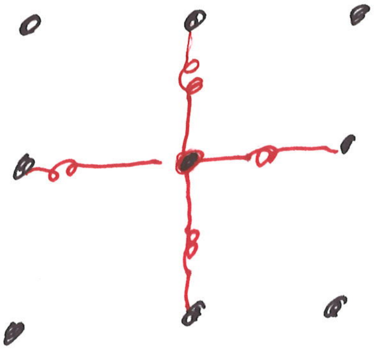
Heat capacity for a crystal

N molecules



"Particle in a cage"

Simple Harmonic Oscillator SHO

3-dimensional

$$\bar{V}(\vec{r}) = V(r) = \bar{V}_0 + \frac{1}{2} k_s r^2 + \dots$$

$$= V_0 + \frac{1}{2} k_s (x^2 + y^2 + z^2)$$

$3N$ 1-dim. SHOs

$$\omega = \sqrt{\frac{k_s}{m}} \Rightarrow k_s = m\omega^2$$

$$E_j = \left(j + \cancel{\tfrac{1}{2}}\right)\hbar\omega$$

Partition function

$$z = \sum_{j=0}^{\infty} e^{-\beta E_j} = \sum_{j=0}^{\infty} e^{-j\beta\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

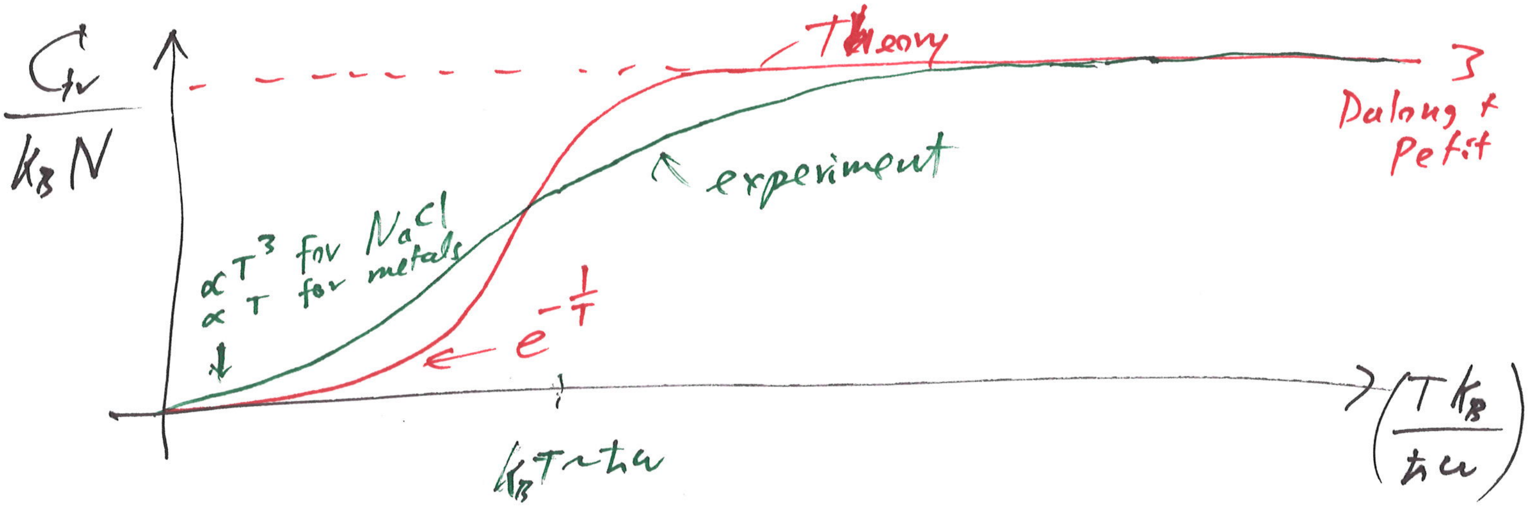
$$Z = z^{3N}$$

$$\ln(z) = -\ln\left(1 - e^{-\beta\hbar\omega}\right) \qquad \ln(Z) = -3N\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

energy $$\epsilon = -\frac{\partial \ln(z)}{\partial \beta} = \frac{+e^{-\beta\hbar\omega}\hbar\omega}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \qquad U = 3N\epsilon$$

$$\beta = \frac{1}{k_B T}$$

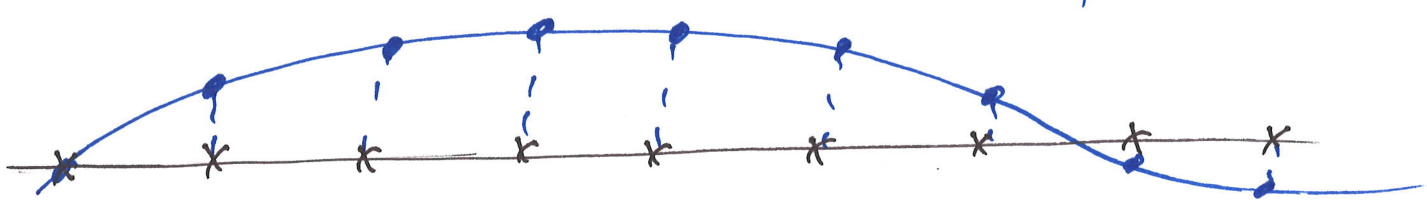
$$c_V = \left(\frac{\partial \epsilon}{\partial T}\right)_{VN} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \left(\frac{1}{e^{\beta\hbar\omega} - 1}\right)^2 e^{\beta\hbar\omega} \qquad C_V = 3N c_V$$



$\propto T^3$ from phonons, $\propto T$ from electrons

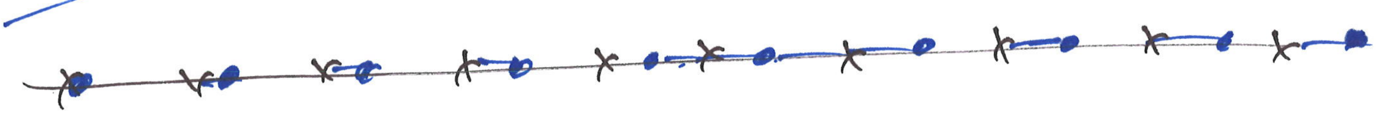
By concentrating on one site in the crystals, we have ignored long-wavelength oscillations.

transverse



Peter Debye

Longitudinal



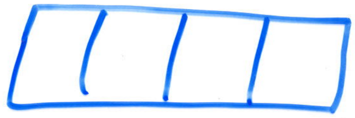
Cf notes for blackbody radiation

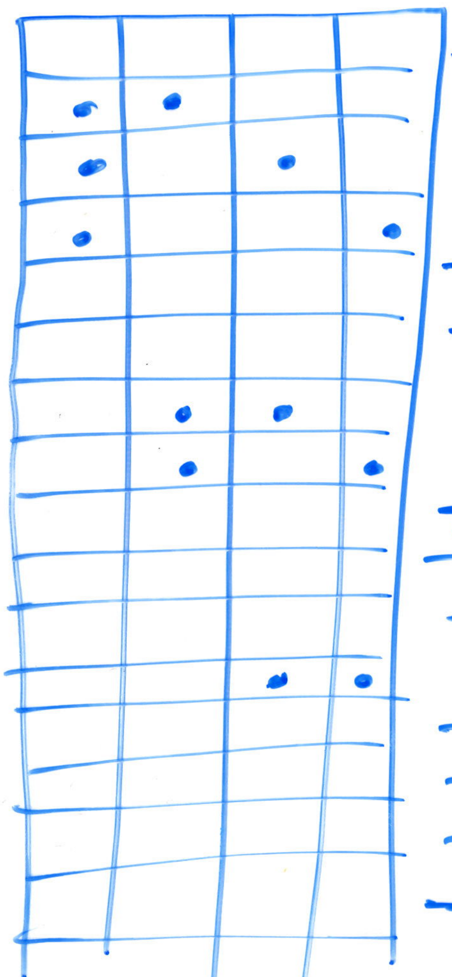
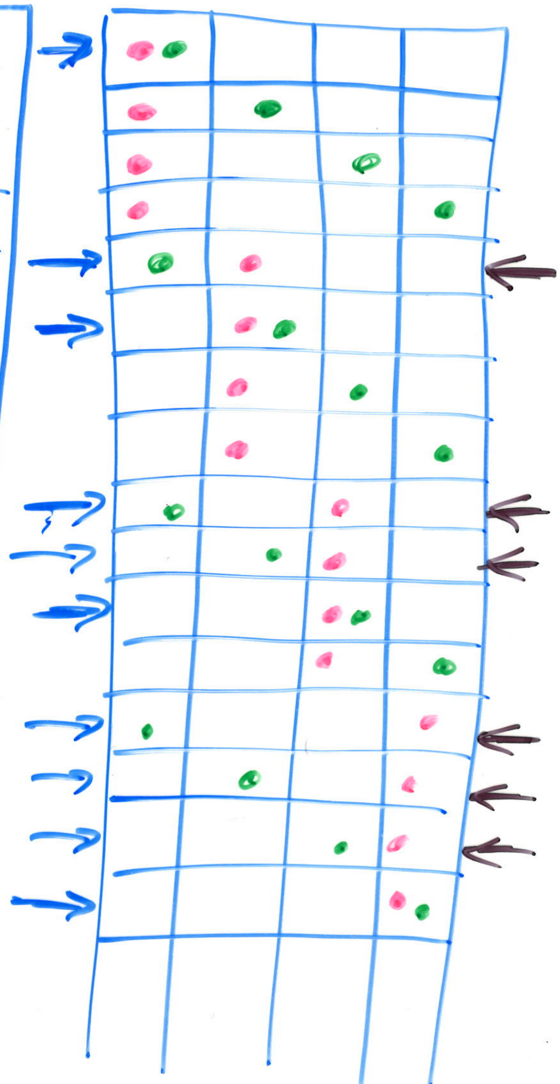
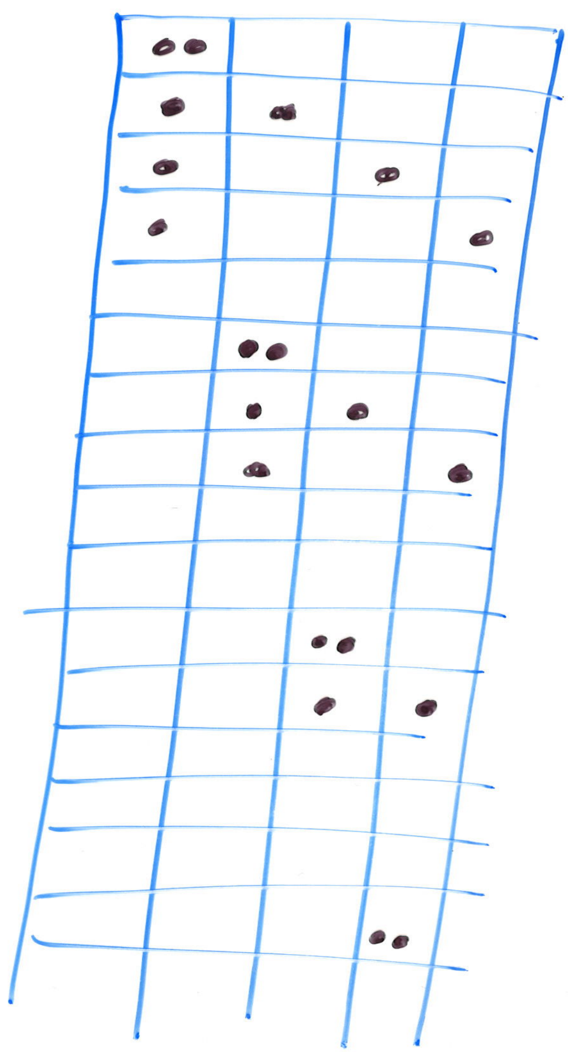
Replace c by v_s (velocity of sound in crystal)

2 polarizations $\rightarrow$ 3 polarization for phonons

$$U \propto T^4, \quad C_v = \frac{dU}{dT} \propto T^3$$

Quantum Statistics

\# Boxes:  M $E = 0$

Indistinguishable Fermions	2 Classical Distinguishable Particles	Indistinguishable Bosons
		
6 states	16 states	10 states
	M^2	

Classical Indistinguishable

$$\frac{M^2}{2!} = 8 \text{ states}$$

cf lecture 11 + 12

$$\frac{S}{k_B} = -N\sum_i p_i \ln(p_i) - \lambda\underbrace{\left(\sum_i p_i - 1\right)}_{\text{unitarity}} - \beta\underbrace{\left(\sum_i p_i E_i - U\right)}_{\text{avg energy}} - \beta\mu\underbrace{\left(\sum_i \nu_i - N_{total}\right)}_{\text{particle number}}$$

$\beta = \frac{1}{k_B T}$

μ is chemical potential

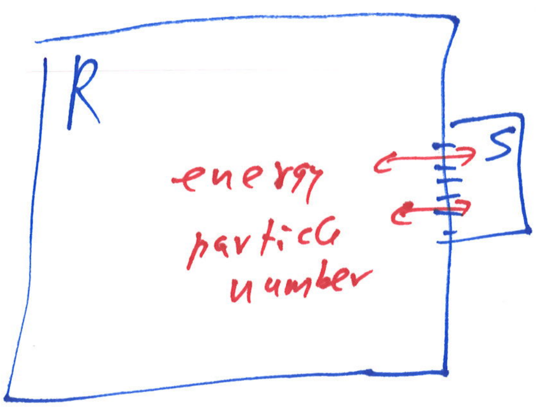
$\mu = \frac{G}{N_{total}}$

Probability that the system state is occupied by n particles

$$P(n) = \frac{e^{-n\beta(\epsilon - \mu)}}{Q}$$

$e^{-n\beta(\epsilon-\mu)}$ ← Gibbs weighting

Q ← grand canonical partition function.



Can put energy into or out of R, and its T temperature will not change

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Can put particles into or out of R, and its μ chemical potential will not change.

$$Q = \sum_{n=0}^{\infty} e^{-n\beta(\epsilon-\mu)}, \qquad Z = \sum_{n=0}^{\infty} e^{-n\beta\epsilon}$$

$$\mathcal{L} = \sum_{n=0}^{\infty} e^{-n\beta H} \quad \text{Gibbs p.f.}$$

$$Q = \sum_{n=0}^{\infty} e^{-n\beta(\epsilon-\mu)}$$

① Fermions, $n = 0$ or 1

$$Q = \underbrace{1}_{n=0} + \underbrace{e^{-\beta(\epsilon-\mu)}}_{n=1}.$$

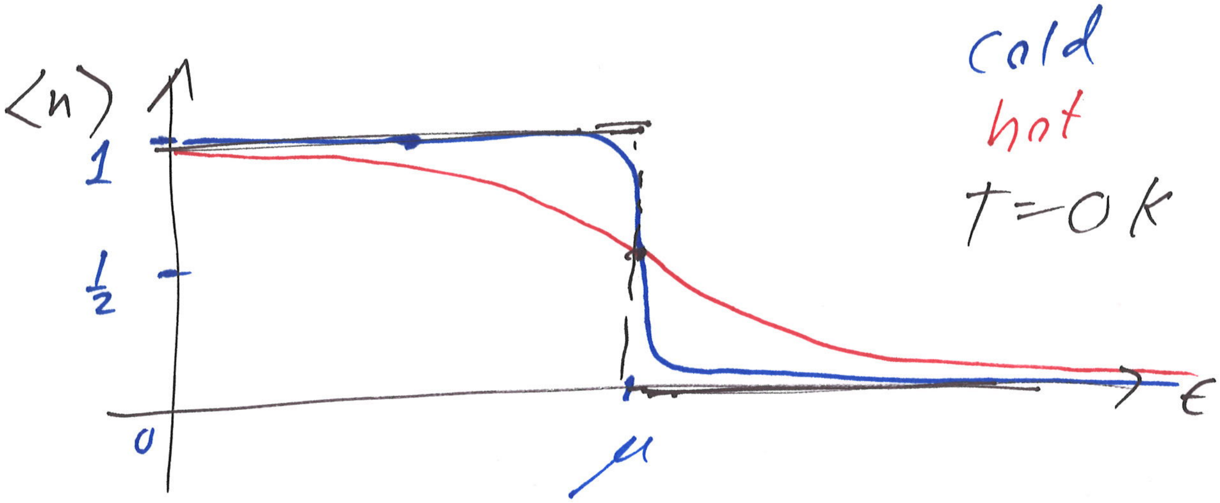
Probability that the state is unoccupied: $P(0) = \dfrac{1}{1+e^{-\beta(\epsilon-\mu)}}$

Prob. that the state is occupied $P(1) = \dfrac{e^{-\beta(\epsilon-\mu)}}{1+e^{-\beta(\epsilon-\mu)}}$

$$\langle n \rangle = \sum_{j=0}^{1} n_j (P_j) = 0\,P(0) + 1\,P(1) = P(1)$$

$$\langle n \rangle = \frac{e^{-\beta(\epsilon-\mu)}}{1+e^{-\beta(\epsilon-\mu)}} \cdot \frac{e^{+\beta(\epsilon-\mu)}}{e^{+\beta(\epsilon-\mu)}} = \frac{1}{e^{+\beta(\epsilon-\mu)}+1}$$

Fermi-Dirac Distribution = occupation number = Average number of particles.



At $T = 0K$ $\quad \mu = \epsilon_{fermi} = k_B T_{fermi}$

Bosons: Any number n can be in the same state.

$$Q = \sum_{n=0}^{\infty} e^{-n\beta(\epsilon-\mu)} \quad \text{geometric series} \quad \frac{1}{1 - e^{-\beta(\epsilon-\mu)}}$$

$$\langle n \rangle = \sum_{j=0}^{\infty} j\, P(j) = 0\, P(0) + 1\, P(1) + 2\, P(2) + \cdots$$

$$\frac{\sum_{j=0}^{\infty} j e^{-j\beta(\epsilon-\mu)}}{Q} = \frac{\sum_{j=0}^{\infty} j e^{-j\beta(\epsilon-\mu)}}{\sum_{k=0}^{\infty} e^{-k\beta(\epsilon-\mu)}}$$

Define $\gamma = \beta(\epsilon - \mu)$

$$\sum_{j=0}^{\infty} j e^{-jr} = -\frac{\partial}{\partial r}\left(\sum_{j=0}^{\infty} e^{-jr}\right) = -\frac{\partial}{\partial r}(Q)$$

$$\langle n \rangle = \frac{-\frac{\partial}{\partial r} Q}{Q} = -\frac{\partial}{\partial r} \ln Q \quad , \quad Q = \frac{1}{1-e^{-r}}$$

$$\langle n \rangle = -\frac{\partial}{\partial r} \ln\left[\frac{1}{1-e^{-r}}\right] = +\frac{\partial}{\partial r}\ln\left[1-e^{-r}\right]$$

$$= \frac{+e^{-r}}{1-e^{-r}} \cdot \left(\frac{e^{+r}}{e^{+r}}\right) = \frac{1}{e^{+r}-1} = \frac{1}{e^{+\beta(\epsilon-\mu)}-1}$$

Bose-Einstein distribution.

Planck Distribution $(\mu=0)$ $\frac{1}{e^{+\beta\epsilon}-1}$

Boltzmann: $\frac{1}{e^{+\beta\epsilon}} = e^{-\beta\epsilon}$ Classical Limit

Fermi-Dirac: $\frac{1}{e^{+\beta(\epsilon-\mu)}+1}$