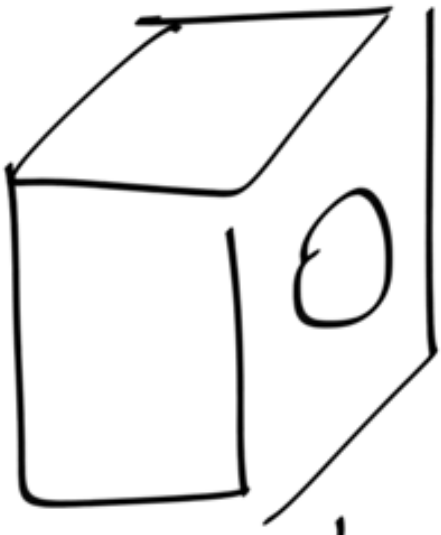
Thermodynamics

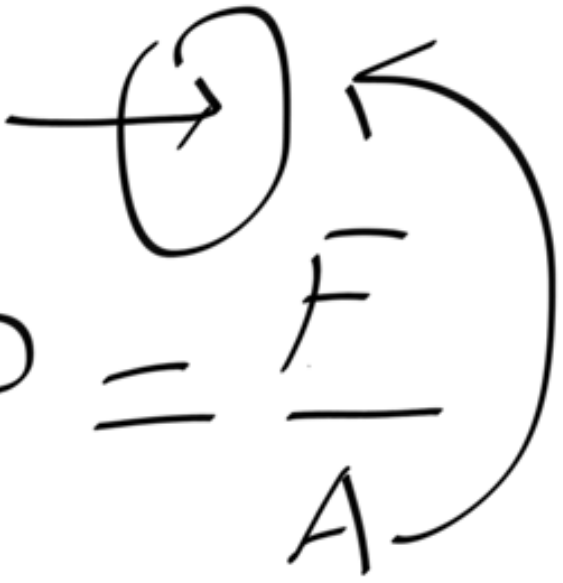
① $dU = \delta Q + \delta W$

② $dS = \frac{\delta Q}{T}$ (reversible)

③ $\lim_{T \to 0} S = 0$

$dU = T\,dS + \delta W$





$$P = \frac{F}{A}$$

$$\delta W = F \cdot L$$

$$= P \cdot A \cdot L = P \cdot dV$$

$$-\delta W = -\delta W' = -P\,dV$$

$$dU = TdS - PdV + \mu dN$$

Isolated sys.

$N, V, \delta Q = 0$ $\Rightarrow S$

$\downarrow$

N, V, T

$F / A \equiv U - TS$ F

$$dF = d(U - TS) = dU - d(TS)$$

$$= TdS - PdV + \mu dN$$

$$- \overline{T}d\overline{S} - S\overline{T}d\overline{T}$$

$$= -SdT - PdV + \mu dN$$

$$G \equiv F + PV \qquad G \downarrow$$

$$dG = -SdT + VdP + \mu dN$$

$$G = \mu N = F + PV$$

$$= U + TS + PV$$

$$H \equiv U + PV$$

$$C_V = \left(\frac{dQ}{dT}\right)_{V,N} = \left(\frac{dU}{dT}\right)_{V,N}$$

$$C_P = \left(\frac{dQ}{dT}\right)_{U,N} = \left(\frac{dH}{dT}\right)_{U,N}$$

$PV = nRT$

macrostate:

microstate:

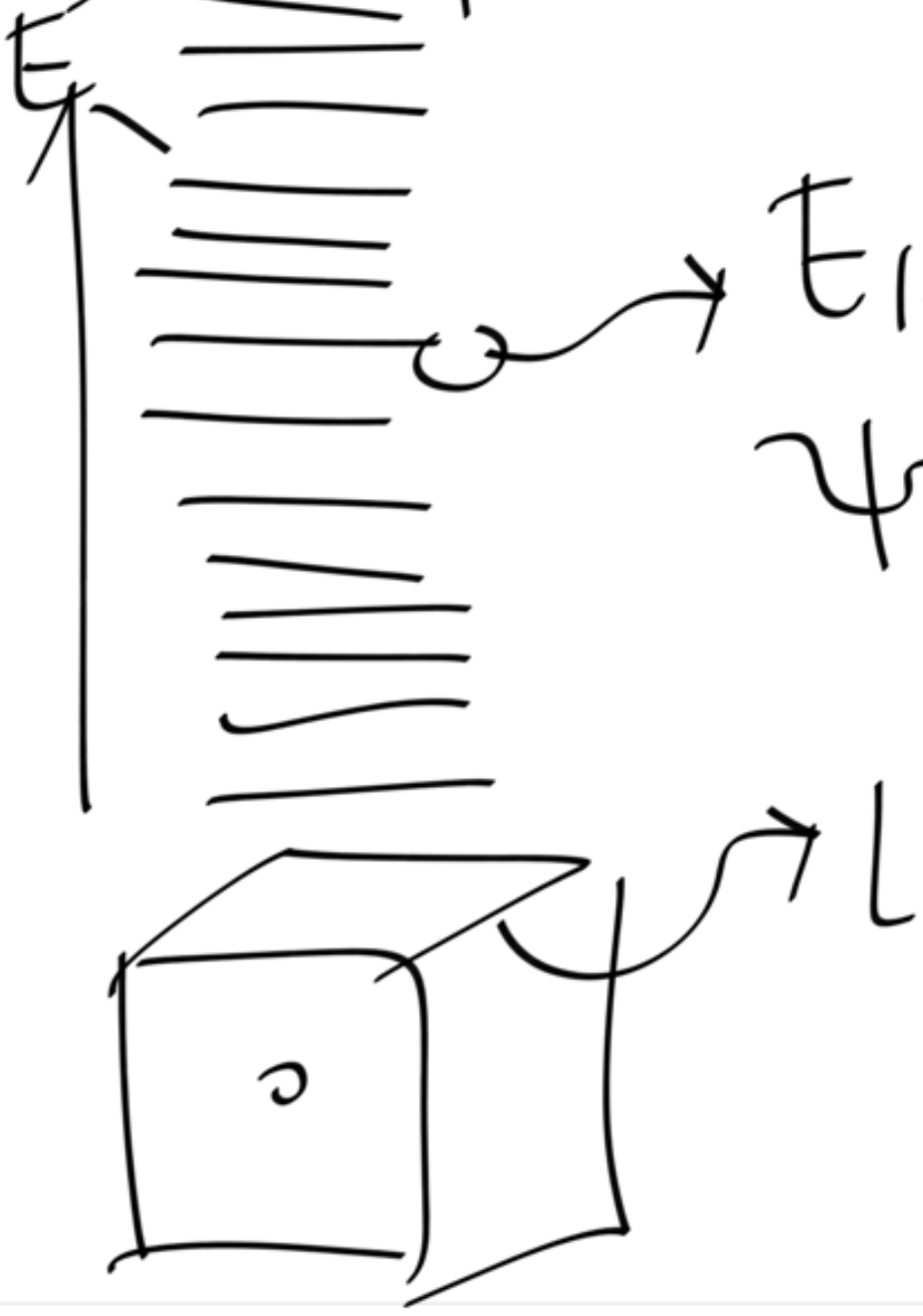
QM: $\psi(\vec{r}, t)$

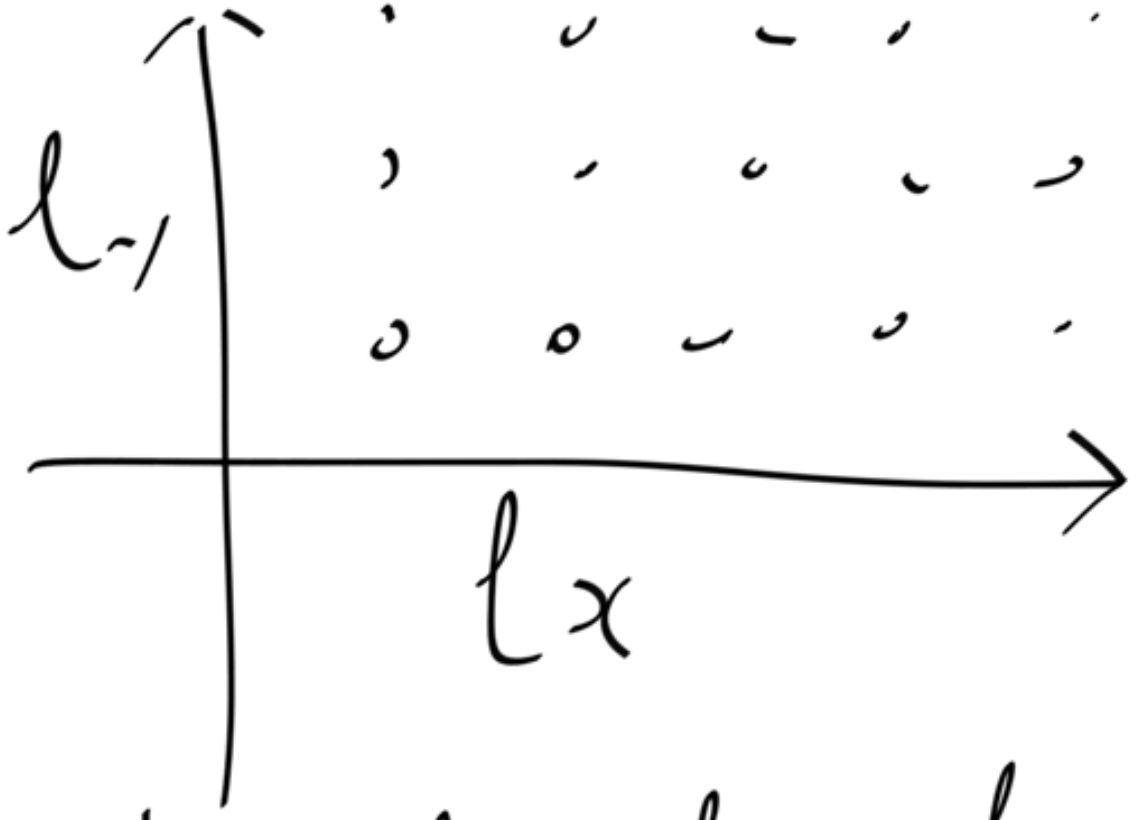
$\hat{H}(\psi(\vec{r}, t)) = i\hbar \frac{\partial \psi}{\partial t}$

$\hat{H} = \hat{K} + \hat{U}$

eg.

$$\hat{H}(\psi_r(\vec{r}) = E\psi_r(\vec{r})$$





$$\psi(l_x, l_y, l_z)$$

$$E_{l_x l_y l_z} = \frac{h^2 (l_x^2 + l_y^2 + l_z^2)}{8mL^3}$$

Mechanical / Non-mech

→ V-λ → A-T

Ensemble:

a collection of

microstates of the system.

$\psi_1, \psi_2, \psi_1, \psi_3 \ldots$

$\Omega \quad P(i) = \frac{n_i}{\Omega}$

SM 1 First postulation

$$A(t) = \lim_{t \to \infty} \frac{\int_{t_0}^{t} A(t)\,dt}{t - t_0}$$

$$= \sum_{i=1}^{M} P_i \cdot A_i$$

$$= \sum_{j=1}^{\Omega} A(j) / \Omega$$

2 postulate:

When $dE \to 0$,

$dN \to 0$

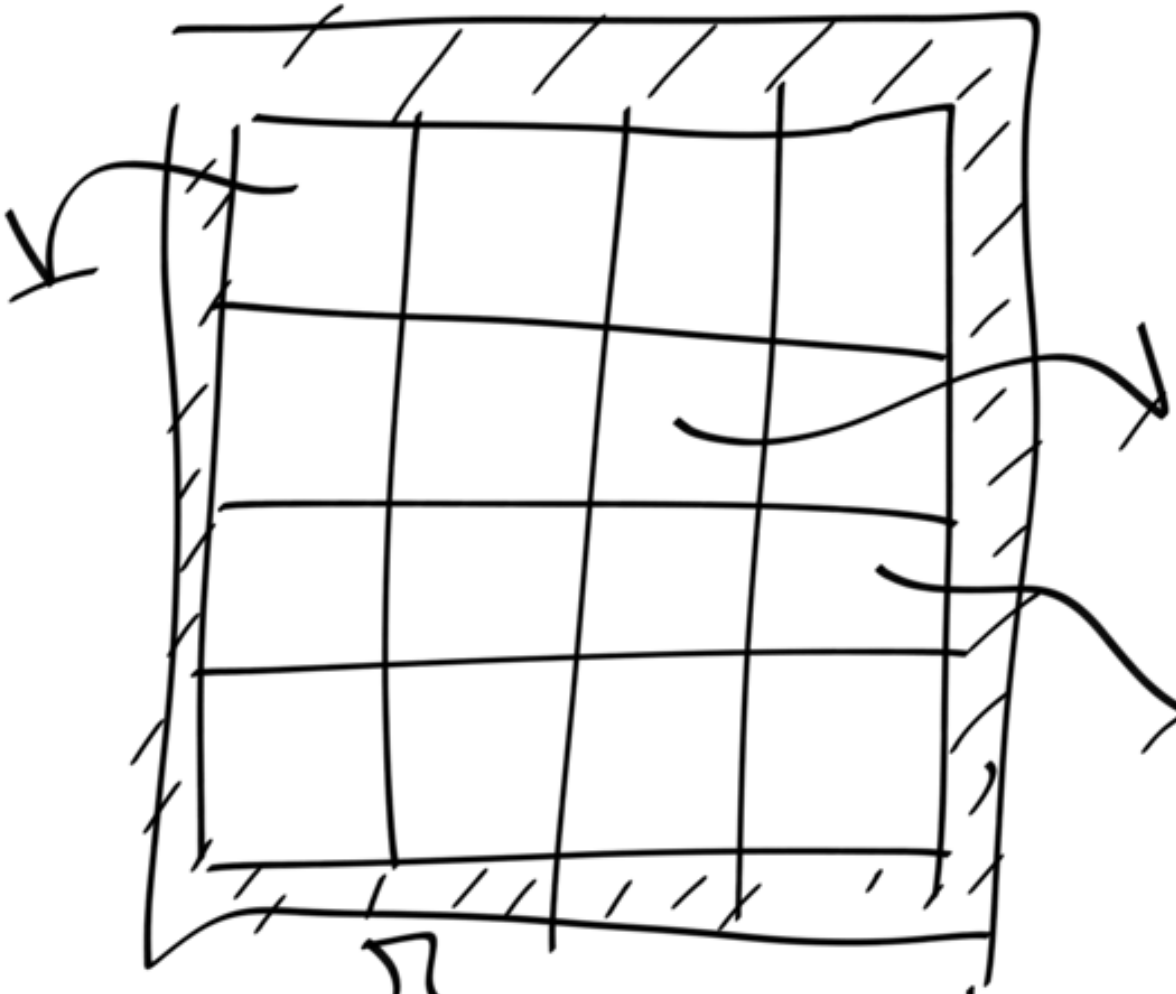
$dV \to 0$,

$$P_i = P_j$$

$$n_i = n_j$$

$$T_i = T_j$$

N, V, T F / A



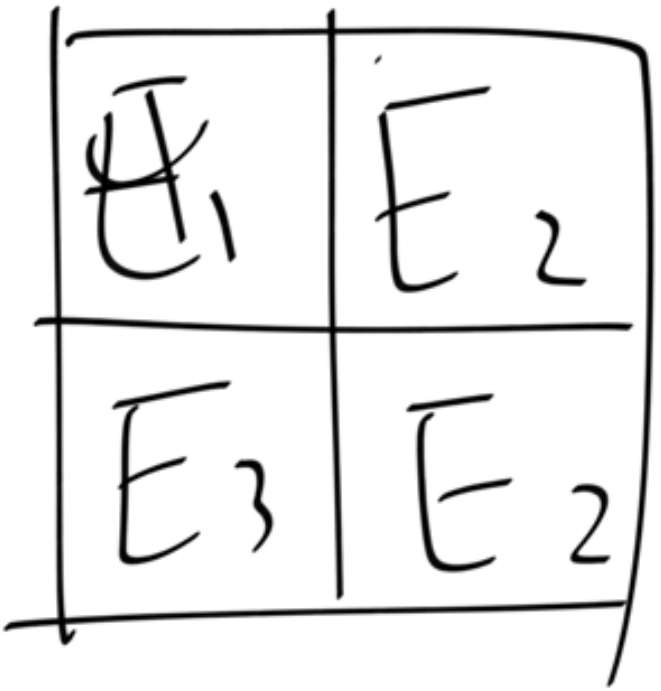
$$E_t = \sum_{i=1}^{n} E_i, \quad N_t = nN$$

$$V_t = nV \rightarrow$$

$E_1 \quad E_2 \quad E_3$

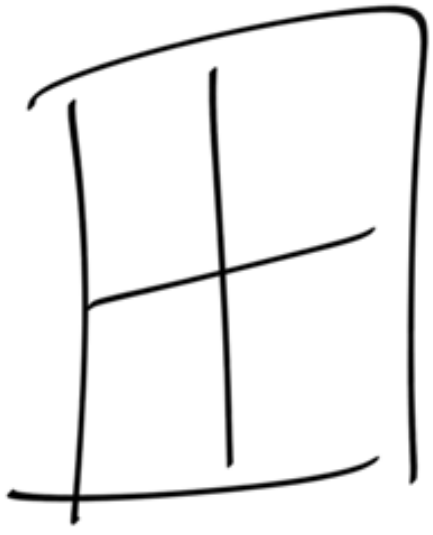
$\psi_1 \quad \psi_2 \quad \psi_3$

$1 \quad 2 \quad +-1$



$$\frac{4!}{2!}$$

$$\Omega_t(\{n\})$$



$$\Omega_t = \sum_{\{n\}} \Omega_t(\{n\})$$

$$\sum_i n_i \epsilon_i = E_t$$

$n_1 = 1 \quad n_2 = 2 \quad n_3 = 1$ I

$n_1 = 2 \quad n_2 = 0 \quad n_3 = 2$ II

$$P_3 = \frac{P_{3,I}\,\Omega_4(I) + P_{3,II}\,\Omega_4(II)}{\Omega_4(I) + \Omega_4(II)}$$

$$\Omega_A(\{n\}) = \frac{\Omega!}{\prod_i n_i!}$$

$$p_3 = \frac{\sum_{|n|} p_3^{n_3} \frac{n!}{\prod_i n_i!}}{\sum_{|n|} \frac{n!}{\prod_i n_i!}}$$

max-term method

$$\ln\left(\sum_{n_0}^{M} \frac{M!}{n!(M-n)!} x^n\right)$$

$$= \int \ln t_n$$

$$(1+x)^M \hookrightarrow \max, n$$

$$\frac{n_1!}{n!(n_1-n)!} x^n$$

$$N \ln(1+x)$$

$$\ln \frac{N!}{N^*! (N - x/*)!} x^{x/*}$$

Stirling

$$\ln N! =$$

$$N \ln N - N$$

$$M \ln M - M$$

$$- \Big[N_* \ln N_* - N_*$$

$$+ (M - N_*) \ln (M - N_*)$$

$$- (M - N_*) \Big]$$

$$+ N_* \ln x$$

$$= M \ln M - N_* \ln N_*$$

$$- (M - N_*) \ln (M - N_*)$$

$$\ln \frac{M!}{N_\perp!\,(M-N_\perp)!}\, x^N$$

$$= M \ln(1+x)$$

$$\{n_i^*\} \longrightarrow \Omega_t(\{n_i^*\})$$

$$\hookrightarrow \max$$

$$p_i = \frac{\bar{n}_i}{n} = \frac{\Omega_t(n^*) n_i^*}{n \Omega_t(n^*)}$$

$$= \frac{n_i^*}{n}$$

$$\sum_i n_i^* = N$$

$$\sum_i n_i^* \bar{t}_i = \bar{t}_1$$

Lagrange Multipliers

$$F(x, y, z)$$

$$dF = 0$$

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = \left(\frac{\partial f}{\partial x}\right)_{x,z}$$

$$= \left(\frac{\partial f}{\partial z}\right)_{x,y} = 0$$

$$G(x, y, z) = C$$

$$dG = 0$$

$$\partial_t G = 0$$

$$dI - \lambda dG = 0$$

$$\left(\frac{\partial f}{\partial x}\right) - \lambda \frac{\partial G}{\partial x} = 0$$

$$\vdots$$

$$dF - \partial d\epsilon_1 - \beta d\mu_n = 0$$

$$\ln \Omega_t(\{n\})$$

$$= \ln \frac{N!}{\prod_i n_i!}$$

$$= N \ln N - \sum_i (n_i \ln n_i)$$

$$F = N_n n - \sum n_i \ln n_i$$

$$\frac{\partial f}{\partial n_j} =$$

$$G_1 = \sum_i n_i = n \frac{\partial G_1}{\partial n_j} = 1$$

$$G_2 = \sum_i n_i E_i = E_t$$

$$\frac{\partial G_2}{\partial n_j} = E_j$$

$$\frac{\partial\left(\sum n_i \ln \sum n_i - \left(\sum n_i \ln n_i\right)\right)}{\partial n_j}$$

$$\rightarrow \sum\left(\frac{n_i}{\sum n_i}\right)$$

$$\sum\left(n_i \frac{\partial \ln \sum n_i}{\partial n_j} + \left(-\frac{\partial n_i}{\partial n_j} \ln \sum n_i\right)\right)$$

$$1 + \ln \sum n_i -$$

$$\sum_i \left(\frac{\partial n_i}{\partial n_j} \ln n_i + n_i \frac{\partial \ln n_i}{\partial n_j} \right)$$

$$\left(\ln n_j + 1 \right)$$

$$\ln \sum n_i - \ln n_j$$

$$= -\frac{\partial f}{\partial n_j}$$

$$\frac{\partial f}{\partial n_j} - \lambda \frac{\partial G_1}{\partial n_j} - \beta \frac{\partial G_2}{\partial n_j}$$

$$= \ln \Omega - \ln n_j - \beta \bar{E}_j = 0$$

$$n_j = \Omega e^{-\alpha} e^{-\beta E_j}$$

$$\hookrightarrow G_1 : \sum n_i = \Omega$$

$$e^{\alpha} = \sum_i e^{-\beta E_i}$$

$$\frac{n_j}{\Omega} = \frac{e^{-\beta E_j}}{\sum e^{-\beta E_i}}$$

$$P_j(N, V, \beta)$$

$$\bar{E} = \sum_i p_i E_i$$

$$dE = T dS - P dV$$

$$d\bar{E} = d\left(\sum p_i E_i\right)$$

$$= \sum p_i dE_i + \sum E_i dp_i$$

$$d\bar{E} = -\delta W$$
$$= -p dV$$

$$\left(\frac{\partial E_i}{\partial V}\right)_{N,T} = -P_i$$

$$dE_i = -P_i \cdot dV$$

$$\sum P_i(-P_i) \cdot dV$$

$$-dV \cdot \bar{P}$$

$$\sum E_i dp_i$$

$$p_i = \frac{e^{-\beta E_i}}{\underbrace{\sum e^{-\beta E_i}}_{\to Q}}$$

$$\ln p_i = -\ln Q - \beta E_i$$

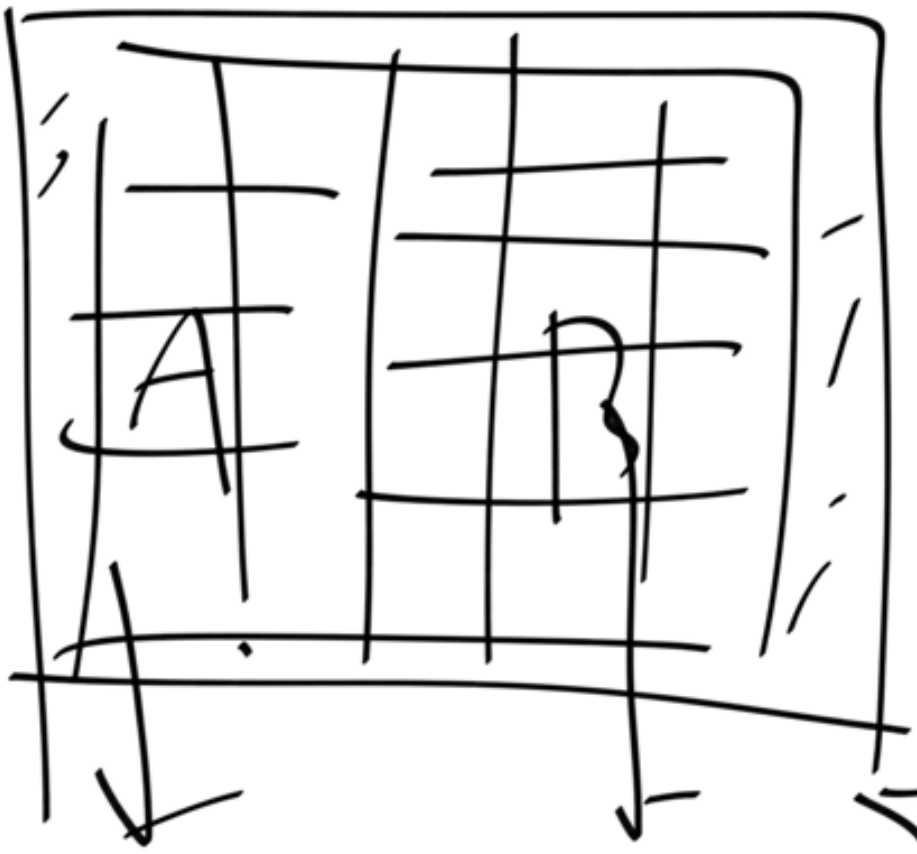
$$\rightarrow, E_i = -\frac{1}{\beta}(\ln p_i + \ln Q)$$

$$-\frac{1}{\beta}\sum(\ln Q + \ln p_i)\,dp_i$$

$$-\frac{1}{\beta}\sum \ln Q \cdot dp_i$$

$$-\frac{1}{\beta}\sum \ln p_i\, dp_i$$

$$-\frac{1}{\beta}\,d\left(\sum p_i \ln p_i\right)$$



$\Omega_t(|n_A|, |n_B)$

$= \Omega_A(|n_A) \cdot \Omega_B(|n_B)$

N_A N_B $\sum n_{Ai} = n$

V_A V_B $\sum n_{Bi} = n$

Ω $\Omega = \sum n_{Ai} E_{Ai}$

$\{n_A|$ $|n_B\}$ $+ \sum n_{Bi} E_{Bi}$

$= E_t$

$$\bar{T}\,dS = -\frac{1}{\beta}\,d\left(\sum p_i \ln p_i\right)$$

$$\Downarrow$$

$$dS = \frac{1}{\beta\bar{T}}\,d\left(-\sum p_i \ln p_i\right)$$

$$G = -\sum p_i \ln p_i$$

$$(N, V, \beta, T)$$

$$dS = \frac{1}{\beta T} dE_T$$

$$\varphi(E_1) = \frac{1}{\beta T}$$

$$dS = \varphi(E_1) dE_1$$

$$\int \varphi(E_1) dE_1 = f(E_1)$$

$$\varphi(E_1) = \frac{\partial f}{\partial E_1}$$

$$df = \varphi(a)\, dG$$

$$dS = d f(G)$$

$$S = f(G) + \text{const}$$

$$f(a) = \int \varphi(a)\, dG$$

$$\Omega_t = \frac{n!}{\prod n_{iA}!} \cdot \frac{n!}{\prod n_{iB}!}$$

$$P_{ij} = \frac{e^{-\beta E_{iA}} e^{-\beta E_{iB}}}{Q_A Q_B \sum e^{-\beta E_{iB}}}$$

$$= P_{Ai} \cdot P_{Aj}$$

$$G_{TAB} = -\sum_{ij} P_{ij} \ln P_{ij}$$

$$= -\sum_{ij} P_{iA} P_{jB} \left(\ln P_{iA} + \ln P_{jB} \right)$$

$$= -\sum_{i} P_{iA} \ln P_{iA} = G_A$$

$$= -\sum_{j} P_{jB} \ln P_{jB} = G_B$$

$$S = -\int (t_1)$$

$$S_{AB} = \int (C_{1AB})$$

$$S_A = f(C_{1A})$$

$$S_B = f(C_{1B})$$

$$S_{AB} = S_A + S_B$$

$$f(C_{1AB}) = f(C_A) + f(C_B)$$

$$f(x+y) = f(x) + f(y)$$

$$d f(x+y)$$

$$= \frac{\partial f}{\partial (x+y)} (dx + dy)$$

$$= \frac{\partial f}{\partial (x-y)} dx + \frac{\partial f}{\partial (x+y)} dy$$

$$d f(x,y)$$

$$= d\left(f(x) + f(y)\right)$$

$$= \frac{\partial f}{\partial x} \cdot dx + \frac{\partial f}{\partial y} dy$$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial (x+y)} = \frac{\partial f}{\partial y}$$

$$f(G) = kG + a$$

$$f(\sigma) = k\epsilon_T$$

$$S = f(\epsilon)$$

$$= -k \sum P_i \ln P_i$$

$$\frac{1}{BT} = \phi(G) = \frac{\partial t}{\partial \epsilon} = k$$

$$\beta = \frac{1}{kT}$$

$$P_i(N, V, T) = \frac{e^{-E_i / k_B T}}{Q}$$

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

$$S(N, V, T) = -k_B \sum p_i \ln p_i$$

$$S = \frac{\bar{E}}{T} + \frac{1}{T} \ln Q$$

$$A = E - TS$$

$$A = -\beta^{-1} \ln Q$$

$$dA = -SdT - PdV + \mu dN$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_{V,N}$$

$$= kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q$$

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$\bar{E} = A + \bar{T}S$$

$$\mu = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

$$= -kT\left(\frac{\partial \ln Q}{\partial n}\right)_{T,V}$$

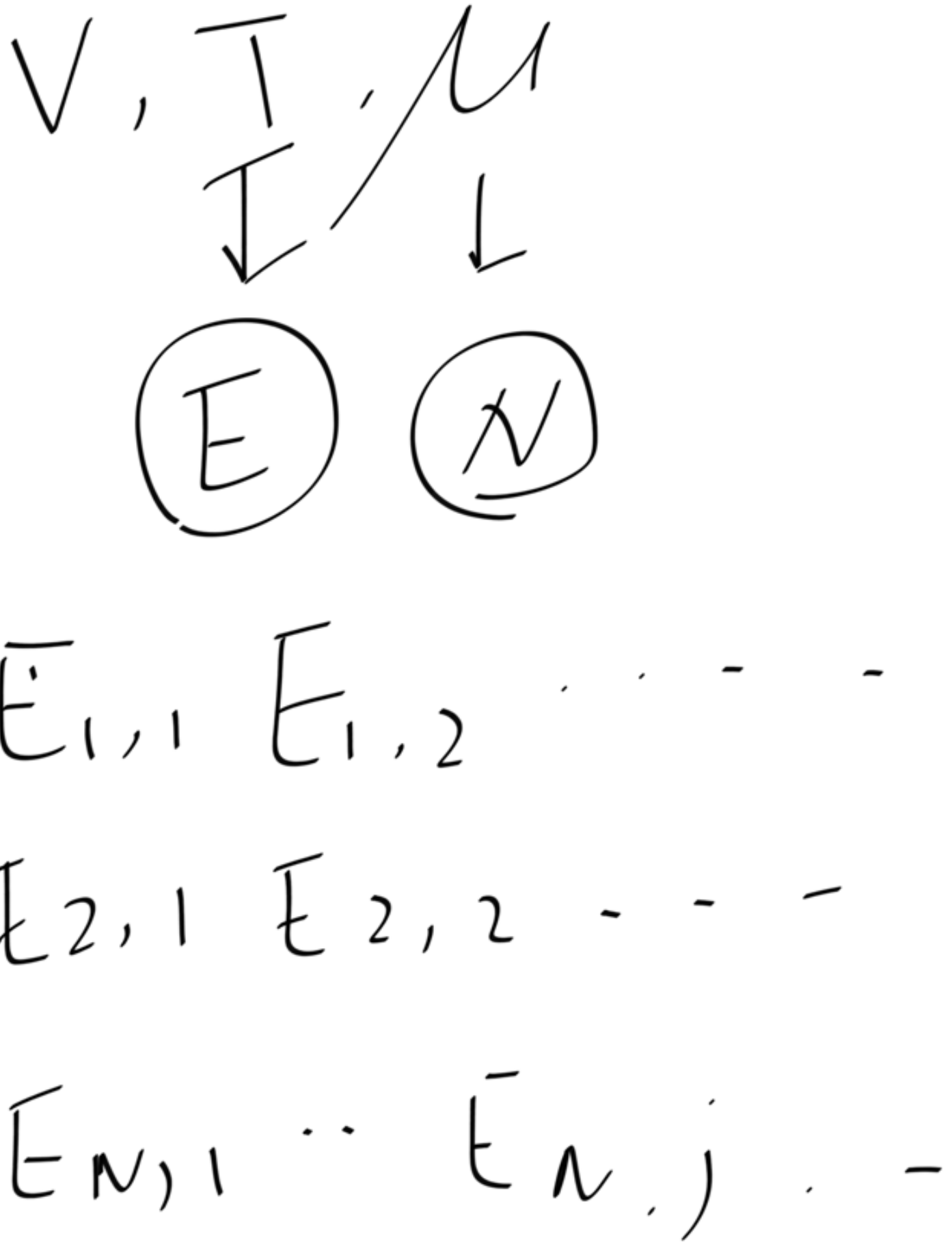
N, V, T:

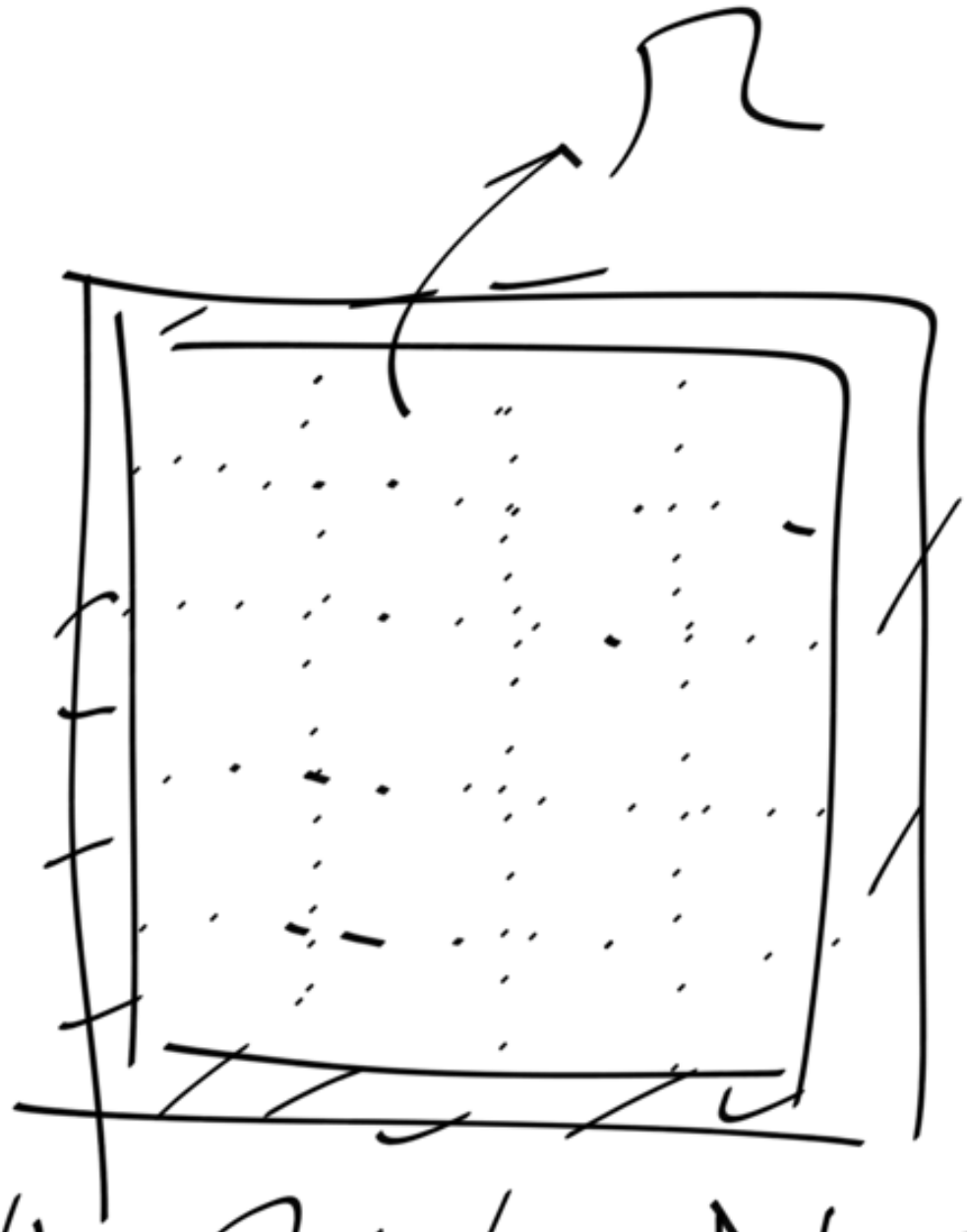
A, E, S, P, μ

$$Q(N, V, T)$$

$$= \sum_i e^{-\beta E_i}$$

$$= \sum_k \Omega(N, V) e^{-\beta E_k}$$


V, I, μ
E
N
E1,1 E1,2 - - -
E2,1 E2,2 - - -
EN,1 .. En,j . -



$$V = \Omega V \qquad N_t = \sum_{i=1}^{n} N_i$$

$$E_t = \sum_{i=1}^{n} E_i$$

$n_1(0)$

$n_1(1), n_2(1) \ldots$

$n_1(2), \ldots\ldots$

$$\sum_j n_j(N) = N$$

$$\sum_{j,N} N \cdot n_j(N) = N_t$$

$$\sum_{j,N} n_j(N) \cdot E_j(N,V) = E_t$$

$$\Omega(\{n_{j,\nu}\}) = \frac{\Omega!}{\prod_{j,\nu} n_{j,\nu}(\nu)!}$$

$$\sum_{j,\nu} n_j(\nu) = \mathcal{N}$$

$$\sum_{j,\nu} n_j(\nu) E_j(\nu, v) = E_t$$

$$\sum_{j,\nu} n_j(\nu) \cdot N = N_t$$

home work ..

$$\Rightarrow n_j^*(\nu) = n e^{-\alpha} e^{-\gamma\nu} e^{-\beta E_j(\nu, v)}$$

$$\beta = \frac{1}{k_B T} \qquad \gamma \to -\frac{\mu}{k_B T}$$

$$P_j(\omega) = \frac{n_j(\omega)}{\mathcal{N}} = \frac{n_j^*(\omega)}{n} = e^{-\alpha} e^{-\gamma\nu} e^{-\beta E_j(\nu)}$$

$$\bar{E} = \sum_{j,N} P_j(N)\, E_j(N,V)$$

$$\bar{N} = \sum_{j,N} P_j(N) \cdot N$$

$$\bar{P} = \sum_{j,N} P_j(N) \cdot \left(\frac{\partial E_j(N,V)}{\partial V}\right)_N$$

$$d\bar{E} = \sum_{j,N} P_j(N)\, dE_j(N,V) + \sum_{j,N} E_j(N,V)\, dP_j(N)$$

$$-p = \left(\frac{\partial E_j}{\partial V}\right)_N \rightarrow \partial E_j(N,V) = -p\, dV$$

$$= -\bar{p}\, dV + \quad -\frac{\gamma}{\beta} d\bar{N}$$

$$= -\bar{p}\, dV - \frac{1}{\beta} d\left[\sum_{j,N} P_j(N) \cdot \ln P_j(N)\right]$$

$$dE = \delta Q - \delta W$$

$$= TdS - pdV + \mu dN$$

$$S_{grand} = -k_B \sum_{j,N} P_j(N) \ln P_j(N)$$

$$S_{canonical} = -k_B \sum_j P_j \ln P_j$$

$$P_j(N; T, \mu, V) = \frac{e^{\beta \mu N} e^{-\beta E_j(N,V)}}{\Xi(T, V, \mu)}$$

$$\Xi = \sum_{N \geq 0} e^{\beta \mu N} \cdot \sum_j e^{-\beta E_j(N,V)}$$

$$= \sum_{N \geq 0} e^{\beta \mu N} \cdot Q(N, V, \beta)$$

$$P_N(V,\beta,\mu) = \frac{e^{-\beta\mu N} Q(N,V,\beta)}{\Xi}$$

$$S = -k_B\left(\sum_{j,N} \frac{e^{\beta(\mu N - E_j(N))}}{\Xi} \ln \frac{e^{\beta(\mu N - E_j(N))}}{\Xi}\right)$$

$$= -k_B\left(\sum_{j,N} \frac{e^{\beta(\mu N - E_j(N))}}{\Xi}\left[\beta\mu N - E_j(N) - \ln \Xi\right]\right)$$

$$= -\frac{\mu \bar{N}}{T} + \frac{\bar{E}}{T} + k_B \ln \Xi$$

$$F = E - TS \qquad S = -\frac{\mu N}{T} + \frac{E}{T} + \frac{PV}{T}$$

$$G = E - TS + PV \qquad \uparrow$$

$$G = N\mu \qquad N\mu = E - TS + PV$$

$$T k_B \ln \Xi = \underline{PV}$$

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

$$F = E - TS = -k_B T \ln Q$$

$$\Phi = -k_B T \ln \Xi = -PV$$

$$\phi = F - N\mu$$

$$-PV = E - TS - N\mu$$

$$d(-PV) = dE - d(TS) - d(N\mu)$$

$$= TdS - pdV - TdS - SdT - Nd\mu - \mu dN + \mu dN$$

$$d(PV) = SdT + Nd\mu + pdV$$

$$d(k_B T \ln \Xi) = \ldots$$

$$S = \left(\frac{\partial (kT \ln \Xi)}{\partial T}\right)_{V,\mu}$$

$$= kT\left(\frac{\partial \ln \Xi}{\partial T}\right)_{V,\mu} + k \ln \Xi$$

$N = ?$

$p = ?$

Microcanonical Ensemble

E, V, N

$\Omega(E, V, N)$

$$S = -k_B \sum p_i \ln p_i$$

$$= -k_B \ln \frac{1}{\Omega} \sum \frac{1}{\Omega} = k_B \ln \Omega$$

Characteristic function: variables

$$\ln \Omega(N,V,E) = \beta T S \nearrow \quad N \quad V \quad E$$

$$\ln\Big(\sum_{E_j} \underbrace{\Omega(N,V,E_j)}_{\Omega} e^{-\beta E_j}\Big) = \beta T S - \beta E \quad N \quad V \quad \beta$$

$$= -\beta F \,.$$

$$\ln \sum_N \sum_{E_j} \Omega(N,V,E_j) e^{-\beta E_j + \beta\mu N} \quad \beta\mu \quad V \quad \beta$$

$$= \beta T S - \beta E + \beta\mu N$$

$$\sum_N e^{\beta\mu N} Q(N,V,\beta) = \beta P V$$

$$\downarrow$$

$$\Xi$$

$$\ln\left(\sum_N \Omega(N,V,E)\, e^{\beta\mu N}\right) = \beta TS + \beta\mu N \quad (\beta\mu,\ V,\ E)$$

$$\downarrow$$

$$G$$

$$\downarrow$$

$$H - TS$$

$$= \beta H \nearrow$$

$$\ln\left(\sum_V \Omega\, e^{-\beta PV}\right) = \beta TS - \beta PV \qquad N \quad \beta P \quad E$$

$$= \beta E - \beta\mu N$$

$$N \quad \beta P \quad \beta$$

$$\ln\left(\sum_V \sum_E \Omega\, e^{-\beta E_j}\, e^{-\beta PV}\right) = \beta TS - \beta E - \beta PV$$

$$\downarrow$$

$$\Delta$$

$$= -\beta\mu N = -\beta G \searrow$$

$$\beta\mu \quad \beta P \quad E$$

$$\ln\left(\sum_V \sum_N \Omega\, e^{-\beta PV}\, e^{\beta\mu N}\right) = \beta TS - \beta PV + \beta\mu N$$

$$= \beta E$$

βμ βP β

$$\ln\left(\sum_{E}\sum_{V}\sum_{N}\Omega e^{-\beta E_j - \beta PV + \beta\mu N}\right)$$

$$= \beta TS - \beta E - \beta PV$$

$$p\beta\mu N = 0$$

1

Gibbs Phase Rule

$$F = C - P + 2$$

$\underline{\underline{E}}, V, N, P$

$$\langle (E - \langle E \rangle)^2 \rangle = \sigma_E^2$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \rangle$$

$$\langle E^2 \rangle - 2\langle E\langle E \rangle \rangle + \langle \langle E \rangle^2 \rangle$$

$$= \langle E^2 \rangle - 2 \cdot \langle E \rangle \langle E \rangle + \langle E \rangle^2$$

,

$$\langle E \rangle = \frac{\sum E_j e^{-\beta E_j}}{Q}$$

$$\rightarrow Q\langle E \rangle = \sum_j E_j e^{-\beta E_j}$$

$$\left(\frac{\partial Q}{\partial \beta}\right)\langle E \rangle + Q \cdot \frac{\partial \langle E \rangle}{\partial \beta}$$

$$= -\sum_j E_j^2 e^{-\beta E_j}$$

$$\frac{\partial Q}{\partial \beta} = -\sum_j E_j e^{-\beta E_j}$$

$$-\langle E \rangle^2 + \frac{\partial \langle E \rangle}{\partial \beta} = -\langle E^2 \rangle$$

$$\rightarrow \frac{\partial \langle E \rangle}{\partial \beta} = -\int_E^2$$

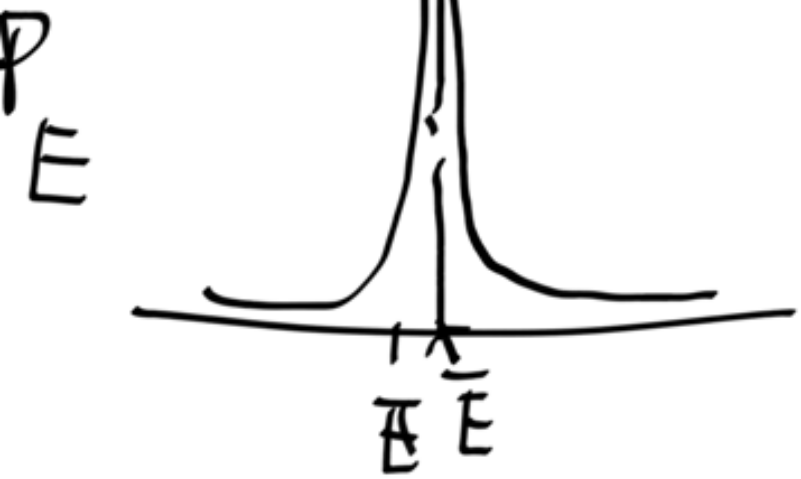
$$\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{N,V} = -k_B T^2 \left(\frac{\partial E}{\partial T}\right)_{N,V}$$

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

$$\Rightarrow \quad \sigma_E^2 = k_B T^2 \cdot C_V$$

$$\frac{\sigma_E}{\bar{E}} \sim \frac{(k_B T C_V)^{1/2}}{\bar{E}} \to O(N) \Rightarrow O(N^{-1/2})$$

$$\bar{E} \to O(N)$$



$$\delta_N^2 = \langle N^2 \rangle - \langle N \rangle^2$$

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

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{V,T} = \delta_N^2$$

$$\left(\frac{\partial \mu}{\partial N} \right)_{V,T} \longrightarrow \mu(N, V, T)$$

$$E - TS + PV - \mu N = 0$$

$$+\mu dN$$

$$TdS - PdV - TdS - SdT + PdV + VdP$$

$$-\mu dN - N d\mu = 0$$

assume $T \to$ const.

$$-SdT + VdP - N d\mu = 0 \to N d\mu = V dP$$

$$d\mu = \frac{V}{N} dp \quad (T \text{ const}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = \frac{1}{V}\left(\frac{\partial \mu}{\partial N/V}\right)_{V,T}$$

$$\mu(N,V,T) \qquad = \frac{1}{V}\left(\frac{\partial \mu}{\partial \rho}\right)_{V,T}$$

$$= \frac{1}{V}\left(\frac{\partial \mu}{\partial \rho}\right)_{T}$$

$$p(N,V,T)$$

$$\left(\frac{\partial P}{\partial V}\right)_{N,T} = -\frac{N}{V^2}\left(\frac{\partial P}{\partial N/V}\right)_{N,T}$$

$$= -\frac{N}{V^2}\left(\frac{\partial P}{\partial \rho}\right)_{T} \qquad \rho d\mu$$

$$V\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = -\frac{V^3}{N^2}\left(\frac{\partial P}{\partial V}\right)_{N,T} \qquad \left(\frac{\partial V}{\partial P}\right)_{N,T}$$

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

$$\left(\frac{\delta N}{N}\right)^2 = \frac{k_B T K}{\bar{V}} = \left(\frac{\delta \rho}{\rho}\right)^2$$

$$\frac{\delta N}{N} \propto O(N^{-1/2})$$

$N, P, T.$

$$\Delta = \sum_V e^{-\beta P V} Q(N, V, T)$$

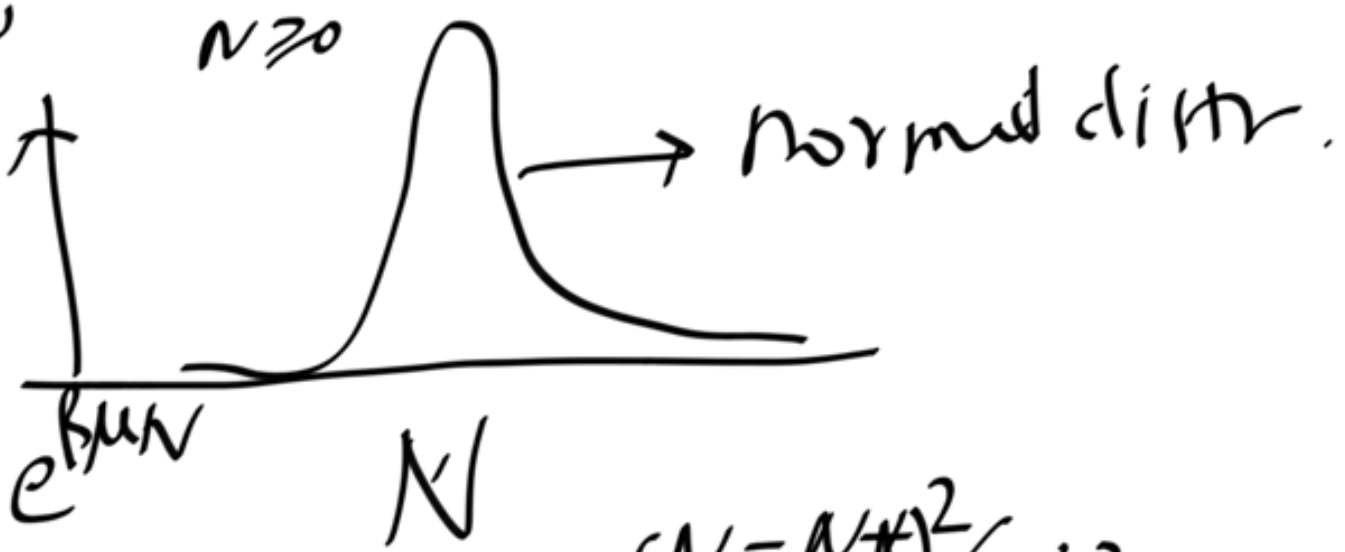
$$\bar{V} = \frac{\sum_V V e^{-\beta P V} Q}{\Delta}$$

$$\left(\frac{\partial \bar{V}}{\partial P}\right)_{N,T} = -\beta(\langle V^2 \rangle - \langle V \rangle^2)$$

$$= -\beta \delta V^2$$

$$\hookrightarrow \left(\frac{\delta \bar{V}}{\bar{V}}\right)^2 = \frac{k_B T K}{\bar{V}} = \left(\frac{\delta N}{N}\right)^2$$

$$\Xi = \sum_{N \geq 0} Q \cdot e^{\beta \mu N}$$



$$t_N = t_N^* e^{-(N-N^*)^2/2\sigma_N^2}$$

$$\ln \Xi = \ln \int_{-\infty}^{+\infty} t_N \, dN$$

$$= \ln t_N^* + \ln \int_{-\infty}^{+\infty} e^{-(N-N^*)^2/2\sigma_N^2} dN$$

$\sim \ln N$

$$= \ln t_N^* + \ln \left[(2\pi)^{1/2} \sigma_N \right]$$

$$\ln t_N^* = \ln Q(N^*, V, T)$$

$$+ \underbrace{\beta \mu N^*}_{O(N^*)}$$

$$\beta PV - \beta \mu N^* = \ln Q^*$$

$$\ln \Xi \approx \ln t_N^* \longrightarrow \beta PV$$

$$\approx \ln Q^* + \beta \mu N^* \quad = \ln Q^* + \beta \mu N^*$$

$$\left(\frac{\partial \ln t_N^*}{\partial N}\right)_{V,T,\mu} = 0^*$$

$$\beta PV - \beta \mu N = \beta(-F)$$

$$-\beta F^* = \ln Q(N^*, V, T)$$