Isolated system : $V$ , $\delta Q = 0$ , $\delta N = 0$

$i$ , $j$ , ....

$P_i = P_j$ $\quad$ $E_i = E_j$

$T$ , $\underline{V}$ , $\underline{N}$ $\quad$ $E_i \neq E_j$

$\delta Q \neq 0$ $\quad$ $P_i = ?$ $P_j = ?$

$T$ , $V$ , $\underline{\mu}$ $\quad$ $P_i = ?$ $P_j = ?$

$E$ $\quad$ $N$

$$P_i = \frac{W_i}{W} \quad W = \sum_i W_i$$

① $\underline{V}$, $\underline{N}$, $\underline{E}$ $\quad$ micro-canonical ensemble

$P_i = P_j$ $\quad$ $\Omega(N, V, E) = \#$ of microstates

$$\underline{P_i = P_j = \frac{1}{\Omega}}$$

$$\underline{E = T \cdot S - PV + \mu \cdot N} \quad E(S, V, N)$$

$$\underline{dE = TdS - Pd\underline{V} + \mu dN}$$

$$dS = \frac{p\,dV}{T} + \frac{dE}{T} - \frac{\mu\,dN}{T}$$

$S(\underline{V, N, E})$

$S$ : characteristic → function of Micro-canonical ensemble.

$$S = -k_B \left( \sum P_i \ln P_i \right)$$

$$= -k_B \left( \sum P_i \ln \frac{1}{\Omega} \right)$$

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

② canonical ensemble

$\underline{T,\ V,\ N}$

$$\underbrace{E - TS} = \underbrace{-pV + \mu N}$$

$$\underbrace{dE - d(TS)}_{d(E-TS)} = T\,dS - p\,dV + \mu\,dN - T\,dS - S\,dT$$

$$= -S\,dT - p\,dV + \mu\,dN$$

$$\underbrace{d(E - TS)}_{-pV + \mu N} \qquad (\underline{T}, \underline{V}, \underline{N})$$

↳ characteristic function of canonical ensemble

$$A = E - TS = -k_B T \ln Q(N, V, T)$$

$$Q = \sum_i e^{-\beta E_i} \qquad P_i = e^{-\beta E_i} / Q$$

③ Grand - Canonical Ensemble

$\underline{T}, V, \underline{\mu}$

$$\underbrace{E - TS - \mu N} = -PV$$

$$d(E - TS - \mu N) = TdS - PdV + \mu dN - TdS - SdT - \mu dN - Nd\mu$$

$$\underset{(-PV)}{d(E - TS - \mu N)} = -SdT - PdV - Nd\mu$$

$$(T, V, \mu)$$

↳ C.F. G.C.E.

$$PV = + k_B T \ln \Xi$$

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q(N, V, T)$$

$$P_i(N) = \frac{e^{\beta\mu N} e^{-\beta E_i(N)}}{\Xi}$$

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\left(\sum_{E_I} \Omega(N, V, E) e^{-\beta E_I}\right)}_{Q(N,V,T)}$$

$$\underline{S} = k_B \ln \Omega$$

$$\beta TS = \ln \Omega$$

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

$$\beta TS - \beta E = \ln Q$$

$$-\beta A = \ln Q$$

$$\beta TS - \beta E + \beta \mu N = \ln \Xi$$

single component / single phase

Control macro state var — Characteristic function — Partition function

$N, V, E$ $\quad \beta TS = \ln \Omega(N,V,E)$

$N, V, T$ $\quad \underbrace{\beta TS - \beta E}_{-\beta A} = \ln \sum_{E_I} \Omega(N,V,E)\, e^{-\beta E_I}$

$\beta PV - \beta \mu N$

$\mu, V, E$ $\quad \underbrace{\beta TS + \beta \mu N} = \ln \sum_{N=0}^{\infty} e^{\beta \mu N}\, \Omega(N,V,E)$

$\underbrace{\beta E + \beta PV}$

$\beta(E + PV) \rightarrow \beta H$

$N, \beta P, E$ $\quad \underline{\beta TS - \beta PV} = \sum_{V} \Omega(N,V,E)\, e^{-\beta PV}$

$\underline{\beta E - \beta \mu N}$

$\mu, V, T$ $\quad \beta TS - \beta E + \beta \mu N = \underbrace{\sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{E_I} \Omega(N,V,E)\, e^{-\beta E_I}}_{\Xi}$

$\beta PV$

$N, P, T$ $\quad \beta TS - \beta E_I - \beta PV = \sum_{V} e^{-\beta PV} \sum_{E_I} \Omega(N,V,E)\, e^{-\beta E_I}$

$-\beta \mu N$ $\quad$ ″ $\quad \Delta$

$$\beta(TS - E - PV)$$

$$-\beta(\underbrace{E + PV - TS}_{\overset{\shortparallel}{G}})$$

$$-\beta G = \ln \Delta$$

$\beta\mu, \beta P, E$

$$= \ln \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{V} \Omega(N,V,E)\, e^{-\beta PV}$$

$$\beta TS - \beta PV + \beta\mu N$$

$$\beta E$$

$\mu, P, T$

$$= \ln\Big( \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{V} e^{-\beta PV} \underbrace{\sum_{E_I} \Omega(N,V,E)\, e^{-\beta E_I}}_{Q(N,V,T)} \Big)$$

$$\beta TS - \underbrace{\beta E}_{6} - \beta PV + \beta\mu N$$

$$= \underbrace{\underbrace{\phantom{Q(N,V,T)}}_{f(N,P,T)}}_{g(\mu,P,T)}$$

Gibbs Phase Role:

max # of independent intensive variables

= # of componts − # of phases + 2

$= 1 - 1 + 2 = 2$

hamiltonian

$$\underbrace{\mathcal{H}}\underbrace{\psi}_{\text{DOF}} = \underbrace{E}\psi$$

DOF

Degrees of freedom

$$\psi \; \{a_1, a_2, a_3 \cdots, b_1, b_2, b_3 \cdots ; c_1, c_2, c_3 \cdots\}$$

① $\mathcal{H} = \mathcal{H}_a + \mathcal{H}_b + \mathcal{H}_c$

$$\underbrace{\{a_1, a_2, a_n\}}_{\text{subsystem}} \quad \underbrace{\{b_1, b_2, b_3 \ldots\}}_{\text{subsystem}} \quad \underbrace{\{c_1, c_2, c_3, \cdots\}}_{\text{subsystem.}}$$

②

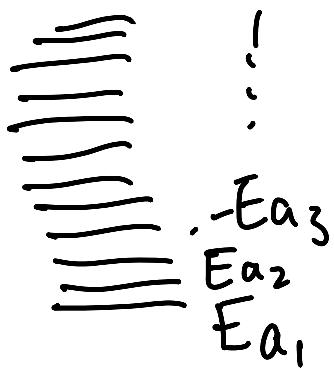
$$\psi(a_1 a_2 a_3 \ldots b_1 b_2 b_3 \ldots)$$

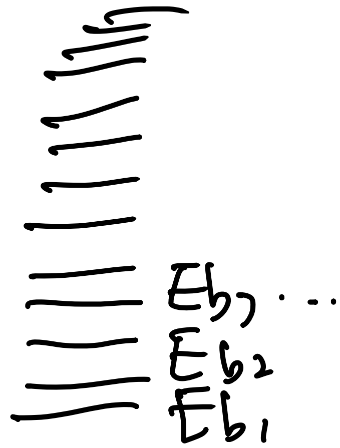
$$= \psi_a(a_1, a_2, \ldots)\psi_b(b_1, b_2 \ldots b_3 \ldots)\psi_c(c_1 c_2 c_3 \ldots) \ldots$$

independent of each other

a, b, c independent subsystems.

$$\mathcal{H}_a \psi_a = E_a \psi_a \qquad \mathcal{H}_b \psi_b = E_b \psi_b$$




$$\mathcal{H}\psi = (\mathcal{H}_a + \mathcal{H}_b)\psi_a \psi_b$$

$$= \psi_b \mathcal{H}_a \psi_a + \psi_a \mathcal{H}_b \psi_b$$

$$= (E_a + E_b)\psi$$

$E_{b1},\ E_{b2}\ E_{b3} \cdots$

$E_{a1},\ E_{a2} \ \cdots$

$$\underbrace{E_{a1} + E_{b1}} \qquad E_{a1} + E_{b2} \qquad E_{a2} + E_{b1} \quad \cdots$$

$$Q = \sum_I e^{-\beta E} = \sum_{i,j} e^{-\beta(E_{ai} + E_{bj})}$$

$$= \sum_{i,j} e^{-\beta E_{ai}} e^{-\beta E_{bj}}$$

$$= \underbrace{\sum_i e^{-\beta E_{ai}}}\ \sum_j e^{-\beta E_{bj}}$$

$$= q_a \cdot q_b$$

Distinguishible systems.

Indistinguishible systems:

$a \qquad a \qquad a$

$$\frac{(E_{a_2} + E_{a_3})}{(E_{a_3} + E_{a_2})} \qquad \frac{1}{2}$$

$$\frac{q_a \cdot q_a}{2} \qquad \frac{q_a^3}{3!}$$

N independent indistinguishible subsystems

$$Q = \frac{q^N}{N!} \qquad Q = \frac{q^N}{N!}$$

$pV = nRT$

↳ mol number

$= \frac{N}{A_0} \cdot RT \qquad \frac{R}{A_0} = k_B$

$pV = N k_B T \qquad \beta pV = \bar{N}$

$\bar{N}$ , $PV$,    Grand Canonical Ensemble

$\Xi \qquad \lambda = e^{\beta\mu}$

$$\Xi = \sum_{N\geq 0} e^{\beta\mu N} \frac{q^N}{N!} = \sum_{N\geq 0}^{\infty} \lambda^N \cdot \frac{q^N}{N!} = \underline{\sum_{N\geq 0}^{\infty} \frac{(\lambda q)^N}{N!}}$$

$$= 1 + \frac{\lambda q}{1} + \frac{(\lambda q)^2}{2!} + \frac{(\lambda q)^3}{3!} + \cdots = e^{\lambda q}$$

$$\ln \Xi = \beta \underline{PV} \qquad \ln \Xi = \lambda q$$

$$\underline{\beta PV} = \lambda q$$

$$\bar{N} = \frac{1}{\Xi} \sum_{N\geq 0}^{\infty} N \cdot e^{\beta\mu N} \cdot Q(N,V,T)$$

---

$$= \frac{1}{\Xi} \sum_{N\geq 0}^{\infty} \cdot \lambda^N \cdot \frac{q^N}{(N-1)!} \qquad N' = N-1$$

$$= \frac{\lambda q}{\Xi} \underbrace{\sum_{N\geq 1}^{\infty} \frac{(\lambda q)^{(N-1)}}{(N-1)!}} \qquad \underbrace{\sum_{N'\geq 0}^{\infty} \frac{\lambda q^{N'}}{N'!}}_{\Xi}$$

$$\bar{N} = \lambda q \qquad \therefore \beta PV = \bar{N}$$

$$\underline{\beta P = \rho}$$

1, 2, 3, ...., .

distinguishible independent subsystem.

$q_1 = \sum_i e^{-\beta E_{1i}}$ $\quad q_2 = \sum_j e^{-\beta E_{2j}}$ $\quad q_3 = \sum_k e^{-\beta E_{3k}}$

$Q = q_1 \cdot q_2 \cdot q_3 \cdot \cdots$

1 at $i$, & 2 at $j$ & 3 at $k$, ....

$$p(1i, 2j, 3k, \cdots) = \frac{e^{-\beta(E_{1i}+E_{2j}+E_{3k}+\cdots)}}{Q}$$

1 at $i$, regardless of other subsystems:

$$\sum_j \sum_k \sum_{\cdots} p(1i, 2j, 3k, \cdots)$$

$$= \frac{1}{Q} \sum_j \sum_k \sum_{\cdots} e^{-\beta E_{1i}} e^{-\beta(E_{2j}+E_{3k}+\cdots)}$$

$$= \frac{e^{-\beta E_{1i}}}{q_1} = \eta_{1i}$$

$N$, indistinguishible independent subsystems

One of subsystem at $i$, regardless of others:

$N$, 1 $q$ $\quad Q = \frac{q^N}{N!}$

$$n_i = \frac{e^{-\beta E_i}\ Q(N-1)}{Q(N)} = \frac{e^{-\beta E_i} \cdot \frac{q^{N-1}}{(N-1)!}}{q^N/N!} = \frac{N \cdot e^{-\beta E_i}}{q}$$

$$\bar{N}_i = n_i = N \cdot \frac{e^{-\beta E_i}}{q}$$

$$\frac{\bar{N}_i}{N} = C_i = \frac{e^{-\beta E_i}}{q}$$ fraction in $i$

Independent :

1 D Ising model :

$\cdots\cdots \uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow \cdots\cdots$

$\sigma : \uparrow\ +1$

$\downarrow\ -1$

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}$$

$J$ , $-J$

$\uparrow\downarrow$ unfavorable

$\uparrow\uparrow$ favorable

$\downarrow\downarrow$

$N=2$

$\uparrow\uparrow$ $\downarrow\downarrow$ $\uparrow\downarrow$ $\downarrow\uparrow$

$e^{+\beta J}$ $e^{+\beta J}$ $e^{-\beta J}$ $e^{-\beta J}$

$$Q_2 = w(\uparrow\uparrow) + w(\downarrow\downarrow) + w(\uparrow\downarrow) + w(\downarrow\uparrow)$$

$$= 2(e^{\beta J} + e^{-\beta J})$$

$$Q_N = \sum_{\sigma_1=-1}^{1}\sum_{\sigma_2=-1}^{1}\cdots\sum_{\sigma_i=-1}^{1}\cdots\sum_{\sigma_N=-1}^{1} e^{+\beta J\sum_{i'=1}^{N-1}\sigma_{i'}\cdot\sigma_{i'+1}}$$

$$\underbrace{\cdots\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow}_{N} \qquad Q_{N-1} \to Q_N$$

$Q_N\uparrow$

$Q_N\downarrow$

$Q_{N-1}\uparrow$

$Q_{N-1}\downarrow$

$$Q_N = Q_N\uparrow + Q_N\downarrow$$

$$Q_{N-1} = \sum_{\sigma_{N-1}=-1}^{1}\underbrace{\sum\cdots\sum}_{1\cdots N-1} e^{\beta J\sum_{i=1}^{N-2}\sigma_i\cdot\sigma_{i+1}}$$

$$= \underbrace{\sum\cdots\sum}_{N-2} e^{-\beta J\sum_{i=1}^{N-2}\sigma_i\cdot\sigma_{i+1}}\,(\sigma_{N-1}=-1)$$

$$+ \underbrace{\sum\cdots\sum}_{N-2} e^{+\beta J\sum_{i=1}^{N-2}\sigma_i\cdot\sigma_{i+1}}\,(\sigma_{N-1}=+1)$$

$$Q_{N-1}\uparrow = \underbrace{\sum\cdots\sum}_{N-2} e^{+\beta J\sum_{i=1}^{N-2}\sigma_i\cdot\sigma_{i+1}}\,(\sigma_{N-1}=+1)$$

$$Q_{N-1}\downarrow = \underbrace{\sum\cdots\sum}_{N-2} e^{+\beta J\sum_{i=1}^{N-2}\sigma_i\cdot\sigma_{i+1}}\,(\sigma_{N-1}=-1)$$

$$Q_N\uparrow = \underbrace{\sum\cdots\sum}_{N-1} e^{+\beta J\underbrace{\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}}}\,(\sigma_N=+1)$$

$$= \underbrace{\sum \cdots \sum}_{N-1} e^{+\beta J\left(\sum_{i=1}^{N-2} \sigma_i \sigma_{i+1}\right)} e^{+\beta J \sigma_{N-1} \sigma_{N}}$$

$$= \underbrace{\sum \sum}_{N-2} e^{+\beta J\left(\sum_{i=1}^{N-2} \sigma_i \sigma_{i+1} (\sigma_{N-1} = +1)\right)} \underline{e^{+\beta J^{+1\,+1}}}$$

$$+ \underbrace{\sum \sum}_{N-2} e^{+\beta J\left(\sum_{i=1}^{N-2} \sigma_i \sigma_{i+1} (\sigma_{N-1} = -1)\right)} \underline{e^{+\beta J^{+1 \times +1}}}$$

$$= e^{+\beta J} \cdot Q_{N-1,\uparrow} + e^{-\beta J} \cdot Q_{N-1,\downarrow}$$

$$Q_{N,\uparrow} = e^{+\beta J} \cdot Q_{N-1\uparrow} + e^{-\beta J} \cdot Q_{N-1\downarrow}$$

$$Q_{N,\downarrow} = e^{-\beta J}\, Q_{N-1\uparrow} + e^{+\beta J} \cdot Q_{N-1\downarrow}$$

$$\begin{bmatrix} Q_{N\uparrow} \\ Q_{N\downarrow} \end{bmatrix} = \underbrace{\begin{bmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{bmatrix}}_{T} \begin{bmatrix} Q_{N-1\uparrow} \\ Q_{N-1\downarrow} \end{bmatrix}$$

$$\begin{bmatrix} Q_N\uparrow \\ Q_N\downarrow \end{bmatrix} = \underline{\underline{T}}^{N-1} \begin{bmatrix} Q_1\uparrow \\ Q_1\downarrow \end{bmatrix} \qquad \begin{bmatrix} Q_2\uparrow \\ Q_2\downarrow \end{bmatrix} = T \begin{bmatrix} Q_1\uparrow \\ Q_1\downarrow \end{bmatrix}$$

$$Q_2\downarrow = e^{\beta J} + e^{-\beta J}$$

$$\underbrace{\underset{=}{\uparrow\uparrow} \quad \underset{=}{\downarrow\downarrow} \quad \underset{=}{\uparrow\downarrow} \quad \underset{=}{\downarrow\uparrow}}$$

$$e^{\beta J} Q_1\uparrow + e^{-\beta J} Q_1\downarrow$$

$$= e^{\beta J} + e^{-\beta J}$$

$$Q_2\uparrow = e^{\beta J} + e^{-\beta J} \qquad Q_1\uparrow = 1$$

$$x = \beta J \qquad Q_1\downarrow = 1$$

$$\overbrace{\underbrace{\begin{bmatrix} e^x & e^{-x} \\ e^{-x} & e^x \end{bmatrix} \begin{bmatrix} & \\ & \end{bmatrix}} \begin{bmatrix} & \\ & \end{bmatrix}}^{N-1}$$

$$\begin{bmatrix} e^x & e^{-x} \\ e^{-x} & e^x \end{bmatrix} \begin{bmatrix} e^x & e^{-x} \\ e^{-x} & e^x \end{bmatrix}$$

$$\downarrow$$

$$\begin{bmatrix} (e^x+e^{-x})^2 & (e^x+e^{-x})^2 \\ (e^x+e^{-x})^2 & (e^x+e^{-x})^2 \end{bmatrix}$$

$$\begin{bmatrix} Q_N\uparrow \\ Q_N\downarrow \end{bmatrix} \qquad T^{N-1} = \begin{bmatrix} (e^x+e^{-x})^{N-1} & (e^x+e^{-x})^{N-1} \\ (e^x+e^{-x})^{N-1} & (e^x+e^{-x})^{N-1} \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$Q_N = 2\,(\underline{e^x + e^{-x}})^{N-1}$$

$$\sinh = \frac{e^x - e^{-x}}{2} \qquad x = \beta J$$

$$\cosh = \frac{e^x + e^{-x}}{2} \qquad Q_N = 2(2\cosh x)^{N-1}$$

$$\tanh = \frac{\sinh^2}{\cosh} \qquad = 2(2\cosh \beta J)^{N-1}$$

$$A = -k_B T \ln Q$$

$\mu$:

$$= -k_B T \ln 2 - k_B T (N-2) \ln(2\cosh \beta J)$$

$$\left(\frac{\partial A}{\partial N}\right) = -k_B T \ln(2\cosh \beta J)$$

$S$:

$$\left(\frac{\partial \mu}{\partial T}\right)_V = k_B \ln(2\cosh \beta J) - \frac{J}{T} \tanh \beta J$$