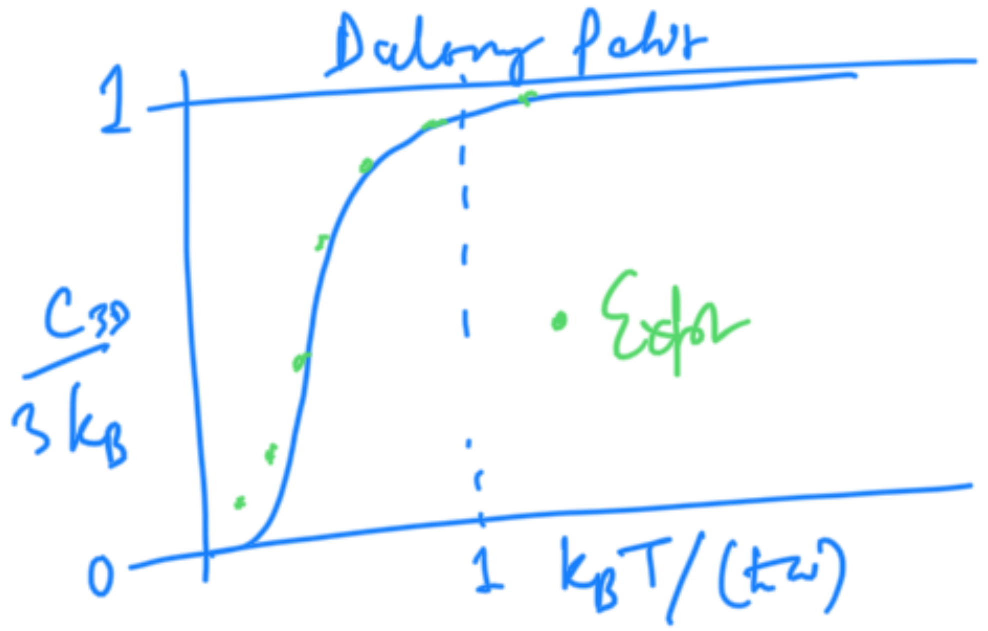
$$\Rightarrow \langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \hbar\omega\left\{\frac{1}{(e^{\beta\hbar\omega} - 1)} + \frac{1}{2}\right\}$$

$\Rightarrow$ heat capacity of single 1D oscillator: $C_{1D} = \frac{\partial \langle E \rangle}{\partial T} = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$

$T \to 0 \Rightarrow (\beta\hbar\omega) \gg 0$: $C_{1D} = k_B(\beta\hbar\omega)^2 \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \longrightarrow 0$ $\because$ higher powers of $(\beta\hbar\omega)$ in denominator.

$T \gg 0 \Rightarrow (\beta\hbar\omega) \to 0$: $C_{1D} = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(1 + \beta\hbar\omega - 1)^2} \approx k_B e^{\beta\hbar\omega} \rightarrow k_B$

In 3D : $Z_{3D} = [Z_{1D}]^3 \Rightarrow C_{3D} = 3\, C_{1D}$



$\Rightarrow$ Deviation from Dulong Petit if $(\beta\hbar\omega)\uparrow \Rightarrow T\downarrow$ or $\omega\uparrow$

ω : fitting parameter : mostly $\hbar\omega < k_BT$

Stronger the bonds : higher the effective k : higher the $\omega = \sqrt{\frac{k}{m}}$

$\Rightarrow$ higher the deviation.

Ex: Diamond. (success!)

$\frac{\hbar\omega}{k_B} = T_E$; E : Einstein

$\Rightarrow \quad C_{3D} \to 3k_B$ as $(\beta\hbar\omega) \to 0 \Rightarrow T \gg 0$ since $\hbar\omega < k_BT$.

$\to 0$ as $(\beta\hbar\omega) \gg 0$: At $T \ll T_E$ degree of freedom freeze out as system gets stuck at the ground state

(see last page)

Einstein model highlights the importance of QM in determining properties of solids at low temp though ω remain a fitting parameter.

Drawback: Does not explain the observed T^3 dependence at low temp. ($T^3 + \alpha T$ for metals.)

Peter Debye 1912 : Oscillation of atoms as sound waves.

$\Rightarrow$ Need to quantize it as light waves following Planck.

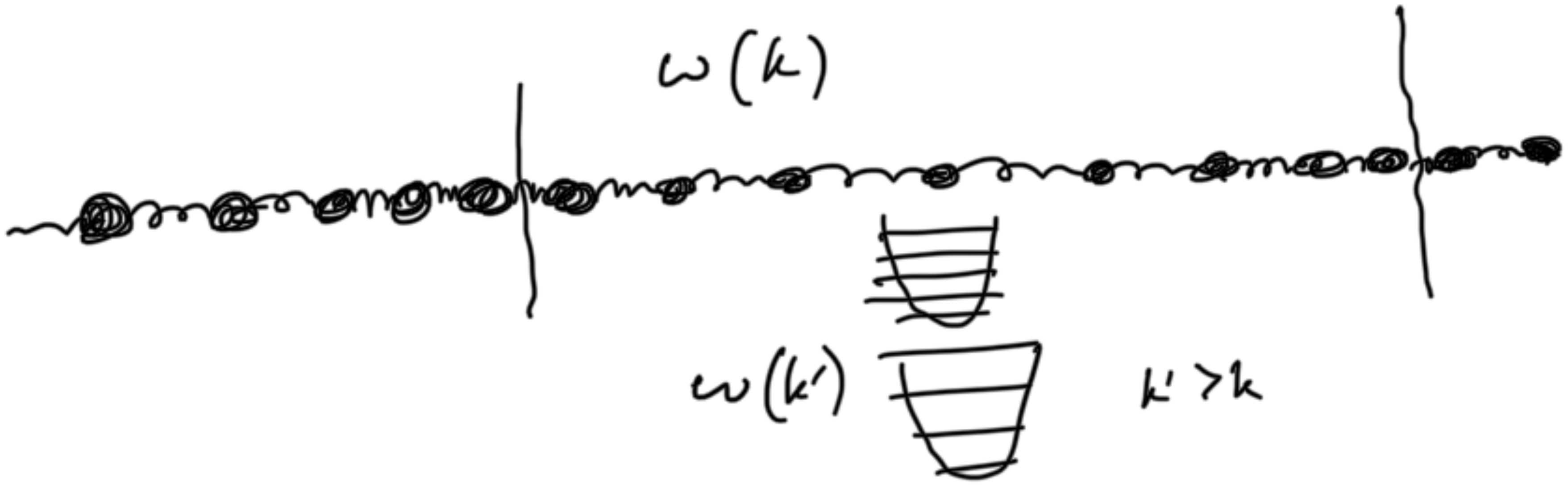
repeats periodically :

Periodic Boundary Condition : L must contain integer # of wavelength : $L = n\lambda$

$\Rightarrow k = \frac{2\pi}{\lambda} = \frac{2\pi n}{L}$: In 3D : $\vec{k} = \hat{i}\frac{2\pi}{L_x}n_x + \hat{j}\frac{2\pi}{L_y}n_y + \hat{k}\frac{2\pi}{L_z}n_z$

$$\omega = \frac{2\pi}{T} = \frac{k\lambda}{T} = \left(\frac{\lambda}{T}\right)k = v k$$

v independent of λ and T
determined by elastic modulus and density.



At temp T
Number of sound (phonon) mode of freq ω: $n_\omega = n_B(\beta\hbar\omega)$, B: Bose

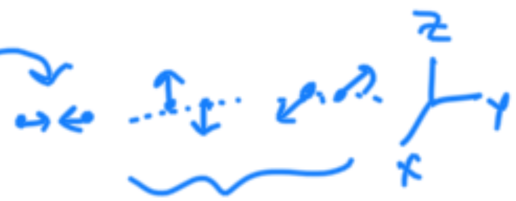
↳ level of excitation of an atomic oscillator of freq ω
Energy of the oscillator at that level: $\hbar\omega\left(n_\omega + \frac{1}{2}\right)$

Consider the nearest integer to $n_B(\beta\hbar\omega)$

$$n_B(x) = \frac{1}{e^x - 1}$$ Bose factor ($\uparrow \infty$ as $x \to 0$ GState.)

$$\therefore \langle E\rangle = 3\sum_{\vec k} \hbar\omega(\vec k)\left(n_B(\beta\hbar\omega(\vec k)) + \frac{1}{2}\right)$$

3 vib modes
1 longitudinal
2 transverse



Note:

$$\sum_k = \frac{1}{\Delta k}\sum \Delta k = \frac{1}{\Delta k}\int dk$$

$$\Delta k = \frac{2\pi}{L}$$

$$\Rightarrow \langle E\rangle = 3\left(\frac{L}{2\pi}\right)^3 \int d\vec k \left[\hbar\omega(\vec k)\left(n_B(\beta\hbar\omega(\vec k)) + \frac{1}{2}\right)\right]$$

Note: $\int d\vec{k} = 4\pi \int k^2 dk$ assuming sph. symmetry to simplify calculation
Mostly valid, best for cubic symmetry.

$$\therefore \langle E \rangle = \frac{3L^3}{8\pi^3} 4\pi \int_0^\infty k^2 dk \left[\hbar\omega(\vec{k}) \left(n_B(\beta\hbar\omega(\vec{k})) + \tfrac{1}{2}\right)\right]$$

Use $k = \frac{\omega}{v}$ $\longrightarrow$ $\langle E \rangle = \frac{3L^3}{2\pi^2} \int_0^\infty \frac{\omega^2 d\omega}{v^3} \hbar\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$

$v \to$ velocity of sound (measurable quantity!)

$$= \int_0^\infty d\omega\, g(\omega)\, \hbar\omega \left(n_B(\beta\hbar\omega) + \tfrac{1}{2}\right)$$

$$g(\omega) \to DOS = \frac{3V\omega^2}{2\pi^2 v^3} = V\frac{3\omega^2}{2\pi^2 v^3} = \frac{N}{n}\frac{3\omega^2}{2\pi^2 v^3} = N\frac{9\omega^2}{\omega_d^3}\ ; \quad \omega_d^3 = 6\pi^2 n v^3$$

$V = L^3$

Debye frequency (Not a fitting param)

$$\therefore \langle E \rangle = \frac{9N\hbar}{\omega_d^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} + \text{Const} \ (T \text{ independent})$$

$\hookrightarrow$ [from the "$\frac{1}{2}$" of $(n_B(\beta\hbar\omega) + \frac{1}{2})$]

$\hbar\omega_d = k_B T_{Debye}$

$$= \frac{9N\hbar}{\omega_d^3(\beta\hbar)^4} \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{\text{Reiman zeta fn.} = \pi^4/15} + \text{Const} = \frac{9N}{(\hbar\omega_d)^3}(k_B T)^4 \frac{\pi^4}{15} + \text{Const} \ (T \text{ indep})$$

$$\Rightarrow C = \frac{\partial \langle E \rangle}{\partial T} = 9N \frac{k_B^4}{k_B^3 T_D^3} 4T^3 \frac{\pi^4}{15} = N k_B \frac{T^3}{T_D^3} \frac{12\pi^4}{5} \Rightarrow C \propto T^3$$

Problem! Varies as T^3 up to arbitrary temp! How to recover Dulong Petit?

Root of the problem: $\int_0^{\infty} d\omega[\quad]$ assumes ∞ number of vib modes.

In reality that must be limited by the number of available vib modes implying a ω_{cutoff} such that

3D motion of N particles: # of vib modes $3N$

$$3N = \int_0^{\omega_{cutoff}} d\omega\, g(\omega) \Rightarrow \langle E\rangle = \int_0^{\omega_{cutoff}} d\omega\, g(\omega)\, \hbar\omega\, n_B(\beta\hbar\omega)$$

At low temp $T \to 0$: $n_B \to 0$ (rapidly) as $x \to 0^+$ $\Rightarrow$ Any finite ω_{cutoff} will have same effect as ∞

$\Rightarrow$ T^3 dependence will show up (only possible to verify numerically)

At high temp limit: $n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega}-1} \to \frac{1}{1+\beta\hbar\omega-1} = \frac{k_BT}{\hbar\omega}$

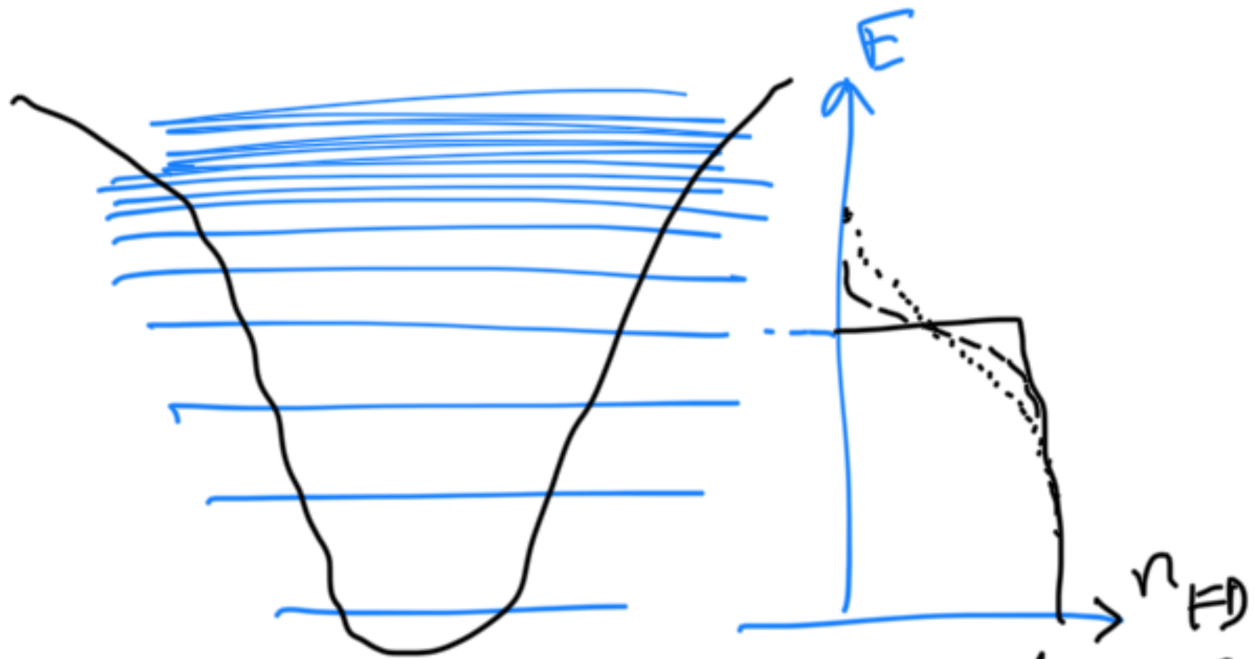
$$\Rightarrow \langle E\rangle = k_BT \underbrace{\int_0^{\omega_{cutoff}} d\omega\, g(\omega)}_{3N} = 3k_BTN \Rightarrow C = \frac{\partial}{\partial T}\langle E\rangle = 3k_BN$$

To find ω_{cutoff}: $3N = \int_0^{\omega_{cutoff}} d\omega\, g(\omega) = 9N\int_0^{\omega_{cutoff}} d\omega\, \frac{\omega^2}{\omega_d^3} = 3N\frac{\omega_{cutoff}^3}{\omega_d^3} \to \omega_{cutoff} = \omega_d$!

$$\lambda_d = \frac{2\pi}{k_d} = \frac{2\pi}{(\omega_d/v)} = \frac{v\,2\pi}{\omega_d} = \frac{v\,2\pi}{(6\pi^2 n)^{1/3} v} = \frac{2\pi}{(6\pi^2)^{1/3}}\left(\underbrace{\frac{L}{N^{1/3}}}_{\text{interatomic separation}}\right) \quad \because n = \frac{N}{V} = \frac{N}{L^3}$$

Very successful theory. Yet. Problem: linear dispersion $\omega = vk$ does not hold as $\omega \nearrow$; the linear dependence due to electronic contribution missing.

How QMech spoils heat capacity?

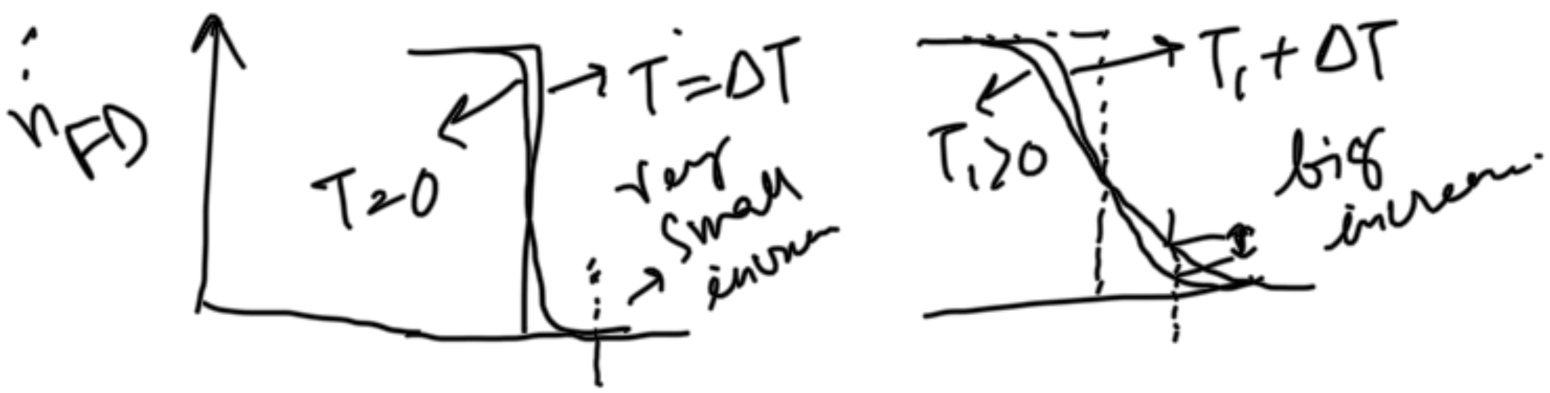


At $T=0$ probability of occupation of state above E_F is zero!

$\Rightarrow$ No excitation possible at $T=0$ $\Rightarrow$ No heat intake!

$\Rightarrow$ $C = \frac{\partial \langle E \rangle}{\partial T} = 0$ since $\Delta \langle E \rangle = 0$

For same increase of temperature ΔT the amount of increase in occupation of states above E_F increases with temperature:



$\Rightarrow$ Heat intake capacity will be lower in lower temperatures.

It will get even lower with increasing value of energies.

$\Rightarrow$ Higher the energy separation lower the heat intake capacity higher the deviation from Dulong Petit Law.

Higher energy separation $\Rightarrow$ higher confinement $\Rightarrow$ stiffer spring (classically)

$\therefore$ lower the temperature and/or higher the confinement higher the deviation.