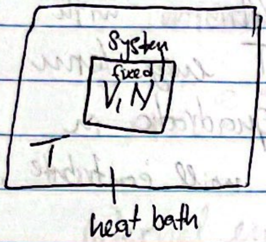
Equillibrium system in heat bath



prob. of state r

$$p_r \propto \Omega_{bath}(E_0 - E_r) \quad , E_r \ll E_0$$

$$\ln(\Omega_{bath}(E_0 - E_r)) \approx \ln(\Omega_{bath}(E_0)) - \left(\frac{\partial \ln(\Omega_b(E_0))}{\partial E}\right)_{E_0} E_r + \frac{1}{2}\left(\frac{\partial^2 \ln(\Omega_b(E_0))}{\partial E^2}\right)_{E_0} E_r^2 \text{ [illegible]}$$

$$\boxed{k_B \ln(\Omega_b) = S}$$

$$= \underbrace{\frac{1}{k} S_{bath}(E_0)}_{C} - \frac{1}{k}\overbrace{\left(\frac{\partial S_{bath}(E_0)}{\partial E}\right)_{E_0}}^{1/T} E_r + \frac{1}{2}\frac{1}{k}\left(\frac{\partial}{\partial E}\underbrace{\frac{\partial S(E_0)}{\partial E}}_{1/T}\right)_{E_0} E_r^2 +$$

$$\left(\frac{\partial}{\partial E}\, 1/T\right) = 0$$

$$\Rightarrow \ln \Omega_{bath}(E_0 - E_r) \approx C - \frac{E_r}{kT}$$

$$\Rightarrow \Omega_{bath}(E_0 - E_r) \approx C' e^{-E_r/kT}$$

$$p_r \propto \Omega_{bath}(E_0 - E_r) \Rightarrow p_r = C'' e^{-E_r/k_BT}$$

find using normalisation

$$\sum_{\text{all states}} p_r = 1 = \sum_{\text{all states}} C'' e^{-E_r/k_BT} \qquad 1/kT = \beta$$

$$\Rightarrow C'' = \frac{1}{Z}, \text{ where } Z = \sum_{\text{all states}} e^{-E_r/\boxed{kT}}$$

↳ partition function

prob. of system with energy E_r:

$$p(E_r) = g(E_r)\,\frac{e^{-\beta E_r}}{Z} \qquad \leftarrow \text{degeneracy}$$

$$Z = \sum_{\text{different energies}} g(E_r)\, e^{-\beta E_r}$$

$$p(x)\,dx = \frac{e^{-\beta E(x)}}{Z}\,dx \Rightarrow Z = \int e^{-\beta E(x)}\,dx$$

Equipartition theorem

- quadratic dependence of energy: $E(x) = \alpha x^2$

e.g. spring motion : $E(x) = \frac{1}{2}kx^2$

rotational -"- : $E(\omega) = \frac{1}{2}I\omega^2 = \frac{1}{2}\frac{L^2}{I}$

Mean energy

$$\langle E \rangle = \int_{-\infty}^{\infty} p(x)\,E(x)\,dx = \int_{-\infty}^{\infty} \frac{e^{-\beta\alpha x^2}}{Z}\,\alpha x^2\,dx =$$

$$x = \frac{y}{\sqrt{\beta}} \quad dx = \frac{dy}{\sqrt{\beta}}$$

$$= \frac{\int_{-\infty}^{\infty} e^{-\beta\alpha x^2}\,\boxed{\alpha x^2}\,dx}{\int_{-\infty}^{\infty} e^{-\beta\alpha x^2}\,dx} = -\frac{\partial}{\partial\beta}\ln\left[\int_{-\infty}^{\infty} e^{-\beta\alpha x^2}\,dx\right] =$$

$$= -\frac{\partial}{\partial\beta}\ln\left[\frac{1}{\sqrt{\beta}}\int_{-\infty}^{\infty} e^{-\alpha y^2}\,dy\right] = -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{1}{\sqrt{\beta}}\right) + \ln\left(\int_{-\infty}^{\infty} e^{-\alpha y^2}\,dy\right)\right]$$

$\ln(ab) = \ln(a) + \ln(b)$

$\frac{\partial}{\partial\beta} = 0$ indep. of β

$$= -\sqrt{\beta}\,\frac{1}{\cancel{\quad}\,2\,\beta^{3/2}} = \frac{1}{2\beta} = \frac{1}{2}k_BT$$

Equipartition Thm:

For a classical system in equilibrium with a heat bath at temperature T every term in the Hamiltonian (energy) that is quadratic in one of the ~~systems~~ indep. coordinate systems will contribute $\frac{1}{2}kT$ to mean energy

$E(x) = \alpha x^2 \Rightarrow \langle E\rangle = \frac{1}{2}k_BT$ per indep. term

suppose dep. on x_i can be separated

$$E = E(x_1, \dots, x_{3N}, p_1, \dots, p_{3N})$$

$$E = E(x_i) + E'(\text{—"— w/o } x_i)$$

$$\langle E(x_i)\rangle = \frac{\int E(x_i)e^{-\beta(E(x_i)+E')}dx\dots dp\dots}{\int e^{-\beta(E(x_i)+E')}dx\dots dp\dots} =$$

$$= \frac{\int E(x_i)e^{-\beta E(x_i)}dx_i \int e^{-\beta E'}dx\dots dp\dots}{\int e^{-\beta E(x_i)}dx_i \int e^{-\beta E'}dx\dots dp\dots}$$

$$= \frac{\int E(x_i)e^{-\beta E(x_i)}dx_i}{\int e^{-\beta E(x_i)}dx_i} \Rightarrow \frac{1}{2}kT$$

Monoatomic gas - N atoms

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \Rightarrow 3 \text{ terms with quadratic dep.}$$

$$\Rightarrow \langle E\rangle = N\times\left(\frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT\right) = \frac{3}{2}NkT$$

Heat capacity $C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{3}{2}Nk = \frac{3}{2}nR = n\cdot 12.47\,JK^{-1}$

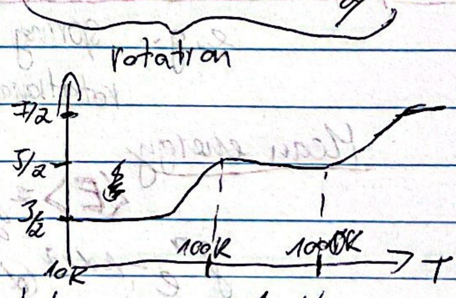
Diatomic gas

neglect → small

$$E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{translation}} + \underbrace{\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 + \cancel{\frac{1}{2}I_3\omega_3^2}}_{\text{rotation}} + \underbrace{\frac{1}{2}\mu v^2 + \frac{1}{2}k}_{\text{vibrations}}$$

$$\Rightarrow \langle E\rangle = \frac{7}{2}NkT$$

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{7}{2}nR$$



Atomic excitation energies
- rotation: 10^{-1} eV
- vibration: 10^0 eV
- atomic excitations: 10^1+ eV

Solids

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \underbrace{\frac{1}{2}k_1x^2 + \frac{1}{2}k_2y^2 + \frac{1}{2}k_3z^2}_{\text{vibration}} \Rightarrow \langle E\rangle = 3k_BT\,N$$

$= 24.94n$

$C_V = 3nR$

Boltzmann distribution

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

- microstate r with energy E_r

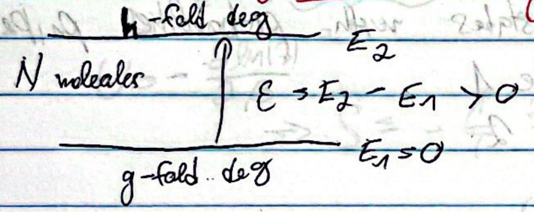
$$p_r = \frac{e^{-\beta E_r}}{Z}, \quad Z = \sum_r e^{-\beta E_r}, \quad \sum_r p_r = 1$$

internal energy $U = \langle E \rangle = \sum_r p_r E_r = \sum_r \frac{e^{-\beta E_r}}{Z} E_r =$

$$= \frac{1}{\sum_r e^{-\beta E_r}} \sum_r E_r e^{-\beta E_r} = -\frac{\partial}{\partial \beta} \ln\left(\sum_r e^{-\beta E_r}\right) = -\frac{\partial \ln Z}{\partial \beta}$$

$$\Rightarrow \boxed{U = -\frac{\partial \ln Z}{\partial \beta}}$$

Two-level system with degeneracies



$U = ?$ < microcanonical (Ω)
canonical (Boltzmann)

Using microcanonical ensemble

$$\Omega(n) = h^n g^{N-n} \frac{N!}{n!(N-n)!}$$ } distributing N particles into 2 groups

n molecules in excited

$U = n\varepsilon + (N-n)\cdot 0$ $\quad S = k\ln(\Omega)$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial n}\frac{\partial n}{\partial U} = \frac{\partial S}{\partial n}\frac{1}{\varepsilon} = \frac{k}{\varepsilon}\frac{\partial \ln(\Omega)}{\partial n}$$

$$\ln(\Omega) = n\ln(h) + (N-n)\ln(g) + \ln(N!) - \ln(n!) - \ln((N-n)!)$$

$\ln(N!) \approx N\ln(N) - N$

$$\approx n\ln(h) + (N-n)\ln(g) + N\ln(N) - \cancel{N} - n\ln(n) + n - (N-n)\ln(N-n) + \cancel{N-n}$$

$$\frac{\partial \ln(\Omega)}{\partial n} = \ln(h) - \ln(g) - \ln(n) - 1 + 1 + \ln(N-n) =$$

$$= \ln(h) - \ln(g) - \ln(n) + \ln(N-n) = \ln\left(\frac{h}{g}\frac{N-n}{n}\right)$$

$$\Rightarrow \frac{1}{T} = \frac{k}{\varepsilon}\frac{\partial \ln(\Omega)}{\partial n} = \frac{k}{\varepsilon}\ln\left(\frac{h}{g}\frac{N-n}{n}\right) = \frac{k}{\varepsilon}\ln\left(\frac{h}{g}\frac{N\varepsilon - n\varepsilon}{n\varepsilon}\right) = \frac{k}{\varepsilon}\ln\left(\frac{h}{g}\frac{N\varepsilon - U}{U}\right)$$

$$\Rightarrow U = \frac{N\varepsilon}{1 + \frac{g}{h} e^{\varepsilon / k_B T}}$$

Using canonical ensemble - partition function

- for 1 molecule:

$$Z_1 = \sum_r e^{-\beta E_r} = \underset{\text{degeneracy}}{g} e^{-\beta \cdot 0} + \underset{}{h} e^{-\beta \varepsilon} = g + h e^{-\beta \varepsilon}$$

$$U_1 = -\frac{\partial \ln Z_1}{\partial \beta} = -\frac{\partial \ln(g + h e^{-\beta \varepsilon})}{\partial \beta} = -\frac{h e^{-\beta \varepsilon} \cdot (-\varepsilon)}{g + h e^{-\beta \varepsilon}} =$$

$$= \frac{\varepsilon}{1 + \frac{g}{h} e^{\beta \varepsilon}}$$

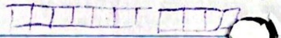
$$\Rightarrow \boxed{U = N U_1 = \frac{N \varepsilon}{1 + \frac{g}{h} e^{\beta \varepsilon}}}$$

Distribution of coloured marbles

- 10 marbles (2y, 3b, 5r)

$$\Rightarrow \Omega = \frac{10!}{\underset{\text{deg}}{5!\,2!\,3!}}$$

← 10! ways of putting them in a row



N copies of same system

each with 1, 2, ..., r states with probabilities $p_1, p_2, \dots, p_r$

$p_1 \cdot N$ systems in state 1

$p_2 \cdot N$ — " — 2

⋮

$$\Omega_N = \frac{N!}{(p_1 N)!\,(p_2 N)! \cdots (p_r N)!}$$

$$\begin{aligned}
\ln(\Omega_N) &= \ln(N!) - \ln((p_1 N)!) - \dots - \ln((p_r N)!) \\
&= N \cdot \ln(N) - N - p_1 N \ln(p_1 N) + p_1 N - \dots \\
&= N \cdot \ln(N) - N - p_1 N \ln(N) - p_1 N \ln(p_1) + p_1 N - \dots \\
&= N \cdot \ln(N) - N + N(p_1 + \dots + p_r) - (p_1 + \dots + p_r) N \ln(N) - N(p_1 \ln(p_1) + \dots) \\
&= N \cdot \ln(N) - N + N \underbrace{\sum_r p_i}_{=1} - N \cdot \ln(N) \underbrace{\sum_i p_i}_{=1} - N \sum_i p_i \ln(p_i) \\
&= -N \sum_i p_i \ln(p_i)
\end{aligned}$$

$$\ln(\Omega_N) = -N \sum_r p_r \ln(p_r)$$

$$S_N = k \ln(\Omega_N) = -kN \sum_r p_r \ln(p_r)$$

$\Rightarrow$ for 1 system $S_1 = \frac{S_N}{N} = -k \sum_r p_r \ln(p_r)$

Microcanonical ensemble

↗ all states have same probability ⇓

$$\overset{p_r = \frac{1}{\Omega}}{S = -k \sum_r^{\Omega} p_r \ln(p_r)} = -k \sum_r^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = +\frac{k}{\Omega} \sum_r^{\Omega} \ln(\Omega) =$$

$$= \frac{k}{\Omega} \cdot \Omega \ln(\Omega) = k \ln(\Omega)$$

Boltzmann distribution

$$p_r = \frac{e^{-\beta E_r}}{Z}$$

upda

$$S = -k \sum_r p_r \ln(p_r) = -k \sum_r \frac{e^{-\beta E_r}}{Z} \ln\left(\frac{e^{-\beta E_r}}{Z}\right) =$$

$$= -k \sum_r \frac{e^{-\beta E_r}}{Z} \left(-\beta E_r \ln(e) - \ln(Z)\right) = k \sum_r \left[\beta E_r \frac{e^{-\beta E_r}}{Z} + \ln(Z) \frac{e^{-\beta E_r}}{Z}\right.$$

$$= k\beta \underbrace{\sum_r E_r \frac{e^{-\beta E_r}}{Z}}_{= U} + k\ln(Z) \overbrace{\sum_r p_r}^{=1} = k\beta U + k\ln(Z) = \frac{U}{T} + k\ln(Z)$$

$$U = -\frac{\partial \ln(Z)}{\partial \beta}$$

$$\Rightarrow S = -\frac{1}{T} \frac{\partial \ln(Z)}{\partial \beta} + k\ln(Z) = -k\beta \frac{\partial \ln(Z)}{\partial \beta} + k\ln(Z) =$$

$$= -k\beta^2 \left(-\frac{1}{\beta^2} \ln(Z) + \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial \beta}\right) =$$

$$\boxed{S = -k\beta^2 \frac{\partial}{\partial \beta}\left(\frac{1}{\beta} \ln(Z)\right)}$$

Helmholtz free energy

$$TS = U + kT \ln Z$$

$$\boxed{F = U - TS \overset{\downarrow}{=} -kT \ln(Z)}$$

Fluctuations

↙ equal if fluctuations are very small

variation in $U = \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

$$\sigma_U^2 = \langle E^2 \rangle - \langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle \left(-\frac{\partial \ln Z}{\partial \beta}\right) =$$

$$= \langle E^2 \rangle + \sum_r \frac{E_r e^{-\beta E_r}}{Z} \cdot \underbrace{\frac{1}{Z}}_{\frac{\partial \ln Z}{\partial Z}} \frac{\partial Z}{\partial \beta} =$$

$$= \langle E^2 \rangle - \left(\sum_r E_r e^{-\beta E_r} \cdot \underbrace{\left(-\frac{1}{Z^2} \frac{\partial Z}{\partial \beta}\right)}_{= \left(\frac{\partial 1/Z}{\partial \beta}\right)}\right) =$$

$$= \sum_r \underbrace{E_r^2 \frac{e^{-\beta E_r}}{Z}}_{\frac{\partial e^{-\beta E_r}}{\partial \beta}} - \sum_r \underbrace{E_r e^{-\beta E_r} \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\right)}_{\frac{\partial}{\partial \beta} \frac{1}{Z}}$$

①

$$= -\frac{\partial}{\partial \beta} \underbrace{\left(\sum_r E_r \frac{e^{-\beta E_r}}{Z}\right)}_{\langle E \rangle} = -\frac{\partial}{\partial \beta} \langle E \rangle = -\frac{\partial^2 \ln(Z)}{\partial \beta^2} = kT^2 C_V$$

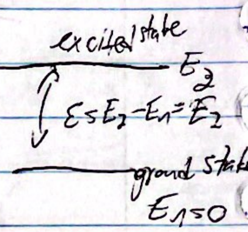
$$-\frac{\partial \langle E \rangle}{\partial T} \overset{!!}{\frac{\partial T}{\partial \beta}} = -\frac{\partial \langle E \rangle}{\partial T} \frac{\partial \left(\frac{1}{k\beta}\right)}{\partial \beta} = \frac{1}{k\beta^2} \frac{\partial U}{\partial T}$$

$$\boxed{\sigma_U^2 = kT^2 C_V}$$

$$\frac{\sigma_U}{U} = \frac{\sqrt{\overbrace{kT^2}^{\text{indep. of } N} C_V}^{\propto N}}{\underbrace{U}_{\propto N}} \propto \frac{\sqrt{N}}{N} = \frac{1}{\underbrace{\sqrt{N}}_{\sim 10^{23} \text{ macroscopic}}} \approx 10^{-11}$$

⇒ fluctuations in the energy of macroscopic system are very small

Two level system

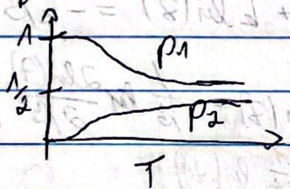


$$Z = \sum e^{-\beta E_r} = e^{-\beta E_1} + e^{-\beta E_2} = 1 + e^{-\beta\varepsilon}$$

$$\boxed{\begin{aligned} p_1 &= \frac{e^{-\beta E_1}}{Z} = \frac{1}{1+e^{-\beta\varepsilon}} \\ p_2 &= \frac{e^{-\beta E_2}}{Z} = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \end{aligned}}$$

$T \to 0 \Leftrightarrow \beta \to \infty \Rightarrow p_1 \to 1,\ p_2 \to 0$ — system in ground state

$T \to \infty \Leftrightarrow \beta \to 0 \Rightarrow p_1 \to \frac{1}{2},\ p_2 \to \frac{1}{2}$ — equal prob.



internal energy $U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln(1+e^{-\beta\varepsilon})}{\partial \beta} = \frac{\varepsilon e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{\varepsilon}{e^{\beta\varepsilon}+1}$

$T \to 0 \Leftrightarrow \beta \to \infty \Rightarrow U \to 0$

$T \to \infty \Leftrightarrow \beta \to 0 \Rightarrow U \to \frac{\varepsilon}{2}$

heat capacity $C_V = +\frac{\partial U}{\partial T} = \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}\frac{\partial U}{\partial \beta} = +\frac{1}{kT^2}\frac{\varepsilon^2 e^{\beta\varepsilon}}{(1+e^{\beta\varepsilon})^2} =$

$$= k\frac{x^2 e^x}{(1+e^x)^2} \quad ; \quad x = \beta\varepsilon = \frac{\varepsilon}{kT}$$

$T \to 0 \Leftrightarrow \beta \to \infty \Leftrightarrow x \to \infty \Rightarrow C_V \to 0$

$T \to \infty \Leftrightarrow \beta \to 0 \Leftrightarrow x \to 0 \Rightarrow C_V \to 0$

} max in between

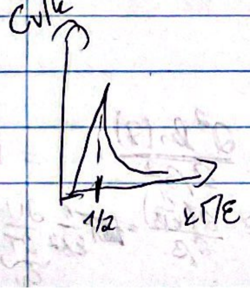
max? $\frac{\partial C_V}{\partial x} = \frac{(2xe^x + x^2e^x)(1+e^x)^2 - x^2e^x\,2(1+e^x)e^x}{(1+e^x)^{3}} = 0$

$$2xe^x + x^2e^x + 2xe^{2x} + x^2e^{2x} - 2x^2e^{2x} = 0$$

$$e^x 2(1+e^x) + x(1 - e^x) = 0$$

$$2 + x + 2e^x - xe^x = 0 \Rightarrow e^x = \frac{x+2}{x-2} \Rightarrow x \approx 2.4$$

$$x = \frac{\varepsilon}{kT} \Rightarrow \boxed{kT \approx \frac{\varepsilon}{2.4}}$$



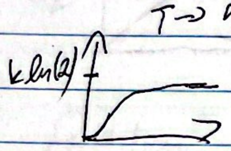
entropy $$S = \frac{U-F}{T} = \frac{U+kT\ln(Z)}{T} = \frac{1}{T}\frac{\varepsilon}{1+e^{\beta\varepsilon}} + k\ln(1+e^{-\beta\varepsilon})$$

$$= k\frac{x}{1+e^{x}} + k\ln(1+e^{-x})$$

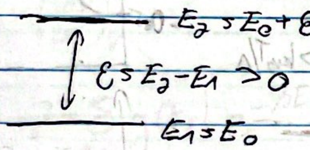
$x \equiv \beta\varepsilon = \frac{\varepsilon}{kT}$

$T \to 0 \Leftrightarrow \beta \to \infty \Leftrightarrow x \to \infty$; $S \to 0$

$T \to \infty \Leftrightarrow \beta \to 0 \Leftrightarrow x \to 0$; $S \to k\ln(2)$



Two-level system



$$U(E_0=0) = \frac{\varepsilon}{1+e^{\beta\varepsilon}}$$

$$\boxed{Z = \sum_r e^{-\beta E_r} = e^{-\beta E_1} + e^{-\beta E_2} = e^{-\beta(E_0)} + e^{-\beta(E_0+\varepsilon)} = e^{-\beta E_0}(1+e^{-\beta\varepsilon})} = e^{-\beta E_0}\cdot Z(E_0=0)$$

$$\boxed{U = -\frac{\partial \ln Z}{\partial\beta} = E_0 + U(E_0=0)} = -\frac{\partial\ln(e^{-\beta E_0}(1+e^{-\beta\varepsilon}))}{\partial\beta} = E_0 + \frac{\varepsilon e^{-\beta E_0}}{1+e^{-\beta E_0}} = E_0 + \underbrace{\frac{\varepsilon}{e^{\beta\varepsilon}+1}}_{U(E_0=0)} =$$

$$\boxed{F = -kT\ln(Z) = E_0 - kT\ln(1+e^{-\beta\varepsilon}) = E_0 + F(E_0=0)}$$

$$\boxed{S = \frac{U-F}{T} = \frac{E_0+U(E_0=0) - E_0 - F(E_0=0)}{T} = \frac{U(E_0=0)-F(E_0=0)}{T} = S(E_0=0)}$$

1D quantum oscillator

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2$$

$$H\Psi = E\Psi \Rightarrow E_n = \hbar\omega(n+\tfrac{1}{2})$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

$t = e^{-\beta\hbar\omega}$

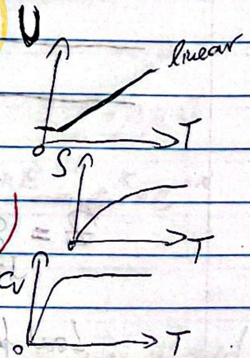
$$\Rightarrow \boxed{Z} = \sqrt{t}\underbrace{\sum_{n=0}^{\infty} t^n}_{\text{geoseries}} = \sqrt{t}\frac{1}{1-t} = \boxed{\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}}$$

$$\Rightarrow U = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$$

$$F = \frac{\hbar\omega}{2} + k_BT\ln(1-e^{-\beta\hbar\omega})$$

$$S = k_B\left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln(1-e^{-\beta\hbar\omega})\right)$$

$$C_V = k_B(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$



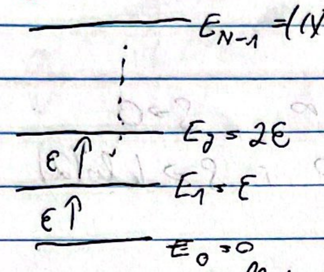
if infinite ladder and $k_BT \gg \hbar\omega$ $\Rightarrow$ $\langle E\rangle$ rises linearly w/ T $\Rightarrow \frac{d\langle E\rangle}{dT} = \text{const}$

$\Rightarrow$ equipartition thm ✓

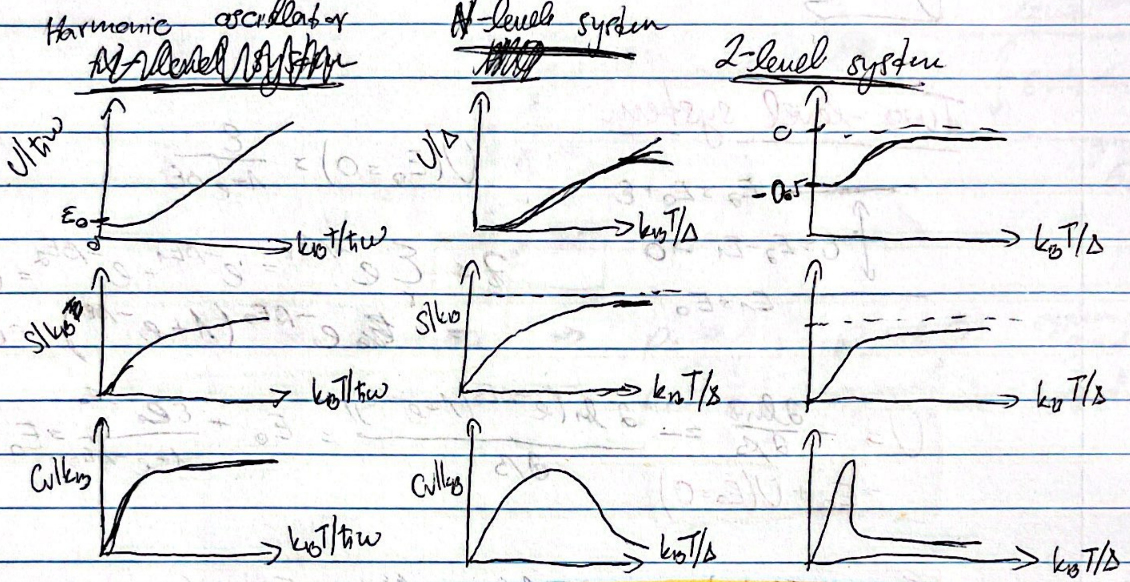
$T \to \infty$, $\beta \to 0$, $S \to -k\ln(\beta\hbar\omega) = k\ln(\frac{1}{\hbar\omega\beta}) = k\ln\underbrace{\left(\frac{k_BT}{\hbar\omega}\right)}_{\sim \#\text{occupied levels}}$

$C_V \to k$

System with N equidistant levels , $E_n = n\mathcal{E}$, $n = 0, \dots, N-1$

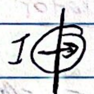


$$\boxed{Z = \sum_{n=0}^{N-1} e^{-\beta E_n} = \sum_{n=0}^{N-1} e^{-\beta n \mathcal{E}} = \underbrace{\sum_{n=0}^{N-1} \left(e^{-\beta\mathcal{E}}\right)^n}_{\text{finite geo series}} \Rightarrow = \frac{1-e^{-N\beta\mathcal{E}}}{1-e^{-\beta\mathcal{E}}}}$$

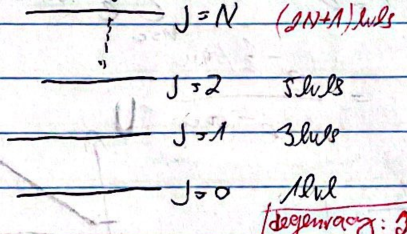


- if $k_BT \ll \Delta E$ between ground & 1st excited ⇒ system in ground state
- finite E-levels and $k_BT \gg \Delta E$ lowest & highest ⇒ each level with same prob.
- infinite E-levels and $k_BT \gg \Delta E$ adjacent lvls ⇒ $\langle E\rangle \propto T$

Rotational energy levels



$E_J = \frac{\hbar^2}{2I} J(J+1)$



$\boxed{\text{degeneracy: } 2J+1}$

$\vec{J}^2 |J, m\rangle = \hbar^2 J(J+1) |J, m\rangle$

$J_z |J, m\rangle = m |J, m\rangle$

$m = -J, -J+1, \dots, 0, \dots J-1, J$

$$Z = \sum_{J=0}^{\infty} (2J+1) e^{-\beta E_J} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\beta\hbar^2}{2I} J(J+1)}$$ ⇒ no closed solution

Low temperature : take only J = 0, 1 ⇒ $Z \approx 1 + 3e^{-\frac{\beta\hbar^2}{2I}}$

High temperature : $\frac{\beta\hbar^2}{2I} \to$ small ⇒ $\sum \Rightarrow \int_0$ ⇒ $Z \approx \frac{2I}{\beta\hbar^2}$

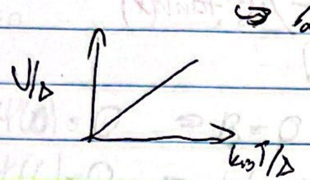
$$Z \approx \int_0^{\infty} (2J+1) e^{-\frac{\beta\hbar^2}{2I} J(J+1)} dJ = \left|\alpha = \frac{\beta\hbar^2}{2I}\right| = \int_0^{\infty} (2J+1) e^{-\alpha J(J+1)} dJ =$$

$$= -\frac{1}{\alpha} \int_0^{\infty} \frac{\partial}{\partial J}\left(e^{-\alpha J(J+1)}\right) dJ = -\frac{1}{\alpha} e^{-\alpha J(J+1)}\Big|_0^{\infty} = \frac{1}{\alpha} = \frac{2I}{\beta\hbar^2}$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln\left(\frac{2I}{\beta\hbar^2}\right) = -\frac{\partial}{\partial \beta}\left[\ln\left(\frac{2I}{\hbar^2}\right) - \ln(\beta)\right] = \frac{1}{\beta}$$

$$U = kT = \frac{1}{2}kT + \frac{1}{2}kT$$

$\Rightarrow$ 2 degrees of freedom by equipartition theorem



Partition function - summary

$$U = -\frac{\partial \ln(Z)}{\partial \beta} \qquad F = -kT\ln(Z) \qquad S = \frac{U-F}{T}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$Z = \sum_{E_r} g(E_r)\, e^{-\beta E_r} \qquad Z = \int g_E(E)\, e^{-\beta E}\, dE$$

sum over different E_r ↗ ↑ degeneracy

$$Z = \int g_x(x)\, e^{-\beta E(x)}\, dx$$

↖ can be anything which E depends on, p, ω, k, ..

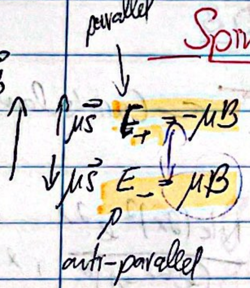
Combining Z's

$$E_{ijk}^{tot} = E_i^{trans} + E_j^{vib} + E_k^{rot}$$

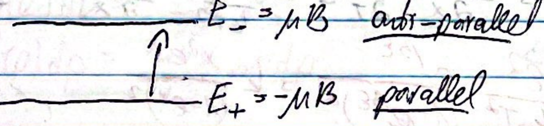
$$\Rightarrow Z^{tot} = \sum_{ijk} e^{-\beta E_i^{trans}} e^{-\beta E_j^{vib}} e^{-\beta E_k^{rot}} = \sum_i e^{-\beta E_i^{trans}} \sum_j e^{-\beta E_j^{vib}} \sum_k e^{-\beta E_k^{rot}} = Z^{trans} Z^{vib} Z^{rot}$$

$$\Rightarrow Z^{tot} = Z^{trans} Z^{vib} Z^{rot}$$

Spin 1/2 in a magnetic field B

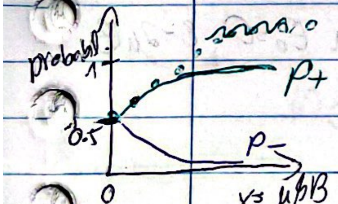


- paramagnetic moment $\boxed{\vec{m} = \mu_B \vec{S}}$, $\mu_B = \frac{e\hbar}{2m}$ = Bohr magneton
- spins align parallel or anti-parallel
- interaction energy of magnetic moment $\boxed{E = -\vec{m}\cdot\vec{B}}$



$x = \beta\mu B$

$$Z_1 = \sum_{r=+,-} e^{-\beta E_r} = e^{-\beta E_+} + e^{-\beta E_-} = e^{\beta\mu B} + e^{-\beta\mu B} = e^{x} + e^{-x}$$



$$p_+ = \frac{e^x}{e^x + e^{-x}}, \quad p_- = \frac{e^{-x}}{e^x + e^{-x}}$$

$x = \mu\beta B$

$x = \frac{\mu B}{kT}$

$T \to 0$, $x \to \infty$ $\Rightarrow$ $p_+ \to 1$, $p_- \to 0$ $\Rightarrow$ spins aligned

$T \to \infty$, $x \to 0$ $\Rightarrow$ $p_+ \to \frac{1}{2}$, $p_- \to \frac{1}{2}$ $\Rightarrow$ both equally possible

dominant at low T

$F = U - TS$ { ..↑↑↑↑↑↑.. - lowest energy (aligned w/ field) but only 1 microstate ⇒ low entropy

balance between U and TS ↙ dominant at high temp $\vec{B}$↑ { ..↓↑↓↑↓↑↓↑.. - higher energy but many microstates

$$\langle E_1\rangle = p_+E_+ + p_-E_- = \frac{e^x}{e^x+e^{-x}}(-\mu B) + \frac{e^{-x}}{e^x+e^{-x}}\mu B =$$
$$= -\mu B\frac{e^x-e^{-x}}{e^x+e^{-x}} \Rightarrow \langle E_1\rangle = -\mu B\tanh(x)$$

$$\langle m_1\rangle = p_+\mu + p_-(-\mu) = \mu\tanh(x)$$

System of N non-interacting spins

$$\boxed{Z_N = Z_1^N} \Rightarrow \ln(Z_N) = N\ln(Z_1)$$
$$\langle E_N\rangle = -\frac{\partial\ln(Z_N)}{\partial\beta} = -N\frac{\partial\ln(Z_1)}{\partial\beta} = N\langle E_1\rangle$$
$$\Rightarrow \langle E_N\rangle = -N\mu B\tanh x$$

$$dU = \text{đ}Q + \text{đ}W$$
$$dU = TdS - mdB$$ ← supplied to magnetic moment m

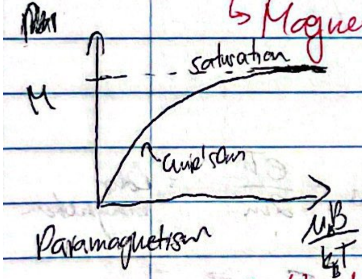
$$dF = dU - TdS - SdT = -SdT - mdB$$

$$\boxed{m = -\left(\frac{\partial F}{\partial B}\right)_T}$$

For 1 spin: $\langle m_1\rangle = -\left(\frac{\partial F_1}{\partial B}\right)_T \overset{\boxed{F=-kT\ln(Z)}}{=} kT\left(\frac{\partial\ln(Z_1)}{\partial\beta}\right)$

For N spins: $\langle m_N\rangle = -\left(\frac{\partial F_N}{\partial B}\right)_T \underset{F_N=-kT\ln(Z_1^N)}{=} kTN\frac{\partial\ln(Z_1)}{\partial\beta} = N\langle m_1\rangle$

↳ Magnetization $\boxed{M = \frac{\langle m_N\rangle}{V} = \frac{N}{V}\langle m_1\rangle = \frac{N}{V}\mu_B\tanh(x) = \frac{N}{V}\mu_B\tanh\left(\frac{\mu_B B}{k_B T}\right)}$



Paramagnetism

- for small B or large T: $x \to 0 \Rightarrow \tanh x \to x$

$$\Rightarrow M \approx \frac{N}{V}\mu_B x = \frac{N\mu_B^2}{Vk_B}\frac{B}{T}$$ ← Curie's law

- for large B or small T: $x \to \infty, \tanh x \approx 1$

$$\Rightarrow M \approx \frac{N}{V}\mu_B$$

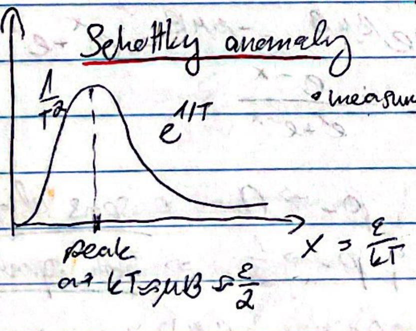
↳ Heat capacity

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial\langle E_N\rangle}{\partial x}\frac{\partial x}{\partial T} = -\frac{\mu B}{kT^2}\frac{\partial\langle E_N\rangle}{\partial x} = \frac{Nk(2x)^2e^{2x}}{(e^{2x}+1)^2}, \quad x = \frac{\mu B}{kT}$$

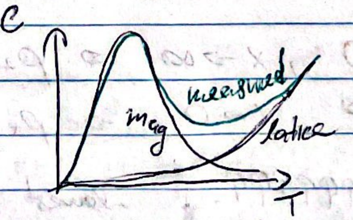
$$\Rightarrow C_V = \frac{\varepsilon^2}{k_BT^2}\frac{e^{\beta\varepsilon}}{(1+e^{\beta\varepsilon})^2} = k\frac{x^2e^x}{(1+e^x)^2}, \quad x = \beta\varepsilon = \frac{\varepsilon}{kT}$$

Schottky anomaly

~ 2-lvl system with $E_0 = 0$, $\varepsilon = 2\mu B$

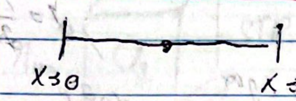


- measured in crystals



Particle in a 1D box

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \underbrace{\frac{2mE}{\hbar^2}}_{k^2} \psi(x) = 0$$ ⇒ wave equation (k = wave #)



⇒ solution: $\psi(x) = A\sin(kx) + B\cos(kx)$

$\psi(0) = 0 \Rightarrow B = 0 \Rightarrow \psi(x) = A\sin(kx)$

$\psi(L) = 0 \Rightarrow kL = n\pi \Rightarrow k = \frac{n\pi}{L}$

$\int_0^L |\psi(x)|^2 dx = 1 \Rightarrow A^2 = \frac{2}{L} \Rightarrow A = \sqrt{\frac{2}{L}} \rightarrow$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$$\left(\frac{n\pi}{L}\right)^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \frac{n^2}{L^2}$$

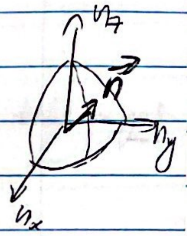
Particle in 3D box

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi(x,y,z) = E\psi(x,y,z)$$

$$\Rightarrow \psi(x,y,z) = \left(\frac{2}{L_x L_y L_z}\right)^{3/2} \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$k_x = \pi\frac{n_x}{L_x}$, $k_y = \pi\frac{n_y}{L_y}$, $k_z = \pi\frac{n_z}{L_z}$

$$\Rightarrow E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \xrightarrow{\text{cube}} \frac{\pi^2\hbar^2}{2mL^2}\underbrace{(n_x^2 + n_y^2 + n_z^2)}_{= |\vec{n}|^2}$$



$$\Rightarrow |\vec{n}| = \frac{L}{\pi\hbar}\sqrt{2mE}$$ ($\frac{L}{\pi\hbar}$: k)

\# states with energy less than E: $\phi(E) = \frac{1}{8}\left(\underbrace{\frac{4}{3}\pi|\vec{n}|^3}_{\text{volume of sphere of rad } |\vec{n}|}\right) = \frac{\pi}{6}\left(\frac{L}{\pi\hbar}\right)^3 (2mE)^{3/2}$

only 1/8 bc $\vec{n} > 0$

states with energy between E and E+dE

$$g(E)dE = \phi(E+dE) - \phi(E) = \frac{\partial\phi}{\partial E}dE$$

$L^3 = V$

$$= \frac{3}{2}\frac{\pi}{6}\left(\frac{L}{\pi\hbar}\right)^3 (2mE)^{1/2} \cdot 2m\, dE = \frac{\pi}{4}\frac{L^3}{\pi^3\hbar^3}(2m)^{3/2}E^{1/2}dE =$$

$\pi^3\hbar^3 = \frac{h^3}{8\pi^3}$

$$= 2\pi\frac{V}{h^3}(2m)^{3/2}E^{1/2}dE$$

$$g(E)dE = \frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}dE$$

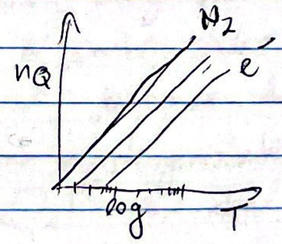
$$g(k)dk = \frac{Vk^2}{2\pi^2}dk$$

$$g(p)dp = \frac{4\pi V}{h^3}p^2 dp$$

$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m}dk$

$E = \frac{p^2}{2m} \Rightarrow p = \hbar k$, $dp = \hbar dk$

n_Q increases w/ temp and mass



Single particle partition function

$$\left.\begin{aligned} Z_1 &= \int_0^\infty g(p)\, e^{-\beta\frac{p^2}{2m}}\, dp \\ g(p)\,dp &= \frac{4\pi V}{h^3}\, p^2\, dp \end{aligned}\right\} \quad Z_1 = \frac{4\pi V}{h^3} \underbrace{\int_0^\infty p^2 e^{-\alpha p^2} dp}_{\equiv I_1(\alpha)} \qquad \alpha = \frac{\beta}{2m}$$

density of states

$$Z_1 = \frac{4\pi V}{h^3} I_1(\alpha) = -\frac{4\pi V}{h^3}\frac{\partial I_0(\alpha)}{\partial \alpha}$$

$$I_0(\alpha) = \int_0^\infty e^{-\alpha x^2} dx \rightarrow I_1(\alpha) = -\frac{\partial I_0(\alpha)}{\partial \alpha} = \int x^2 e^{-\alpha x^2} dx$$

...

$$I_0(\alpha) = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

$$\Rightarrow Z_1 = -\frac{4\pi V}{h^3}\frac{\partial}{\partial \alpha}\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right) = -\frac{4\pi V}{h^3}\cdot\frac{\sqrt{\pi}}{2}\,\frac{1}{-2\alpha^{+3/2}} =$$

$$= \frac{4\pi V}{h^3}\sqrt{\pi}\,\alpha^{-3/2} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

spinless particle

$$\Rightarrow \boxed{Z_1 = \int_0^\infty \frac{V 4\pi p^2}{h^3} e^{-\frac{\beta p^2}{2m}} dp = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}$$

Quantum concentration & thermal wavelength

$$Z_1 = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = V n_Q = V/\lambda_{th}^3 \Rightarrow \boxed{n_Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}$$

quantum concentration

↳ # states available for a system per cubic meter

$$\boxed{\lambda_{th} \equiv \left(\frac{1}{n_Q}\right)^{1/3} = \frac{h}{\sqrt{2\pi m k T}} = \left(\frac{3}{2\pi}\right)^{1/2}\lambda_{dB}}$$

thermal wavelength

de Broglie

or the other way around:

$$\lambda_{dB} = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \underset{\uparrow}{=} \frac{h}{\sqrt{3mkT}} = \left(\frac{2\pi}{3}\right)^{1/2}\lambda_{thermal}$$

$E = KE = \frac{3}{2}k_B T$ in 3D

$$\boxed{n = \frac{N}{V}}$$

$\Rightarrow$ interparticle spacing: $\boxed{\ell = \left(\frac{1}{n}\right)^{1/3}}$

- quantum aspects will show if: $\lambda_{dB} \gg \ell$
  ↳ ψ of particles will overlap

$$\Downarrow$$

$$\frac{\lambda_{dB}}{\ell} \gg 1$$

$$1 \gg \frac{\ell^3}{\lambda_{dB}^3} = \frac{n_Q}{n}$$

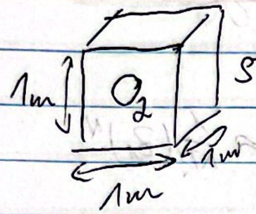
$\Rightarrow$ if $\frac{n_Q}{n} \ll 1$ (particle concentration $\gg$ quantum concentration)

$\Rightarrow$ quantum aspects become important

||

states

Estimate of number of states



STP

$m(O_2) = 5.3 \cdot 10^{-26}$ kg $\Rightarrow$ $\underline{\underline{3 \cdot 10^{25}}}$ molecules (ideal gas law)

$kT \approx 4 \cdot 10^{-21}$ J at STP

- $\boxed{n_Q = \left(\frac{2\pi m kT}{h^2}\right)^{3/2}} \approx \underline{1.7 \cdot 10^{32}}\ m^{-3}$ states

\# molecules << \# available states
⇒ (ideal) gas, neglect quantum.

N particles in a box

- three energy states for 1 particle: $\varepsilon_1, \varepsilon_2, \varepsilon_3$

$$Z_1 = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3}$$

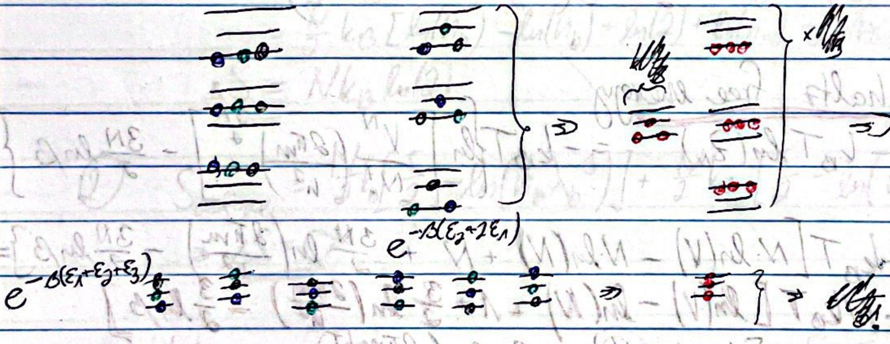
$$\Rightarrow Z_3 = (Z_1)^3 = \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + e^{-\beta\varepsilon_3}\right)^3 =$$

$$= 6e^{-\beta(\varepsilon_1+\varepsilon_2+\varepsilon_3)} + e^{-\beta 3\varepsilon_2} + e^{-3\beta\varepsilon_3} + e^{-3\beta\varepsilon_1} +$$
$$+ 3e^{-\beta(\varepsilon_1+2\varepsilon_2)} + 3e^{-\beta(\varepsilon_1+2\varepsilon_3)} + 3e^{-\beta(\varepsilon_2+2\varepsilon_1)} + 3e^{-\beta}e^{-\beta(\varepsilon_2+2\varepsilon_3)}$$
$$+ 3e^{-\beta(\varepsilon_3+2\varepsilon_1)} + 3e^{-\beta(\varepsilon_3+2\varepsilon_2)}$$

works ~~for~~ only distinguishable particles (e.g. solid) vs. indistinguishable

$Z_3 = Z_1^3$ ← have some label, e.g. position in lattice

↳ no label, e.g. particles in gas



$\Rightarrow Z_3 \neq (Z_1)^3$

⇓

$Z_3 =$ as above but all the coeff. are cancelled

Ideal and classical gas

Ideal ↓ PE << KE

classical ↳ single particle states contain no more than 1 molecule

$$(Z_1)^N = \underbrace{(\ldots)}_{\text{terms representing situations with more than 1 particle in the same single particle state}} + \underbrace{N!}\, e^{-\beta(\varepsilon_1+\varepsilon_2+\ldots+\varepsilon_N)}$$

terms representing situations with more than 1 particle in the same single particle state but these don't occur under assumption of classical gas

→ overcounting with factor $N!$ because every one of these N-particle states is identical because the particles are indistinguishable in gas

$$\boxed{Z_N \approx \frac{1}{N!}(Z_1)^N \text{ for ideal classical gas}}$$

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Partition function ideal (monoatomic) gas

- **single** particle:

$$Z_1 = V\left(\frac{2\pi m k T}{h^2}\right)^{3/2}$$

- **N**-particles: $Z_N \neq (Z_1)^N$ but $Z_N \approx \frac{1}{N!}(Z_1)^N$

$$\Rightarrow \boxed{Z_N = \frac{V^N}{N!}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3N}{2}}}$$

Properties of ideal gas

Internal energy

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln\left[\frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}}\right] = -\frac{\partial}{\partial \beta}\left\{\ln\left[\frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{\frac{3N}{2}}\right] - \frac{3N}{2}\ln(\beta)\right\}$$

$$= \frac{3N}{2}\frac{\partial \ln(\beta)}{\partial \beta} = \frac{3N}{2}\frac{1}{\beta} = \frac{3}{2}N k_B T$$

$$\boxed{U = \frac{3}{2}N k_B T = \frac{3}{2}nRT}$$

$\Rightarrow$ heat capacity

$$\boxed{C_V = \frac{\partial U}{\partial T} = \frac{3}{2}N k_B} \left(= \frac{3}{2}R \text{ for 1 mole}\right)$$

Helmholtz free energy

$$F = -k_B T \ln(Z_N) = -k_B T\left\{\ln\left[\frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{\frac{3N}{2}}\right] - \frac{3N}{2}\ln\beta\right\} =$$

$$= -k_B T\left[N\cdot\ln(V) - N\cdot\ln(N) + N + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{3N}{2}\ln\beta\right] =$$

$$F = -N k_B T\left[\ln(V) - \ln(N) + 1 + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{3}{2}\ln\beta\right]$$

$$F = -N k_B T\left[1 - \ln\left(\underbrace{\frac{N}{V}}_{=n}\right) + \frac{3}{2}\ln\left(\frac{2\pi m k T}{h^2}\right)\right]$$

$$= -N k_B T\left[1 - \ln(n) - 3\ln\left(\overset{=\lambda_{th}}{\frac{h}{\sqrt{2\pi m k T}}}\right)\right]$$

$$= -N k_B T\left[1 - \ln(n) - \ln(\lambda_{th}^3)\right]$$

$$\boxed{F = -N k_B T\left[1 - \ln(n\lambda_{th}^3)\right]}$$

Pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(-N k_B T \ln(V)\right) = N\frac{k_B T}{V}$$

$$\Rightarrow \boxed{p = \frac{N k_B T}{V}} \leftarrow \text{ideal gas law}$$

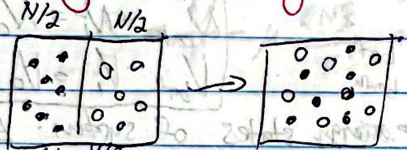
Entropy

$$S = \frac{U-F}{T} = \frac{\frac{3}{2}Nk_BT - \left(-Nk_BT\left(1-\ln(n\lambda_{th}^3)\right)\right)}{T} =$$

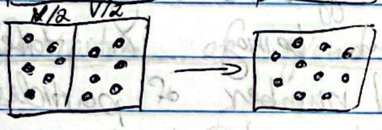
$$= Nk_B\left[\frac{3}{2} + 1 - \ln(n\lambda_{th}^3)\right] \Rightarrow =$$

$$\boxed{S = Nk_B\left[\frac{5}{2} - \ln(n\lambda_{th}^3)\right]}$$ Sackur - Tetrode equation

Entropy of mixing

① 

irreversible : $\Delta S > 0$

② 

reversible : $\Delta S = 0$

b = black
w = white

① $S_{before} = \frac{N}{2}k_B\left[\frac{5}{2} - \ln(n_b\lambda_b^3)\right] + \frac{N}{2}k_B\left[\frac{5}{2} - \ln(n_w\lambda_w^3)\right]$

$S_{after} = \frac{N}{2}k_B\left[\frac{5}{2} - \ln\left(\frac{n_b}{2}\lambda_b^3\right)\right] + \frac{N}{2}k_B\left[\frac{5}{2} - \ln\left(\frac{n_w}{2}\lambda_w^3\right)\right]$

$\Delta S = S_{after} - S_{before} = \frac{N}{2}k_B\left[-\ln\left(\frac{n_b}{2}\right) - \ln(\lambda_b^3) - \ln\left(\frac{n_w}{2}\right) - \ln(\lambda_w^3) + \ln(n_b) + \ln(\lambda_b^3) + \ln(n_w) + \ln(\lambda_w^3)\right]$

$= \frac{N}{2}k_B\left[\ln(n_b) - \ln\left(\frac{n_b}{2}\right) + \ln(n_w) - \ln\left(\frac{n_w}{2}\right)\right] =$

$= \frac{N}{2}k_B\left[\ln(n_b) - \ln(n_b) + \ln(2) + \ln(n_w) - \ln(n_w) + \ln(2)\right] =$

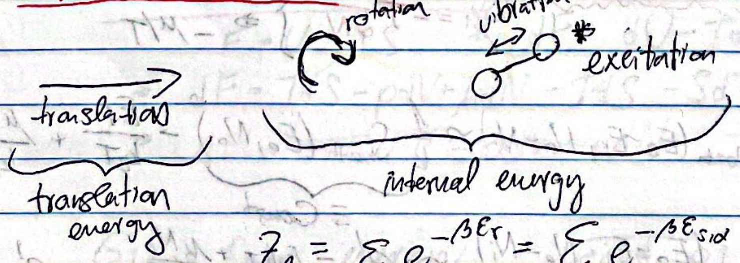
$$\boxed{\Delta S = Nk_B\ln(2)}$$

② $S_{before} = \frac{N}{2}k_B\left[\frac{5}{2} - \ln(n_b\lambda_b^3)\right] + \frac{N}{2}k_B\left[\frac{5}{2} - \ln(n_b\lambda_b^3)\right] = S_{after}$

$\Rightarrow \underline{\underline{\Delta S = 0}}$

Partition function

$\varepsilon_r = \varepsilon_{s,\alpha} = \varepsilon_s^{tr} + \varepsilon_\alpha^{int}$



$$Z_1 = \sum_r e^{-\beta\varepsilon_r} = \sum_{s,\alpha} e^{-\beta\varepsilon_{s\alpha}} = \sum_{s,\alpha} e^{-\beta\varepsilon_s^{tr}} e^{-\beta\varepsilon_\alpha^{int}} =$$

$$= \sum_s e^{-\beta\varepsilon_s^{tr}} \cdot \sum_\alpha e^{-\beta\varepsilon_\alpha^{int}} = z_1^{tr} \cdot z_1^{int}$$

$$\Rightarrow \boxed{Z_N = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}\left[z^{int}(T)\right]^N}$$

Partition function of ideal gas

Gibbs distribution

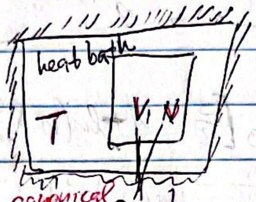
grand canonical ensemble

isolated system

microcanonical

$S = k_B \ln(\Omega(E,V,N))$

↳ isolated from everything



canonical

$\downarrow$

$F = -k_B T \ln(Z(T,V,N))$

↳ can exchange E w/ heat bath

↳ system << heat bath

system

can exchange both heat and energy with bath

system >> bath

⇓

interaction with the heat bath won't change μ & T of the bath

$\Phi_G = -k_B T \ln(\mathcal{Z}(T,V,N))$

$$\left.\begin{array}{l} E_{bath} + E_i = E_0 \\ N_{bath} + N_i = N_0 \\ V_{bath} + V_i = V_0 \end{array}\right\} \text{conserved}$$

⇒ energy states of system: $E_1, E_2, \dots, E_i, \dots$

Probability of the system being in state i with energy E_i and number of particles N_i :

$$p_i \propto \underbrace{\Omega_{bath}(\underbrace{E_0 - E_i}_{E_{bath}}, \underbrace{N_0 - N_i}_{N_{bath}})}_{\text{states of heat bath}} \times 1$$

↖ only 1 state i

Equilibrium with heat and particle bath

$E_i \ll E_0 \quad , N_i \ll N_0$:

Taylor expand $\ln \Omega_{bath}(E_0 - E_i) \approx \ln \Omega_{bath}(E_0, N_0) - \left(\frac{\partial \ln \Omega_{bath}(E,N)}{\partial E}\right)_{E_0} E_i + \left(\frac{\partial \ln \Omega_{bath}}{\partial N}\right)_{N_0} N_i + \dots$

$\ln \Omega = \frac{S}{k}$

$$\ln \Omega_{bath}(E_0 - E_i, N_0 - N_i) \approx \frac{1}{k} S_{bath}(E_0, N_0) - \frac{1}{k}\overbrace{\left(\frac{\partial S_b(E,N)}{\partial E}\right)_{E_0}}^{1/T} E_i - \frac{1}{k}\underbrace{\left(\frac{\partial S_b(E,N)}{\partial N}\right)_{N_0}}_{} N_i$$

$\left\{ \text{Chemical potential:} \quad \boxed{\mu = -T \frac{\partial S}{\partial N}} \right\} \Rightarrow -\mu/T$

$$\ln \Omega_{bath}(E_0 - E_i, N_0 - N_i) \approx \underbrace{\frac{1}{k} S_{bath}(E_0, N_0)}_{\equiv \text{Const.}} - \frac{E_i}{k_B T} + \frac{\mu N_i}{k_B T}$$

$\boxed{p_i \propto} \Rightarrow \Omega_{bath}(E_0 - E_i, N_0 - N_i) \approx C' e^{-E_i/kT + \frac{\mu N_i}{kT}} = C' e^{\beta(\mu N_i - E_i)}$

Gibbs distribu. / Grand canonical ensemble

$$\boxed{p_i = \underset{1/\mathcal{Z}}{C} e^{\beta(\mu N_i - E_i)}}$$

$\sum p_i = 1 = \sum C e^{\beta(\mu N_i - E_i)}$

$\Rightarrow C = \frac{1}{\mathcal{Z}}$

$$\Rightarrow \boxed{\mathcal{Z} = \sum_i e^{\beta(\mu N_i - E_i)}}$$

= Grand partition function

Thermodynamics properties - Gibbs distributions.

$$S = -k \sum_i p_i \ln(p_i) = -k \sum_i p_i \ln\left(\frac{e^{\beta(\mu N_i - E_i)}}{Z} \right) =$$

$$= -k \sum_i p_i \left[\beta \mu N_i - \beta E_i - \ln(Z) \right] =$$

$$= -\underbrace{k \beta}_{=\frac{1}{T}} \mu \underbrace{\sum_i p_i N_i}_{\langle N \rangle = N} + \overset{1/T}{k\beta} \underbrace{\sum_i p_i E_i}_{\langle E \rangle = U} + k \underbrace{\left(\sum p_i \right)}_{=1} \cdot \ln(Z) =$$

$$\boxed{S = \frac{U}{T} - \mu \frac{\langle N \rangle}{T} + k \ln(Z)}$$

$$\Rightarrow kT \ln(Z) = TS + \mu N - U$$

Definition of grand potential

$$\boxed{\Phi_G = -kT \ln(Z) = U - TS - \mu N}$$

Generalization of Helmholtz free energy

$$F = -kT \ln(Z) = U - TS$$

~~slide 52~~

Internal energy

$$S(U, V, N) \Rightarrow dS = \underbrace{\frac{\partial S}{\partial U}}_{1/T} dU + \underbrace{\frac{\partial S}{\partial V}}_{p/V} dV + \underbrace{\frac{\partial S}{\partial N}}_{-\mu/T} dN$$

$$\Rightarrow dS = \frac{1}{T} dU + \frac{p}{V} dV - \frac{\mu}{T} dN$$

$$\Rightarrow \boxed{dU = TdS - pdV + \mu dN}$$

Helmholtz free energy - $\boxed{\text{Const. } V}$

$$F = U - TS \Rightarrow dF = dU - TdS - SdT$$

$$\Rightarrow dF = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT$$

$$\Rightarrow \boxed{dF = -SdT - pdV + \mu dN}$$

Gibbs free energy - $\boxed{\text{const. } p}$

$$G = U + p\cancel{V} - TS \Rightarrow dG = dU + pd\cancel{V} + \cancel{V}dp - TdS - SdT$$

$$\Rightarrow dG = \cancel{TdS} - p\cancel{dV} + \mu dN + p\cancel{dV} + Vdp - \cancel{TdS} - SdT$$

$$\boxed{dG = -SdT + Vdp + \mu dN}$$

~~Chemic~~

Chemical potential

$dF = -SdT - pdV + \mu dN \Rightarrow \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

$dG = -SdT + Vdp + \mu dN \Rightarrow \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$

$\downarrow$ extensive $\Rightarrow G \propto N$

$\Rightarrow G(N,T,p) = N g(T,p) \Rightarrow \boxed{\mu = g(T,p)}$

Gibbs energy per particle

chemical potential is the gibbs free energy per particle

$\Phi_G(T,V,N) = -k_B T \ln(\mathcal{Z})$

$\Phi_G = U - TS - \underbrace{\mu N}_{=G} = U - TS - G = U - TS - U - pV + TS = -pV$

$\Rightarrow \boxed{\Phi_G = -pV}$

$d\Phi_G = dU - TdS - SdT - \mu dN - Nd\mu$

$= \cancel{TdS} - pdV + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu$

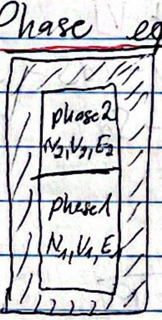
$\Rightarrow \boxed{d\Phi_G = -pdV - SdT - Nd\mu}$

$\Rightarrow \boxed{N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}} \quad \boxed{p = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}} \quad \boxed{S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu}}$

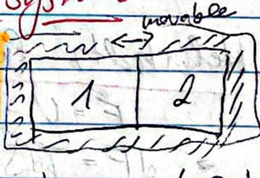
$$\boxed{\begin{aligned} N &= k_B T\left(\frac{\partial \ln \mathcal{Z}(T,V,\mu)}{\partial \mu}\right)_{T,V} \\ U &= -\left(\frac{\partial \ln \mathcal{Z}(T,V,\mu)}{\partial \beta}\right)_{\mu,V} + \mu N \end{aligned}}$$

Equillibrum of an isalated system

Phase equillibrum



equilibrium $\boxed{\begin{aligned} T_1 &= T_2 \\ p_1 &= p_2 \\ \mu_1 &= \mu_2 \end{aligned}}$



$E_1 + E_2 = E$

$N_1 + N_2 = N$

$V_1 + V_2 = V$

$S_1 + S_2 = S$

$$\boxed{\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \quad ① \\ p &= T\frac{\partial S}{\partial V} \quad ③ \\ \mu &= -T\frac{\partial S}{\partial N} \quad ② \end{aligned}}$$

$dS = \left(\frac{\partial S}{\partial E_1}\right)_{V_1N_1} dE_1 + \left(\frac{\partial S}{\partial N_1}\right)_{V_1E_1} dN_1 + \left(\frac{\partial S}{\partial V_1}\right)_{E_1,N_1} dV_1$

$dS = \left(\frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1}\right)_{V_1,N_1} dE_1 + \left(\frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_1}\right)_{V_1,E_1} dN_1 + \left(\frac{\partial S_1}{\partial V_1} + \frac{\partial S_2}{\partial V_2}\right)_{E_1,}$ d

- isaleted system

$N_1 + N_2 = N$

$V_1 + V_2 = V$

$E_1 + E_2 = E$

- equilibrium: $dS = 0$

$\frac{\partial S_2}{\partial E_1} = -\frac{\partial S_2}{\partial E_2}$ and similar for N_1, V_1

$= \underbrace{\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)_{V_1N_1}}_{} dE_1 + \underbrace{\left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)_{V_1E_1}}_{=0} dN_1 + \left(\frac{\partial S_1}{\partial V_1}\right.$

$dS = 0$ in equilibrium $\Rightarrow = 0$

$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$ ① $\frac{1}{T_1} = \frac{1}{T_2}$ $\Rightarrow T_1 = T_2$

② $\mu_1 = \mu_2$

$= 0$ ③ $p_1 = p_2$

$$\left(\frac{\partial S}{\partial t}\right)_{E_1,N_1} = \left(\frac{\partial S_1}{\partial t}\right)_{E_1,N_1} + \left(\frac{\partial S_2}{\partial t}\right)_{E_1,N_1}$$

const. E_1, ~~V_1~~ N_1

$$\left(\frac{\partial S}{\partial t}\right)_{E_1,N_1} = \frac{\partial S_1}{\partial V_1}\frac{\partial V_1}{\partial t} + \frac{\partial S_2}{\partial V_2}\frac{\partial V_2}{\partial t}$$ } connected: $\frac{\partial V_1}{\partial t} = -\frac{\partial V_2}{\partial t}$

$$= \frac{\partial S_1}{\partial V_1}\frac{\partial V_1}{\partial t} - \frac{\partial S_2}{\partial V_2}\frac{\partial V_1}{\partial t}$$

$$\left(\frac{\partial S}{\partial t}\right)_{E_1N_1} = \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1,N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{E_1,N_1}\right]\left(\frac{\partial V_1}{\partial t}\right) \geq 0$$ by second law

$\boxed{\left(\frac{\partial S}{\partial V}\right) T = p}$ ⇝ $\boxed{T_1 = T_2}$ = const. E

$$\left(\frac{\partial S}{\partial t}\right) = \frac{1}{T}(p_1 - p_2)\left(\frac{\partial V_1}{\partial t}\right) \geq 0$$

$\Rightarrow$ if $p_1 > p_2 \Rightarrow \frac{\partial V_1}{\partial t} \geq 0 \Rightarrow$ volume with larger pressure expands

$$\left(\frac{\partial S}{\partial t}\right)_{E_1,V_1} = \left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t}\right)_{E_1,V_1} = \left(\frac{\partial S_1}{\partial N_1}\frac{\partial N_1}{\partial t} + \frac{\partial S_2}{\partial N_2}\frac{\partial N_2}{\partial t}\right)_{E_1,V_1} \overset{\Downarrow}{=} \quad \frac{\partial N_1}{\partial t} = -\frac{\partial N_2}{\partial t}$$

$$= \left(\frac{\partial S_1}{\partial N_1}\frac{\partial N_1}{\partial t} - \frac{\partial S_2}{\partial N_2}\frac{\partial N_1}{\partial t}\right)_{E_1,V_1} = \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)_{E_1,V_1}\left(\frac{\partial N_1}{\partial t}\right) \geq 0 \text{ by 2nd law}$$

$\boxed{\mu = -T\frac{\partial S}{\partial N}}$ ⇝

$$\left(\frac{\partial S}{\partial t}\right)_{E_1V_1} = -\frac{1}{T}(\mu_1 - \mu_2)\frac{\partial N_1}{\partial t} \geq 0$$

$\Rightarrow$ if $\mu_1 > \mu_2 \Rightarrow \frac{\partial N_1}{\partial t} < 0 \Rightarrow$ particles leave compartment with higher chemical potential

Ideal classical gas

canonical: $Z_N = \frac{1}{N!}[Z_1]^N$ with $Z_1 = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$

grand cannonical: $\mathcal{Z}(T,V,\mu) = \sum_i e^{\beta(\mu N_i - E_i)} = \sum_{N,r} e^{\beta(\mu N - E_{N,r})} =$

$$= \sum_{N=0}^{\infty}\sum_r e^{\beta(\mu N - E_{N,r})} = \sum_{N=0}^{\infty} \underset{(e^{\beta\mu})^N}{e^{\beta\mu N}} \underbrace{\sum_r e^{-\beta E_{N,r}}}_{= Z(T,V,N) = \frac{1}{N!}[Z_1(T,V)]^N} =$$

$$= \sum_{N=0}^{\infty}\frac{1}{N!}\left(e^{\beta\mu}Z_1\right)^N \Bigg\} \sum \frac{1}{N!}x^N = e^x$$

$$\boxed{\mathcal{Z}(T,V,\mu) = e^{e^{\beta\mu}Z_1(T,V)}}$$

$$\left.\begin{aligned}\Phi_G &= -kT\ln\mathcal{Z} = -kT\ln e^{e^{\beta\mu}Z_1} = -kT Z_1 e^{\beta\mu}\\ \Phi_G &= -pV\end{aligned}\right\} pV = k_BTe^{\beta\mu}Z_1(T,V)$$

with $\underbrace{e^{\beta\mu}Z_1(T,V)}_{=N}$

$$N = -\left(\frac{\partial\Phi_G}{\partial\mu}\right)_{T,V} = \left(\frac{\partial kT\ln\mathcal{Z}}{\partial\mu}\right)_{T,V} = kT\left(\frac{\partial e^{\beta\mu}Z_1}{\partial\mu}\right)_{T,V} = \cancel{kT}\,\cancel{\beta}\,Z_1e^{\beta\mu} = Z_1e^{\beta\mu}$$

$\Downarrow$

$$pV = Nk_BT$$

Internal energy U

$$U = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu N = -\left(\frac{\partial e^{\beta\mu} Z_1}{\partial \beta}\right)_\mu + \mu N =$$

$$= -\mu \underbrace{Z_1 e^{\beta\mu}}_{N} - e^{\beta\mu}\left(\frac{\partial Z_1}{\partial\beta}\right)_\mu + \mu N = -e^{\beta\mu}\left(\frac{\partial Z_1}{\partial\beta}\right)_\mu$$

$$Z_1 = V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \Rightarrow \left(\frac{\partial Z_1}{\partial\beta}\right)_\mu = -\frac{3}{2}V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\frac{1}{\beta} = -\frac{3}{2}kTZ_1$$

$$\Rightarrow U = -e^{\beta\mu}\left(-\frac{3}{2}kTZ_1\right) = \frac{3}{2}k_BT\underbrace{Z_1 e^{\beta\mu}}_{N} = \frac{3}{2}k_BTN$$

$$\Rightarrow \boxed{U = \frac{3}{2}k_BTN}$$

$\boxed{N = Z_1 e^{\beta\mu}}$

$\Downarrow$

$\frac{N}{Z_1} = e^{\beta\mu}$

$\beta\mu = \ln\left(\frac{N}{Z_1}\right)$

$\mu = \frac{1}{\beta}\ln\left(\frac{N}{Z_1}\right)$

Entropy S

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_\mu = \left(\frac{\partial kT\ln\mathcal{Z}}{\partial T}\right)_\mu = \left(\frac{\partial kTe^{\beta\mu}Z_1}{\partial T}\right)_\mu =$$

$$= \frac{\partial\beta}{\partial T}\frac{\partial \frac{1}{\beta}e^{\beta\mu}Z_1}{\partial\beta} = -k\beta^2\left[-\frac{1}{\beta^2}\underbrace{e^{\beta\mu}Z_1}_{N} + \frac{\mu}{\beta}\underbrace{e^{\beta\mu}Z_1}_{N} + \frac{1}{\beta}e^{\beta\mu}\left(\frac{\partial Z_1}{\partial\beta}\right)_\mu\right]$$

$$= -k\beta^2\left[-\frac{N}{\beta^2} + \frac{\mu}{\beta}N - \frac{1}{\beta}e^{\beta\mu}\frac{3}{2}\underbrace{kT}_{1/\beta}Z_1\right] = \quad (e^{\beta\mu}Z_1 = N)$$

$$= -k\beta^2\left[-\frac{N}{\beta^2} + \frac{\mu}{\beta}N - \frac{1}{\beta^2}\frac{3}{2}N\right] = kN\left[1 - \mu\beta + \frac{3}{2}\right] = kN\left[\frac{5}{2} - \mu\beta\right]$$

$$= kN\left[\frac{5}{2} - \ln\left(\frac{N}{Z_1}\right)\right]$$

$$\hookrightarrow Z_1 = V\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}$$

$$\Rightarrow \boxed{S = kN\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)\right]}$$ Sackur -Tetrode

Chemical potential μ

$$\mu = \frac{1}{\beta}\ln(N/Z_1) = kT\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right)$$

$$= kT\ln\left(\frac{N}{V}\lambda_{th}^3\right) = -kT\ln\left(\frac{n_Q}{n}\right) \qquad \lambda_{th} = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

$$n_Q = \lambda_{th}^{-3} \qquad \Rightarrow \boxed{\mu = -kT\ln\left(\frac{n_Q}{n}\right)} = kT\ln(n\lambda_{th}^3)$$

CO poisoning

$N = 0 \quad , \varepsilon = 0\,eV$ ⇒ unoccupied

- two states: $N = 1 \quad , \varepsilon_0 = -0.7$ ⇒ occupied by O_2

$$\mathcal{Z} = \sum_{N=0}^{1}\sum_r e^{\beta(\mu N - E_{N,r})} = e^{0-0} + e^{\beta(\mu_0 - \varepsilon)} = 1 + e^{-\frac{\varepsilon_0 - \mu_0}{kT}}$$

↳ assume equillibrium between O_2 in blood and in air ⇒ $\boxed{\mu_{O_{blood}} = \mu_{O_{air}} = \mu_O}$

Suppose O_2 ideal ⇒ $\mu = -kT\ln\left(\frac{n_Q}{n}\right)$

$1m^3$ of air at $T = 37°C$ ⇒ $kT \approx 4.3\cdot10^{-21}J = 0.027eV$

⇒ $m(O_2) = 5.3\cdot10^{-26}kg$

⇒ $n_Q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \approx 1.9\cdot10^{32}\,m^{-3}$ states

↳ 20% O_2 ⇒ $\approx 5.4\cdot10^{24}$ O_2 molecules

$\mu_O = -kT \ln\left(\frac{n_Q}{n}\right) \searrow$ $n_Q \approx 1.9 \cdot 10^{32}$ states/m3
$n \approx 5.4 \cdot 10^{24}$ O_2 molec./m3
$kT \approx 0.027 eV$

$\mu_O = -0.47 eV$

$\Rightarrow \mathcal{Z} = 1 + e^{-\frac{\varepsilon_0 - \mu_0}{kT}} =$
$= 1 + e^{-\frac{(-0.7+0.47)}{0.027}} \approx 1 + 5006 = 5007$

$P_{O_2} = \frac{e^{-\frac{\varepsilon_0 - \mu_0}{kT}}}{\mathcal{Z}} = \frac{5006}{5007} \approx 1$

$\nearrow$ prob. of state occupied by O_2

- now CO present $\Rightarrow$ 3 states

$N = 0 \quad \varepsilon = 0$ occupied by:
$N = 1 \quad \varepsilon = \varepsilon_0 = -0.7 eV$ - oxygen
$N = 1 \quad \varepsilon = \varepsilon_{CO} = -0.85 eV$ - CO

$$\mathcal{Z} = \sum_{N=0}^{1} \sum_{r} e^{\beta(\mu N - E_{N,r})}$$

$$\mathcal{Z} = e^{0-0} + e^{\beta(\mu_O - \varepsilon_O)} + e^{\beta(\mu_{CO} - \varepsilon_{CO})} = 1 + e^{-\frac{\varepsilon_0 - \mu_0}{kT}} + e^{-\frac{\varepsilon_{CO} - \mu_{CO}}{kT}}$$

↳ assume equillibrium between CO in blood and air:

$\mu_{CO \text{ in blood}} = \mu_{CO \text{ in air}} = \mu_{CO}$
and $n_{CO} = 0.01 n_0$

$$\mu_{CO} = -kT \ln\left(\frac{n_Q}{n_{CO}}\right) = -kT \ln\left(\frac{n_Q}{0.01 n_0}\right) = -\underbrace{kT\left(\ln\left(\frac{n_Q}{n_0}\right)}_{=\mu_0} - \ln(0.01)\right) =$$
$$= \mu_0 + k_B T \ln(0.01)$$
$$= -0.047 + 0.027(-4.6) = -0.59 eV \Rightarrow \mu_{CO} = -0.59 eV$$

$$\mathcal{Z} = 1 + e^{-\frac{-0.7+0.47}{0.027}} + e^{-\frac{-0.85+0.59}{0.025}} = 1 + 5006 + 15210 \approx 20200$$

$$p(\text{occupied by Oxygen}) = \frac{e^{-\frac{\varepsilon_0 - \mu_0}{kT}}}{\mathcal{Z}} = \frac{5006}{20200} \approx 0.25$$

$\Rightarrow$ 25% oxygen, 75% CO

More particle types:

$$\boxed{\begin{aligned} dU &= TdS - pdV + \overbrace{\sum_i \mu_i dN_i}^{\text{one term for each particle type}} \\ dF &= -pdV - SdT + \sum_i \mu_i dN_i \\ dG &= Vdp - SdT + \sum_i \mu_i dN_i \end{aligned}}$$

const. T, V: $dF = \sum_i \mu_i dN_i$
const. T, p: $dG = \sum_i \mu_i dN_i$

Particle conservation laws

at const. T and V $\Rightarrow$ equilibrium when $dF=0$

★suppose N is not fixed

↳ e.g. photons in a box - can vary by interactions with the wall (absorption/emission)

$$dF = -SdT - pdV + \mu dN$$

$$\boxed{\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \underset{dF=0}{\uparrow} = 0}$$

chemical potential of particles w/o particle conservation is 0

★ electrons, positrons, photons in box $\boxed{e^+ + e^- \Leftrightarrow \gamma + \gamma}$

$$\underbrace{\text{conservation law}}: \quad \underset{e^+ \nearrow}{N_+} - \underset{e^- \nearrow}{N_-} = N = \text{const.} \Rightarrow dN_+ - dN_- = 0$$

$$dN_+ = dN_-$$

$$dF = \sum \mu_i N_i = 0$$

$$\Rightarrow \mu(e^+)\,dN_+ + \mu(e^-)\,dN_- + \cancel{\mu(\gamma)}\,dN_\gamma = 0 \quad \xleftarrow{} 0 \text{ from above}$$

$$\mu(e^+)\,dN_+ + \mu(e^-)\,dN_+ = 0$$

$$\mu(e^+) + \mu(e^-) = 0$$

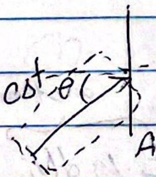
T4

Photons and black body radiation

emitted rad. is purely function of temperature

(black body) ← absorbs all em radiation

Photon gas



- photon: $E = pc$
- γ density: n
- E density: $u = nE$

$\#\gamma = nc\Delta t A\cos\theta$ (as # γ hitting wall)

- momentum transfer at collision: $\Delta p_\gamma = 2\frac{E}{c}\cos\theta$ (1 γ)

$\Rightarrow$ pressure at wall: $p = \frac{F}{A} = \frac{\Delta p}{\Delta t A} \cdot nc\Delta t A\cos\theta =$

$$= \Delta p n c \cos\theta = 2nE(\cos\theta)^2 = 2u\cos^2\theta$$

$\Rightarrow$ average over all angles: $\langle\cos^2\theta\rangle = \frac{1}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos^2\theta \sin\theta d\theta =$

$$= -\frac{1}{2}\int_0^{\pi/2} \cos^2\theta \, d\cos\theta = -\frac{1}{2}\cdot\frac{1}{3}\cos^3\theta\Big|_0^{\pi/2} = \frac{1}{6}$$

$$\int_0^{2\pi}\int_0^{\pi/2} \sin\theta \, d\theta d\varphi$$

$\Rightarrow$ $\boxed{p = \frac{u}{3}}$

⇒ particle flux at wall

$$\phi = \frac{n c \Delta t A \cos\theta}{\Delta t A} = nc\cos\theta$$

$$\langle\phi\rangle = nc\langle\cos\theta\rangle = nc\frac{1}{4\pi}\int_0^{\pi/2}\int_0^{2\pi}\cos\theta\sin\theta \, d\theta \, d\varphi =$$

$$= -\frac{1}{2}\int_0^{\pi/2}\cos\theta \, d\cos\theta = -\frac{1}{4}\cos^2\theta\Big|_0^{\pi/2} = \frac{1}{4}$$

$$\Rightarrow \boxed{\Phi = nc\langle\cos\theta\rangle = \frac{1}{4}nc}$$

⇒ energy flux at wall

$$F = \phi E = \frac{1}{4}nEc = \frac{1}{4}uc \Rightarrow \boxed{\overset{\text{energy flux}}{F} = \frac{1}{4}uc}$$

Thermodynamics of photon gas

$$dU = TdS - pdV$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \quad \longleftarrow \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{T}{3}\left(\frac{\partial u}{\partial T}\right)_V - \frac{1}{3}u \quad \longleftarrow p = \frac{1}{3}u$$

$$\parallel$$

$$u = \frac{1}{3}T\frac{\partial u}{\partial T} - \frac{1}{3}u$$

$$\frac{4}{3}u = \frac{1}{3}T\frac{\partial u}{\partial T}$$

$$4\frac{dT}{T} = \frac{du}{u} \quad \Rightarrow \text{solve:} \quad 4\ln T = \ln(u) + a = \ln(u) + \ln(a')$$

$$\ln T^4 = \ln(u \cdot a')$$

$$u = \frac{T^4}{a'} = AT^4$$

$$\Rightarrow F = \frac{1}{4}uc = \frac{1}{4}cAT^4 = \sigma T^4 \hookrightarrow \boxed{A = \frac{4\sigma}{c}}$$

Steffen-Boltzman law: $\boxed{\overset{\text{energy flux}}{F} = \sigma T^4}$

↗ Steffen-Boltzmann constant

energy flux $= 5.67 \cdot 10^{-8}\, Js^{-1}m^{-2}K^{-4}$

Blackbody radiation

$$U = \int_0^\infty E\langle n\rangle g(\omega)d\omega = \int_0^\infty \underset{\text{photon energy}}{\hbar\omega}\, \underset{\text{mean }\#\gamma}{\langle n(\omega)\rangle}\, \underset{\#\text{states}}{g(\omega)}\, d\omega$$

Partition function of photon gas

- $n_i = \#\gamma$ with energy ε_i
- no conservation law ⇒ any number possible for any energy lvl

$$Z_\gamma = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots)} = \underbrace{\sum_{n_1=0}^{\infty} e^{-\beta n_1\varepsilon_1}}_{\frac{1}{1-e^{-\beta\varepsilon_1}}}\ \underbrace{\sum_{n_2=0}^{\infty} e^{-\beta n_2\varepsilon_2}}_{\frac{1}{1-e^{-\beta\varepsilon_2}}} \cdots\cdots$$

geometric series →

$$= \prod_{r=1}^{\infty}\frac{1}{1-e^{-\beta E_r}}$$

Mean $\#\gamma$ at level i

$$\frac{\partial \ln(Z_\gamma)}{\partial \varepsilon_i} = \frac{1}{Z_\gamma}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots -\beta n_i e^{-\beta(n_1\varepsilon_1+\cdots)} =$$

$$= -\beta \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots n_i \frac{e^{-\beta(n_1\varepsilon_1+\cdots)}}{Z_\gamma} = -\beta \sum_{n_1=0}\sum_{n_2=0}^{\infty}\cdots n_i \cdot p(n_1,n_2,\cdots)$$

$$= -\beta \langle n_i \rangle$$

$$\Rightarrow \boxed{\langle n_i\rangle = -\frac{1}{\beta}\frac{\partial \ln Z_\gamma}{\partial \varepsilon_i}}$$

$$\ln Z_\gamma = \ln\left(\prod_{r=1}^{\infty}\frac{1}{1-e^{-\beta\varepsilon_r}}\right) = \sum_{r=1}^{\infty}\ln\frac{1}{1-e^{-\beta\varepsilon_r}} = -\sum_{r=1}^{\infty}\ln(1-e^{-\beta\varepsilon_r})$$

$$\Rightarrow \langle n_i\rangle = -\frac{1}{\beta}\frac{\partial \ln Z_\gamma}{\partial \varepsilon_i} = \frac{1}{\beta}(1-e^{-\beta\varepsilon_i})^{-1}(+e^{-\beta\varepsilon_i})(-\beta) =$$

$$= \frac{1}{1-e^{-\beta\varepsilon_i}}e^{-\beta\varepsilon_i} = \frac{1}{e^{\beta\varepsilon_i}-1} \quad \text{and} \quad \varepsilon_i = \hbar\omega$$

continuous

$$\Rightarrow \boxed{\langle n(\omega)\rangle = \frac{1}{e^{\beta\hbar\omega}-1}}$$

Density of states – ideal gas of spinless particles

$$g(p)dp = V\frac{4\pi p^2}{h^3}dp \quad E = \hbar\omega = pc \Rightarrow p = \frac{\hbar\omega}{c} \Rightarrow dp = \frac{\hbar}{c}d\omega$$

$$g(\omega)d\omega = V\frac{4\pi}{h^3}\left(\frac{\hbar\omega}{c}\right)^2\frac{\hbar}{c}d\omega = \frac{V\omega^2}{2\pi^2c^3}d\omega$$

photons have 2 polarisation directions $\times 2$

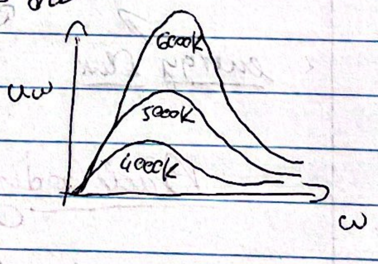
$$\boxed{g(\omega)d\omega = \frac{V\omega^2}{\pi^2c^3}d\omega}$$

$$U = \int_0^\infty \hbar\omega\langle n(\omega)\rangle g(\omega)\,d\omega = \frac{V\hbar}{\pi^2c^3}\int_0^\infty\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

$$u = \frac{U}{V} = \int_0^\infty u_\omega\, d\omega = \int_0^\infty \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

Planck's law $\Rightarrow \boxed{u_\omega(T) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}}$

energy density



Maximum in energy density

$$\frac{\partial u}{\partial\omega} = 0 = \frac{3\omega^2}{e^{\beta\hbar\omega}-1} - \left(\frac{\omega^3}{(e^{\beta\hbar\omega}-1)^2}e^{\beta\hbar\omega}\beta\hbar\right)$$

$$0 = 3\omega^2(e^{\beta\hbar\omega}-1) - \omega^3\beta\hbar e^{\beta\hbar\omega}$$

$$3 = (3-\beta\hbar\omega)e^{\beta\hbar\omega} \Rightarrow \text{solve numerically:}$$

$$\beta\hbar\omega_{max} = 2.822$$

Wien's displacement law

$$\Rightarrow \boxed{\omega_{max} = \frac{2.822k_BT}{\hbar} \approx 3.6\cdot 10^{11}T}$$

$K^{-1}s^{-1}$

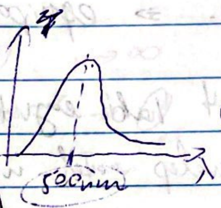
The Sun as blackbody

$T_{Sun} \approx 5800K$, $\lambda = \frac{2\pi c}{\omega}$

$\omega_{max} \approx 3.6 \cdot 10^{11} T = 2.1 \cdot 10^{15} s^{-1}$

$\lambda_m = \frac{2\pi c}{\omega_m} \approx \underline{\underline{900nm}}$

but from measurements:



(?) (?) (!)

$$u = \frac{U}{V} = \int_0^\infty u_\omega d\omega = \int_0^\infty u_\lambda d\lambda$$

$$u = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega = \frac{\hbar}{\pi^2 c^3}\int_\infty^0 \frac{\left(\frac{2\pi c}{\lambda}\right)^3}{e^{\frac{\beta hc}{\lambda}}-1}\left(-\frac{2\pi c}{\lambda^2}\right)d\lambda =$$

flip boundaries

$\omega = 2\pi c/\lambda$

$d\omega = -\frac{2\pi c}{\lambda^2}d\lambda$

$$= \frac{8\pi^3 c^3 h \cdot 2\pi c}{\pi^2 c^3\, 2\pi}\int_0^\infty \frac{1}{\lambda^5\left(e^{\beta hc/\lambda}-1\right)}d\lambda = \int_0^\infty u_\lambda d\lambda$$

$$\boxed{u_\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{(\beta hc/\lambda)}-1}}$$

energy density

$$\frac{\partial u}{\partial \lambda} = 0 \Rightarrow \left(5 - \frac{hc}{\lambda kT}\right)e^{\frac{hc}{\lambda kT}} = 5 \Rightarrow \frac{hc}{\lambda_m kT} = 4.97$$

$$\Rightarrow \boxed{\lambda_m = \frac{hc}{4.97kT} = \frac{2.9\cdot 10^{-3}}{T}}\ Km$$

$\Rightarrow$ 500nm for Sun ✓

Stefan-Boltzmann law

$x = \beta\hbar\omega = \frac{\hbar}{kT}\omega$

$$u = \int_0^\infty u_\omega(T)d\omega = \int_0^\infty \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega \overset{\downarrow}{=}$$

~~Stefan Boltzmann~~

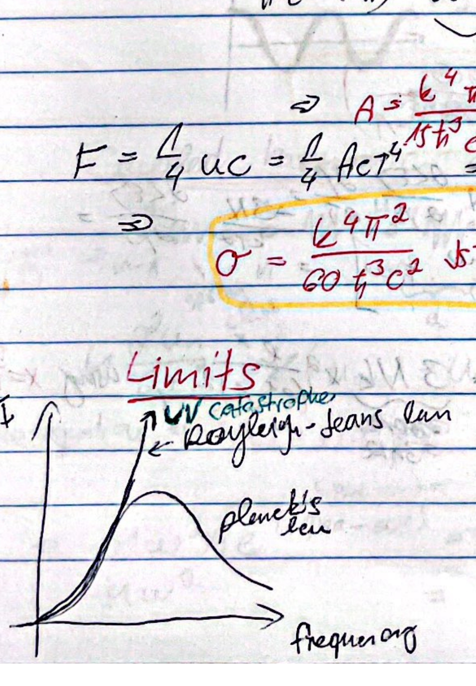
$$= \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{x^3}{e^x-1}dx}_{\pi^4/15} = \underbrace{\frac{\hbar}{\pi^2 c^3}\frac{k^4}{\hbar^4}\frac{\pi^4}{15}}_{A} T^4 = AT^4$$

$$\Rightarrow A = \frac{k^4\pi^2}{15\hbar^3 c^3}\ Jm^{-3}K^{-4}$$

$$F = \frac{1}{4}uc = \frac{1}{4}AcT^4 = \sigma T^4 \Rightarrow \sigma = \frac{Ac}{4} = \frac{c}{4}\frac{k^4\pi^2}{15\hbar^3c^3}$$

$$\Rightarrow \boxed{\sigma = \frac{k^4\pi^2}{60\hbar^3c^2}\ Js^{-1}m^{-2}K^{-4}}$$

Limits



low freq.

$\underline{\hbar\omega \ll kT}$: $u_\omega(T) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{\underbrace{e^{\beta\hbar\omega}-1}_{\sim\frac{\hbar\omega}{kT}}} \approx \underline{\underline{\frac{\omega^2}{\pi^2c^3}kT}}$

Rayleigh-Jeans (classical)

high freq.

$\hbar\omega \gg kT$:

$u_\omega(T) = -\,''\,- \approx \underline{\underline{\frac{\hbar\omega^3}{\pi^2c^3}e^{-\beta\hbar\omega}}}$

Wien's law, experimental result

Heat capacity of solids

$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} k_1 x^2 + \frac{1}{2} k_2 y^2 + \frac{1}{2} k_3 z^2$

↳ 6 deg free. ⇒ equipartition theorem: $\langle E \rangle = N \cdot 6 \cdot \frac{1}{2} kT = 3NkT$

$C_V = \frac{\partial \langle E \rangle}{\partial T} = 3Nk = 3nR$

But doesn't hold everywhere...

⇒ develop model which explains: $\begin{cases} T \to 0 \Rightarrow C \propto T^3 \\ T \gg 0 \Rightarrow C = 3R \end{cases}$

Einstein model

- 3N quantum oscillators with frequency ω $E_j = \hbar\omega(j + \frac{1}{2})$
  - ↳ calculate $\langle \varepsilon \rangle$ for 1 osc. in eq. with heat bath at T
  - ↳ multiply by 3N: $U = 3N \langle \varepsilon \rangle$
  - ↳ find $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$Z_1 = \sum_{j=0}^{\infty} e^{-\beta E_j} = \sum_{j=0}^{\infty} e^{-\beta\hbar\omega(j+1/2)} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{j=0}^{\infty} e^{-\beta\hbar\omega j} =$$

$x := \beta\hbar\omega$ $$= e^{-\frac{1}{2}x} \underbrace{\sum_{j=0}^{\infty} (e^{-x})^j}_{\text{geometric}} = e^{-\frac{1}{2}x} \frac{1}{1-e^{-x}}$$

$$\boxed{Z_1 = e^{-\frac{1}{2}x} \frac{1}{1-e^{-x}}}$$

$$F_1 = -kT \ln Z_1 = -\frac{1}{\beta} \ln Z_1 = -\frac{1}{\beta} \ln\left(e^{-x/2} \frac{1}{1-e^{-x}}\right) =$$
$$= +\frac{1}{\beta}\left(\frac{x}{2} + \ln(1-e^{-x})\right)$$

$$\langle \varepsilon \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\partial \beta F_1}{\partial \beta} = \frac{\partial \beta F_1}{\partial x}\frac{\partial x}{\partial \beta} = \hbar\omega \frac{\partial \beta F_1}{\partial x} = \hbar\omega \frac{\partial}{\partial x}\left(\frac{x}{2} + \ln(1-e^{-x})\right)$$
$$= \hbar\omega \left(\frac{1}{2} + \frac{e^{-x}}{1-e^{-x}}\right) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{x}-1}\right) = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$\boxed{\langle \varepsilon \rangle = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}}$$

$$\boxed{U = 3N\langle \varepsilon \rangle = 3N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N \frac{\partial \langle \varepsilon \rangle}{\partial T} = 3N \frac{\partial \langle \varepsilon \rangle}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{3N}{kT^2}\frac{\partial \langle \varepsilon \rangle}{\partial \beta} =$$
$$= -\frac{3N}{kT^2}\left[\frac{-\hbar\omega}{(e^{\beta\hbar\omega}-1)^2} e^{\beta\hbar\omega} \cdot \hbar\omega\right] =$$

Einstein temp.

$$= 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = \underbrace{3Nk}_{=3nR} x^2 \frac{e^x}{(e^x-1)^2}, \text{ using } x = \frac{\hbar\omega}{kT} = \frac{\Theta_E}{T}$$

$$C_V = 3nR\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$$

High temperature limit $T \to \infty$, $x \to 0$

for 1 mole:

$$C_V = 3Rx^2 \frac{(1+x+\dots)}{(1+x+\frac{x^2}{2}+\dots-1)^2} \approx 3R\frac{x^2(1+x)}{(x+\frac{x^2}{2})^2} = 3R\frac{1+x}{(1+\frac{x}{2})^2} \xrightarrow{x\to 0} 3R \checkmark$$

Low temperature limit $T \to 0$, $x \to \infty$

$$C_V = 3Rx^2\frac{e^x}{(e^x-1)^2} \to 3Rx^2e^{-x} \to 0$$ goes to 0 exponentially but not T^3 ✗

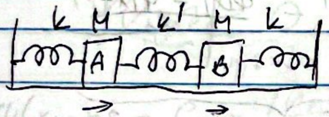
Debey model

- 3N coupled oscillators with characteristic frequencies

$$U = \sum_{j=1}^{\infty} \langle \varepsilon_j \rangle$$

$$\langle \varepsilon_j \rangle = \frac{1}{2}\hbar\omega_j + \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1}$$

Two coupled harmonic oscillators



Ⓐ $$M\frac{\partial^2 x_1}{\partial t^2} = -kx_1 - k'x_1 + k'x_2$$

$$M\frac{\partial^2 x_1}{\partial t^2} + (k+k')x_1 - k'x_2 = 0$$

Ⓑ $$M\frac{\partial^2 x_2}{\partial t^2} + (k+k')x_2 - k'x_1 = 0$$

add and subtract

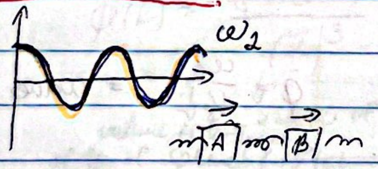
$$\frac{\partial^2(x_1+x_2)}{\partial t^2} + \omega_1^2(x_1+x_2) = 0$$

$$\frac{\partial^2(x_1-x_2)}{\partial t^2} + \omega_2^2(x_1-x_2) = 0$$

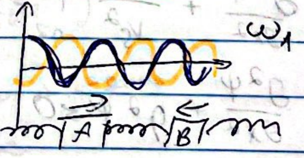
wave equations

characteristic frequencies $$\boxed{\omega_{1,2}^2 = \frac{k+k'}{M} \pm \frac{k'}{M}}$$

a) acoustic mode



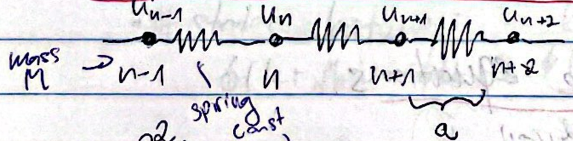
b) optical mode



, $\boxed{\omega_1 > \omega_2}$

#characteristic freq. = #oscillators

Coupled harmonic oscillators



spring const

$$M\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) - K(u_n - u_{n-1}) = K(u_{n+1} + u_{n-1} - 2u_n)$$

wave equation ⇒ $u_n = Ae^{i(qna - \omega t)}$ wave number frequency

$$\Rightarrow -M\omega^2 Ae^{i(qna-\omega t)} = +KA\left(e^{(iq(n+1)a-\omega t)} + e^{i(q(n-1)a-\omega t)} - 2e^{i(qna-\omega t)}\right)$$

$$-M\omega^2 = K(e^{iqa} + e^{-iqa} - 2)$$

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$$\omega^2 = \frac{K}{M}\left(2 - \frac{\cancel{2}(e^{iqa}+e^{-iqa})}{\cancel{2}}\right) = \frac{2K}{M}\underbrace{(1-\cos(qa))}_{=2\left(\sin\frac{qa}{2}\right)^2}$$

$$\boxed{\omega^2 = \frac{4K}{M}\sin^2\left(\frac{qa}{2}\right)}$$ - dispersion relation

for low temperature → Long-wavelength approximation

$$q = \frac{2\pi}{\lambda} \xrightarrow[\lambda\to\infty]{} 0 \Rightarrow qa \to 0 \Rightarrow \sin\left(\frac{qa}{2}\right) \to \frac{qa}{2}$$

$$\Rightarrow \omega^2 = \frac{4K}{M}\left(\frac{qa}{2}\right)^2 \Rightarrow \boxed{\omega = aq\sqrt{\frac{K}{M}} \equiv V_s q}$$

slide 102

$$V_s = a\sqrt{\frac{K}{M}}$$ velocity of sound → acoustic freq.

same order of magnitude as sound

Continuity of eq.

$$M\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1}+u_{n-1}-2u_n), \quad u_n = \Psi(na)\underbrace{e^{-i\omega t}}_{\text{cancel out}}$$

$$-M\omega^2\Psi(na) = K[\Psi((n+1)a)-\Psi(na)] - K[\Psi(na)-\Psi((n-1)a)]$$

$$-\frac{M}{Aa}\omega^2\Psi(x) = \frac{aK}{A}\underbrace{\frac{\frac{\Psi(x+a)-\Psi(x)}{a}-\frac{\Psi(x)-\Psi(x-a)}{a}}{a}}_{\Psi''(x) = \frac{\partial^2\Psi(x)}{\partial x^2}} \qquad x = na$$

A: cross-section area

$$\frac{M}{\underbrace{Aa}_{V}} = \rho \text{ density}$$

$$\frac{aK}{A} = Y \text{ Young's modulus}$$

$$\boxed{-\rho\omega^2\Psi(x) = Y\frac{\partial^2\Psi(x)}{\partial x^2}}$$

$$\sqrt{\frac{aK}{A}\frac{Aa}{M}} = a\sqrt{\frac{K}{M}} = V_s \text{ as above}$$

$$\frac{\partial^2\Psi(x)}{\partial x^2} + \frac{\omega^2}{\underbrace{\left(\frac{Y}{\rho}\right)}_{V_s}}\Psi(x) = 0$$

$$\boxed{V_s = \sqrt{\frac{Y}{\rho}}} = \text{velocity of sound}$$

$$\frac{\partial^2\Psi}{\partial x^2} + \underbrace{\frac{\omega^2}{V_s^2}}_{q^2}\Psi = 0$$

$$\boxed{q = \frac{\omega}{V_s}} = \text{wave number}$$

$$\frac{\partial^2\Psi}{\partial x^2} + q^2\Psi = 0$$

$$\boxed{\omega = qV_s \text{ linear dispersion relation}}$$

Time-dependent wave equations

Matter waves: $$\frac{\partial^2\Psi(\vec r,t)}{\partial t^2} = \underbrace{\frac{Y}{\rho}}_{V_s^2}\nabla^2\Psi(\vec r,t), \quad \Psi(\vec r,t) = \Psi(\vec r)e^{-i\omega t}$$

$$v^2\nabla^2\Psi(\vec r) = -\omega^2\Psi(\vec r)$$

$$\Rightarrow \boxed{\frac{\partial^2\Psi(\vec r)}{\partial x^2} + \frac{\partial^2\Psi(\vec r)}{\partial y^2} + \frac{\partial^2\Psi(\vec r)}{\partial z^2} + \underbrace{\frac{\omega^2}{v^2}}_{q^2 = k^2 \text{ wave number}}\Psi = 0}$$

EM waves: $\frac{\partial^2 \psi(\vec{r},t)}{\partial t^2} = \underbrace{\boxed{\frac{1}{\mu_0 \varepsilon_0}}}_{= c^2} \nabla^2 \psi(\vec{r},t)$

$\psi(\vec{r},t) = \psi(\vec{r}) e^{-i\omega t}$ ↪

$$-\omega^2 \psi(\vec{r}) = c^2 \nabla^2 \psi(\vec{r},t)$$

$$\Rightarrow \frac{\partial^2 \psi(\vec{r})}{\partial x^2} + \frac{\partial^2 \psi(\vec{r})}{\partial y^2} + \frac{\partial^2 \psi(\vec{r})}{\partial z^2} + \underbrace{\boxed{\frac{\omega^2}{c^2}}}_{= k^2} \psi(\vec{r}) = 0$$

Particles: $i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r},t)$ - Schrödinger eq. for $V = 0$

$\psi(\vec{r},t) = \psi(\vec{r}) e^{-iEt/\hbar}$ $\quad E\psi(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r})$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \underbrace{\boxed{\frac{2mE}{\hbar^2}}}_{= k^2} \psi = 0$$

↪ all: $\nabla^2 \psi + k^2 \psi = 0$

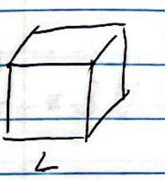
Density of states

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + k^2 \psi = 0$$

3D

boundary condition:

$\psi(x,y,z)\big|_{x,y,z = L} = 0$ on cube with sides L

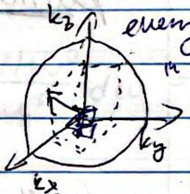


$$\psi(x,y,z) = C \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right), \quad n = 1, 2, 3, \ldots$$

↪ substitute into wave equation and solve for k

$$k^2 = \frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\vec{k} = \left(\frac{n_x \pi}{L}, \frac{n_y \pi}{L}, \frac{n_z \pi}{L}\right)$$



every cube in k-space = state

- volume of cube $\left(\frac{\pi}{L}\right)^3$

- number of cubes with $|\vec{k}| \leq k$:

$$\boxed{\phi(k) = \frac{\frac{1}{8}\left(\frac{4\pi}{3} k^3\right)}{\left(\frac{\pi}{L}\right)^3} = \frac{Vk^3}{6\pi^2}}$$

↓ volume of 1 cube in k-space

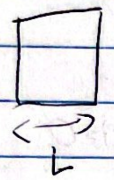
↓ volume in k-space of 1/8 of sphere $\vec{k}$: $|\vec{k}| \leq k$ = sphere but also $\vec{k} > 0 \Rightarrow 1/8$

- # states between: $k < |\vec{k}| < k + dk$

$$\phi(k + dk) - \phi(k) = \underbrace{\frac{\phi(k+dk) - \phi(k)}{dk}}_{\text{derivative}} dk = \frac{d\phi}{dk} dk = \underbrace{\frac{Vk^2}{2\pi^2}}_{g(k)} dk$$

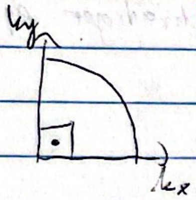
$$\boxed{g(k)\,dk = \frac{Vk^2}{2\pi^2} dk}$$

2D



$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+k^2\psi=0 \quad , \quad \psi(L,L)=0$$

$$\Rightarrow \psi(x,y)=C\sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)$$



$$k^2=\frac{\pi^2}{L^2}(n_x^2+n_y^2)$$

every square in k-space represents a state

↳ area of square: $\left(\frac{\pi}{L}\right)^2$

squares with $|\vec{k}| \leq k$: $\boxed{\phi(k)=\frac{\frac{1}{4}(\pi k^2)}{\left(\frac{\pi}{L}\right)^2}=\frac{Ak^2}{4\pi}}$

states between $k<|\vec{k}|<k+dk$

$$\Rightarrow \frac{\phi(k+dk)-\phi(k)}{dk}dk = \frac{d\phi}{dk}dk = \underbrace{\frac{Ak}{2\pi}}_{g(k)}dk$$

$$\boxed{g(k)dk=\frac{Ak}{2\pi}dk}$$

1D

similarly $\Rightarrow$ $\boxed{g(k)dk=\frac{L}{\pi}dk}$

particles

$$\left.\begin{matrix} g(p)dp \\ g(k)dk \\ g(E)dE \end{matrix}\right\} = \delta\frac{Vk^2}{2\pi^2}dk = \delta\frac{Vp^2}{2\pi^2\hbar^3}dp = \delta\frac{Vp^2 8\pi^3}{h^3 2\pi^2}dp$$

$$= \delta\frac{Vp^2 4\pi}{h^3}dp$$

$p=\hbar k \Rightarrow k=\frac{p}{\hbar}$, $dk=\frac{dp}{\hbar}$

$$= \delta\frac{4\pi V}{h^3}2mE\,dp$$

$$= \delta\frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}dE$$

$E=\frac{p^2}{2m} \Rightarrow p=\sqrt{2mE}$

$$dp=\frac{\sqrt{2m}\,dE}{2\sqrt{2mE}}=\frac{1}{2}E^{-1/2}dE$$

$$\boxed{\begin{aligned} g(k)dk &= \delta\frac{Vk^2}{2\pi^2}dk \\ g(p)dp &= \delta\frac{4\pi V}{h^3}p^2dp \\ g(E)dE &= \delta\frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}dE \end{aligned}}$$

$$\delta=\begin{cases} 1 & \text{- bosons (spin 0)} \\ 2 & \text{fermions (spin 1/2)} \Rightarrow \text{2 spin states} \end{cases}$$

photons

$$\boxed{\begin{aligned} g(k)dk &= \delta\frac{Vk^2}{2\pi^2}dk \\ g(\omega)d\omega &= \delta\frac{V}{2\pi^2c^3}\omega^2d\omega \\ g(\lambda)d\lambda &= \delta\frac{4\pi V}{\lambda^4}d\lambda \end{aligned}}$$

$\downarrow k=\frac{\omega}{c}$ $\quad E=\hbar\omega=pc$

$\downarrow k=\frac{2\pi}{\lambda}$

$\Downarrow$ $\delta=2$ Two polarisation directions

elastic wave

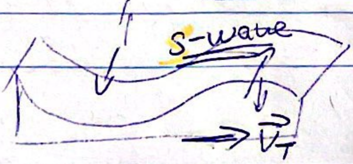
$$\boxed{\begin{aligned} g(k)dk &= \delta\frac{Vk^2}{2\pi^2}dk \\ g(q)dq &= \delta\frac{Vq^2}{2\pi^2}dq \\ g(\omega)d\omega &= \delta\frac{V\omega^2}{2\pi^2v^3}d\omega \end{aligned}}$$

$\downarrow q=k$ $\quad \delta=1,2,3$ # indep. modes

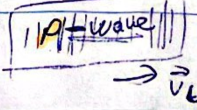
$\downarrow q=\frac{\omega}{v}$

$$\longrightarrow \frac{V\omega^2d\omega}{2\pi^2}\overbrace{\left(\frac{2}{v_T^3}+\frac{1}{v_L^3}\right)}^{=3/v_s^3}$$

2 transverse directions



1 longitudal direction $\Rightarrow 1+2=3$



Internal energy

$$U = \sum_{j=1}^{3N} \langle \varepsilon_j \rangle$$

$$g(\omega)d\omega = V \frac{3\omega^2 d\omega}{2\pi^2 V_s^2} \quad , \quad \langle \varepsilon_j \rangle = \frac{1}{2}\hbar\omega_j + \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1} \quad , \quad \omega = V_s q$$

$$U = \sum_{j=1}^{3N} \langle \varepsilon_j \rangle \underset{\uparrow}{=} \int_0^{\text{? max. freq.}} \langle \varepsilon(\omega) \rangle g(\omega)\, d\omega$$

how continuous? Can we $\Sigma \to \int$

$$q^2 = \frac{\pi^2}{L^2} n^2 \quad , \quad \omega = V_s q = V_s \frac{\pi}{L} n = V_s \frac{\pi}{Na} n$$

inv. propto size / # particles of system ⇒ for macroscopic system: ↑N, ↑L ⇒ ↓ steps

⇒ continuous ✓

max = Debey freq.

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

as said before # ω = # ~~part~~ oscillators

$$\int_0^{\omega_D} g(\omega)\, d\omega = V \int_0^{\omega_D} \frac{3\omega^2}{2\pi^2 V_s^3} d\omega = \frac{V\omega^3}{2\pi^2 V_s^3}\Big|_0^{\omega_D} = \frac{V\omega_D^3}{2\pi^2 V_s^3} = 3N$$

$$\Rightarrow \boxed{\omega_D = \left(\frac{6N\pi^2 V_s^3}{V}\right)^{1/3}} \quad \Rightarrow \quad \boxed{g(\omega)d\omega = \frac{9N\omega^2}{\omega_D^3} d\omega}$$

$$U = \int_0^{\omega_D} \langle \varepsilon(\omega) \rangle g(\omega)\, d\omega = \int_0^{\omega_D} \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right) \frac{9N\omega^2}{\omega_D^3} d\omega =$$

$$= \underbrace{\frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{1}{2}\hbar\omega^3 d\omega}_{\text{indep. of } T} + \underbrace{\frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1} d\omega}_{\text{depends on } T} \Rightarrow C_V = \frac{\partial U}{\partial T}$$

~~energy of free space~~

Heat capacity

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}\frac{\partial U}{\partial \beta} = \frac{-1}{kT^2}\frac{\partial}{\partial \beta}\left(\frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1} d\omega\right)$$

$\frac{\partial}{\partial\beta} \to 0$

$$= -\frac{1}{kT^2} \frac{9N}{\omega_D^3} \int_0^{\omega_D} \left(\frac{-\hbar\omega^3}{(e^{\beta\hbar\omega}-1)^2} e^{\beta\hbar\omega} \cdot \hbar\omega\right) d\omega =$$

$$= + \frac{\hbar^2}{kT^2} \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} d\omega =$$

$$= \left(\frac{\hbar}{kT}\right)^2 \frac{9Nk}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} d\omega =$$

$x = \beta\hbar\omega = \frac{\hbar\omega}{kT}$

$x_D = \frac{\hbar\omega_D}{kT} = \frac{\Theta_D}{T}$

$\Rightarrow \Theta_D = \frac{\hbar\omega_D}{k_B}$

↑ needs to be obtained from experiment

$$\boxed{C_V = 3Nk\left[\frac{3}{x_D^3}\int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2} dx\right]}$$

$$C_V = 3Nk\left[\frac{3}{x_D^3}\int_0^{x_D}\frac{x^4 e^x}{(e^x-1)^2}dx\right]$$

↳ high temperature limit $T >> \Theta_D \Rightarrow x_D = \frac{\Theta_D}{T} << 1$ ✓

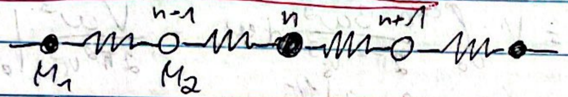
$$\frac{x^4 e^x}{(e^x-1)^2} = \frac{x^4(1+x+...)}{(1+x+\frac{x^2}{2}+...-1)^2} \approx \frac{x^4}{x^2} = x^2$$

$$C_V = 3Nk\left[\frac{3}{x_D^3}\int_0^{x_D} x^2 dx\right] = 3Nk = 3nR$$ Dulong-Petit ✓

↳ low temperature limit $T << \Theta_D \Rightarrow x_D = \frac{\Theta_D}{T} >> 1$ ✓

$$C_V \approx 3Nk\left(\frac{T}{\Theta_D}\right)^3\left[3\underbrace{\int_0^{\infty}\frac{x^4 e^x}{(e^x-1)^2}dx}_{\frac{4\pi^4}{15}}\right] = \frac{12\pi^4}{5}Nk\frac{T^3}{\Theta_D^3}$$ ✓

Coupled harmonic oscillators - diatomic chain



$$\begin{cases} M_1\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1}+u_{n-1}-2u_n) \\ M_2\frac{\partial^2 u_n}{\partial t^2} = K(u_{n+2}+u_n-2u_{n+1}) \end{cases}$$

$u_n = Ae^{i(qna-\omega t)}$

$u_{n+1} = Be^{i(q(n+1)a-\omega t)}$

$$\begin{cases} (2K-M_1\omega^2)A-(2K\cos(qa))B=0 \\ -(2K\cos(qa))A+(2K-M_1\omega^2)B=0 \end{cases}$$

↳ non-trivial solution as determinant = 0

$$(2K-M_1\omega^2)(2K-M_1\omega^2)-4K^2\cos^2(qa) = 0$$

$$\Rightarrow \boxed{\omega^2 = K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm K\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2-\frac{4\sin^2(qa)}{M_1M_2}}}$$