Review

$E = \mathcal{H}(p,q)$ $\qquad \rho(p,q) = \dfrac{e^{-\beta \mathcal{H}(p,q)}}{Z}$ $\qquad Z = \int e^{-\beta \mathcal{H}(p,q)} d\Gamma$

$$d\Gamma = \frac{dp^{3N} dq^{3N}}{(N!) h^{3N}}$$

discrete energy levels: $\rho_r = \dfrac{e^{-\beta E_r}}{Z}$ $\qquad Z = \sum_r e^{-\beta E_r}$

classical example: ideal gas

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

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$E = F + TS$ $\qquad$ and $\Rightarrow S(E,V,N)$

example: quantum oscillators (N 1-dim)

$\varepsilon_{n_k} = \hbar\omega\left(n_k + \tfrac{1}{2}\right)$ $\qquad n_k = 0,1,2,\dots$ $\qquad k = 1,2,3,\dots,N$

$$E_{n_1 n_2 \dots n_N} = \sum_{k=1}^{N} \hbar\omega\left(\tfrac{1}{2} + n_k\right) = \sum_{k=1}^{N} \varepsilon_{n_k}$$

$$\rho(n_1, n_2, \dots, n_N) = \frac{e^{-\beta E_{n_1 n_2 \dots n_N}}}{Z}$$

$$Z = \sum_{n_1, n_2, \dots, n_N} e^{-\beta E_{n_1 n_2 \dots n_N}} = \sum_{n_1, n_2, \dots, n_N} e^{-\beta \sum_{k=1}^{N} \varepsilon_{n_k}} = \sum_{n_1, n_2, \dots, n_N} \prod_{k=1}^{N} e^{-\beta \varepsilon_{n_k}}$$

$$= \prod_{k=1}^{N} \sum_{n_k=0}^{\infty} e^{-\beta \varepsilon_{n_k}} = \prod_{k=1}^{N} Z_1 = Z_1^N$$

$$Z = Z_1^N$$

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

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

$$Z_N = e^{-\frac{\beta\hbar\omega N}{2}} \frac{1}{[1-e^{-\beta\hbar\omega}]^N}$$

$$\boxed{F(T,N) = \frac{\hbar\omega N}{2} + NkT \ln(1-e^{-\beta\hbar\omega})}$$

$$P = 0, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_T = \frac{F}{N} = \frac{\hbar\omega}{2} + kT\ln(1-e^{-\beta\hbar\omega})$$

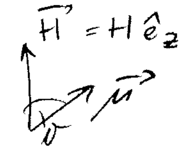
$$S = -\left(\frac{\partial F}{\partial T}\right)_N = -\left\{Nk\ln(1-e^{-\frac{\hbar\omega}{kT}}) + NkT\frac{e^{-\frac{\hbar\omega}{kT}}\left(-\frac{\hbar\omega}{kT^2}\right)}{1-e^{-\frac{\hbar\omega}{kT}}}\right\}$$

$$= -Nk\ln(1-e^{-\frac{\hbar\omega}{kT}}) + \frac{N\hbar\omega}{T}\frac{e^{-\frac{\hbar\omega}{kT}}}{1-e^{-\frac{\hbar\omega}{kT}}} \qquad = \frac{1}{e^{\frac{\hbar\omega}{kT}}-1}$$

$$\boxed{E = F + TS = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}}$$

(compare with microcanonical result in class)

Classical Description of Paramagnetism



dipole gas: N identical localised magnetic moments $\quad \varepsilon_i = -\vec{\mu}_i \cdot \vec{H} = -\mu H \cos\vartheta$

distinguishable ! $\quad |\vec{\mu}_i| = \mu = \text{fix} \quad E = \sum_{i=1}^{N} \varepsilon_i \quad$ indep!

$$Z_N = Z_1^{\,N}$$

$$\boxed{Z_1 = \int \sin\vartheta\, d\vartheta\, d\varphi \; e^{-\beta(-\mu H \cos\vartheta)} = 2\pi \int_0^{\pi} \sin\vartheta\, d\vartheta \; e^{\beta\mu H \cos\vartheta}}$$

$$\langle \mu^z \rangle = \frac{\int \sin\vartheta\, d\vartheta\, d\varphi \; \mu\cos\vartheta \; e^{\beta\mu H \cos\vartheta}}{Z_1}$$

total magnetisation:

$$M_z = \langle \sum_{i=1}^{N} \mu_i^z \rangle = N\langle \mu^z \rangle = N\mu\langle \cos\vartheta \rangle = N\frac{\partial}{\partial(\beta H)} \ln Z_1$$

$$M_x = M_y = \langle \sum_{i=1}^{N} \mu_i^{x,y} \rangle = N\langle \mu^{x,y} \rangle = N\mu \left\langle \begin{matrix} \sin\vartheta\cos\varphi \\ \sin\vartheta\sin\varphi \end{matrix} \right\rangle = \emptyset$$

axial symmetry

$$Z_1 = 2\pi \int_0^{\pi} \sin\vartheta\, d\vartheta \; e^{\beta\mu H\cos\vartheta} = 2\pi \int_0^{\pi} -d(\cos\vartheta)\; e^{\beta\mu H \cos\vartheta} \underset{x \equiv \cos\vartheta}{=}$$

$$= 2\pi \int_{-1}^{1} dx\, e^{\beta\mu H x} = 2\pi\, \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{\beta\mu H} = \frac{4\pi}{\beta\mu H} \sinh(\beta\mu H)$$

magnetisation per spin:

$$m_z \equiv \frac{M_z}{N} = \langle \mu^z \rangle = \frac{\partial}{\partial(\beta H)} \ln Z_1 = \frac{\partial}{\partial(\beta H)} \ln\left[\frac{4\pi}{\beta H\mu} \sinh(\beta H\mu)\right] =$$

$$= \frac{\cosh(\beta H\mu)}{\sinh(\beta H\mu)} \cdot \mu - \frac{1}{\beta H} = \mu \underbrace{\left\{ \coth(\beta H\mu) - \frac{1}{\beta H\mu} \right\}}_{\text{Langevin function}}$$

$$\langle \mu^z \rangle = \mu \left\{ \coth(u) - \frac{1}{u} \right\} = \mu L(u) \qquad u = \beta H \mu$$

$\swarrow$ Langevin function

$$u = \frac{H\mu}{kT} \to \infty \qquad \text{(low temperatures / strong field limit)}$$

$$\langle \mu^z \rangle \simeq \mu \qquad \text{(fully alligned with } \vec{H}\text{)}$$

$$u = \frac{H\mu}{kT} \ll 1 : \qquad \text{(high temperature / weak field limit)}$$

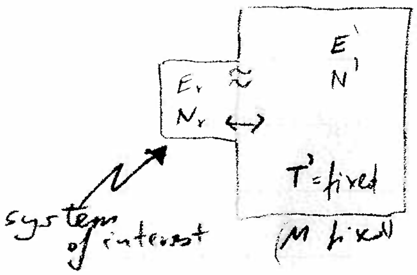
$$\coth(u) \simeq \frac{1}{u} + \frac{1}{3} u + o(u^3)$$

$$L(u) = \frac{1}{3} u + o(u^3)$$

$$m_z \quad \langle \mu^z \rangle \simeq \frac{1}{3} \mu \beta H \mu = \frac{1}{3} \frac{H\mu^2}{kT}$$

$$\chi = \lim_{H \to 0} \left(\frac{\partial M_z}{\partial H} \right) \simeq \frac{1}{3} \frac{N\mu^2}{kT} = \frac{\text{const.}}{T} \qquad \text{Curie-law}$$

Grand Canonical Ensemble



$$E_r + E' = E^{(0)} \qquad E_r \ll E' \lesssim E^{(0)}$$

$$N + N' = N^{(0)} \qquad N \ll N' \lesssim N^{(0)}$$

state r: E_r, N $\qquad$ classical systems: $r \to (p, q)$

$$\rho_{r,N} = \frac{\Omega'(E^{(0)} - E_r,\ N^{(0)} - N)}{\Omega^{(0)}(E^{(0)}, N^{(0)})} \qquad \begin{array}{l} E_r \ll E^{(0)} \\ N \ll N^{(0)} \end{array}$$

$$\ln \rho_{r,N} \simeq \text{const.} - \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E' = E^{(0)}} E_r - \left.\frac{\partial \ln \Omega'}{\partial N'}\right|_{N' = N^{(0)}} N$$

$$\frac{1}{kT'} = \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{N'} \qquad -\frac{\mu'}{kT'} = \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{E'}$$

$$\frac{1}{kT'} = \frac{1}{kT} \qquad -\frac{\mu'}{kT'} = -\frac{\mu}{kT}$$

$$\ln \rho_{r,N} \simeq \text{const.} - \left(\frac{E_r}{kT} - \frac{\mu N}{kT}\right)$$

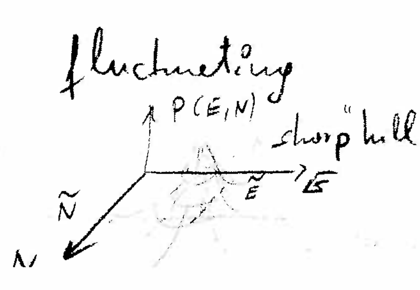
$$\rho_{r,N} = \frac{e^{-\beta(E_r - \mu N)}}{Z_G}$$

probability that the system is in state r with energy E_r and N particles

$$Z_G = \sum_{N,r} e^{-\beta(E_r - \mu N)} \qquad N = 0, 1, 2, \ldots, N^{(0)}$$

both E and N are fluctuating variables!

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E\rangle} \sim \frac{1}{\sqrt{N}} \qquad \frac{\sqrt{\langle(\Delta N)^2\rangle}}{\langle N\rangle} \sim \frac{1}{\sqrt{N}}$$



$$P(E,N) = \frac{g_N(E)\, e^{-\beta(E-\mu N)}}{Z_G}$$ E, N are fluctuating

$$Z_G = \sum_{N=0}^{\infty} \int g_N(E)\, e^{-\beta(E-\mu N)}\, dE$$ grand partition function

$$Z_G \approx g_{\tilde{N}}(\tilde{E})\, e^{-\beta(\tilde{E}-\mu\tilde{N})}\, \delta E$$

$$\ln Z_G \approx \ln g_{\tilde{N}}(\tilde{E}) - \beta\tilde{E} + \beta\mu\tilde{N}$$ $\tilde{E} \approx E$, $\tilde{N} \approx N$

$$\underbrace{-kT \ln Z_G}_{} = -T\,\underbrace{k \ln g_N(E)}_{S} + E - \mu N$$

Landau or Grand Thermodynamic Potential $E(S,V,N)$

$$\boxed{\phi = E - TS - \mu N} = \phi(T,V,\mu) = -PV$$

$$dE = T\,dS - P\,dV + \mu\,dN$$
$$d\phi = -S\,dT - P\,dV - N\,d\mu$$

$$S = -\left(\frac{\partial\phi}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial\phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial\phi}{\partial \mu}\right)_{T,V}$$

$$\boxed{\phi(T,V,\mu) = -kT \ln Z_G}$$

example: ideal Gas $\quad \tau : (p,q)$ $\quad \mathcal{H}(p,q) = \sum_{i=1}^{N} \frac{p_i^2}{2m}$ $\quad e^{-\beta(\mathcal{H}_N(p,q) - \mu N)}$

$$Z_G = \sum_{N=0}^{\infty} \int \frac{dp^{3N} dq^{3N}}{N! h^{3N}} e^{-\frac{\beta}{2m}\sum_{i=1}^{3N} p_i^2} e^{+\beta\mu N} = \sum_{N=0}^{\infty} \frac{1}{N!} Z_1^N e^{\beta\mu N}$$

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

$$\phi(T,V,\mu) = -kT \ln Z_G$$

$$\boxed{\phi(T,V,\mu) = -kT Z_1 \, e^{\mu/kT}}$$

from last class
$$Z_1 = \frac{V}{h^3}(2\pi m kT)^{3/2}$$

$$\phi(T,V,\mu) = -kT \frac{V}{h^3}(2\pi m kT)^{3/2} e^{\mu/kT}$$

$$\left.\begin{aligned} N &= -\left(\frac{\partial \phi}{\partial \mu}\right)_{T,V} = -\frac{1}{kT}\phi \\ P &= -\left(\frac{\partial \phi}{\partial V}\right)_{T,\mu} = -\frac{\phi}{V} \end{aligned}\right\} \quad PV = NkT \quad \Rightarrow \phi = -NkT$$

$$S = -\left(\frac{\partial \phi}{\partial T}\right)_{V,\mu} = -\frac{5}{2}\frac{1}{T}\phi + \frac{\mu}{kT^2}\phi = \frac{5}{2}Nk + \frac{\mu}{kT^2}\phi =$$

$$= \frac{5}{2}Nk - \frac{\mu}{kT^2}PV = \frac{5}{2}Nk - \frac{\mu N}{T}$$

$$E = \phi + TS + \mu N = -NkT + \frac{5}{2}NkT - \mu N + \mu N = \frac{3}{2}NkT$$