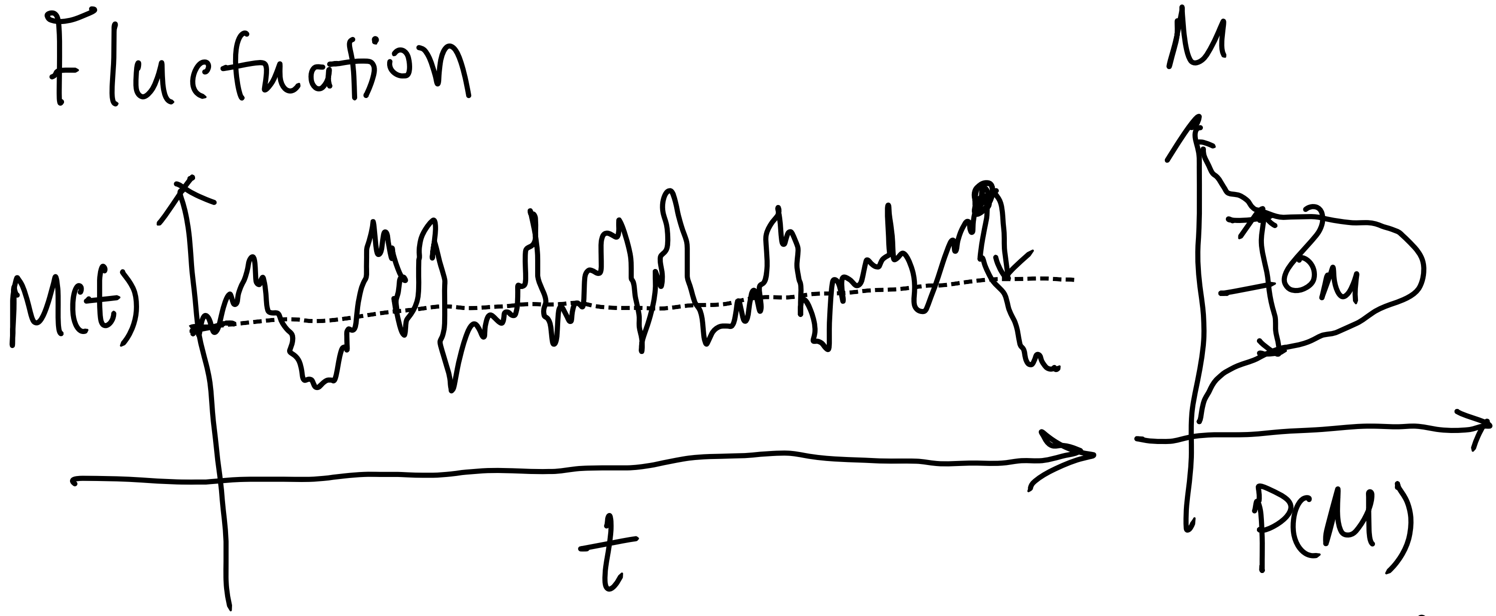
$i \rightarrow P(i) \rightarrow \bar{M}$

Flucfuation



① whether or not ignore fluctuation

② property ⟷ fluctuation .. C_v

③ nonequibrium

variance

$$\delta_M^2 = \frac{\sum_{i=1}^{N} (M(t_i) - \bar{M})^2}{N}$$

$$= \overline{\left(M(t_i) - \overline{M(t_i)}\right)^2}$$

$$\underline{\overline{M(t_i)}} = \underline{\underline{\sum_j M_j \cdot P(j)}} = \langle M(i) \rangle$$

$$= \left\langle \left(M(i) - \langle M(i)\rangle\right)^2 \right\rangle$$

$$= \left\langle M^2(i) - 2M(i)\langle M(i)\rangle + \langle M(i)\rangle^2 \right\rangle$$

$$= \langle M^2(i)\rangle - \langle 2M(i)\langle M(i)\rangle\rangle + \underbrace{\left\langle \langle M(i)\rangle^2 \right\rangle}_{\langle M(i)\rangle^2}$$

$$\sum_j P(j) \cdot \underbrace{\langle \quad \rangle^2}_{\langle \quad \rangle^2 \sum_j P_j}$$

$$= \langle M(i)^2 \rangle - \langle M(i) \rangle^2 = \delta_M^2$$

N, V, T

$\bar{E} = \langle E_i \rangle = \frac{1}{Q} \sum E_i e^{-\beta E_i}$

$e^{-\beta E_i}$: weight for each state i

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

$$\underline{\left.\frac{\partial \langle E_i \rangle}{\partial \beta}\right|_{N,V}} = \frac{\partial \left(\frac{1}{Q} \left(\sum_i E_i e^{-\beta E_i} \right) \right)}{\partial \beta}$$

$$= \frac{1}{Q} \cdot \sum_i (-\beta) \cdot E_i^2 e^{-\beta E_i} + \left(\sum E_i e^{-\beta E_i} \right) \frac{-1}{Q^2} \cdot \frac{\partial \sum_i e^{-\beta E_i}}{\partial \beta}$$

$$= -\frac{\beta}{Q} \sum_i E_i^2 e^{-\beta E_i} + \frac{\beta}{Q^2} \left(\sum_i E_i e^{-\beta E_i} \right) \left(\sum_i E_i e^{-\beta E_i} \right)$$

$$= -\beta \left(\underline{\frac{1}{Q} \sum_i E_i^2 e^{-\beta E_i}} - \left(\frac{1}{Q} \sum_i E_i e^{-\beta E_i} \right)^2 \right)$$

$$-\beta(\langle E_i^2 \rangle - \langle E_i \rangle^2)$$

$$= -\beta \sigma_E^2 \qquad \beta = \frac{1}{k_B T}$$

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

$$dE = \delta Q - \delta W + \mu dN$$

$$\delta W = 0, \quad \mu dN = 0$$

$$dE = \delta Q$$

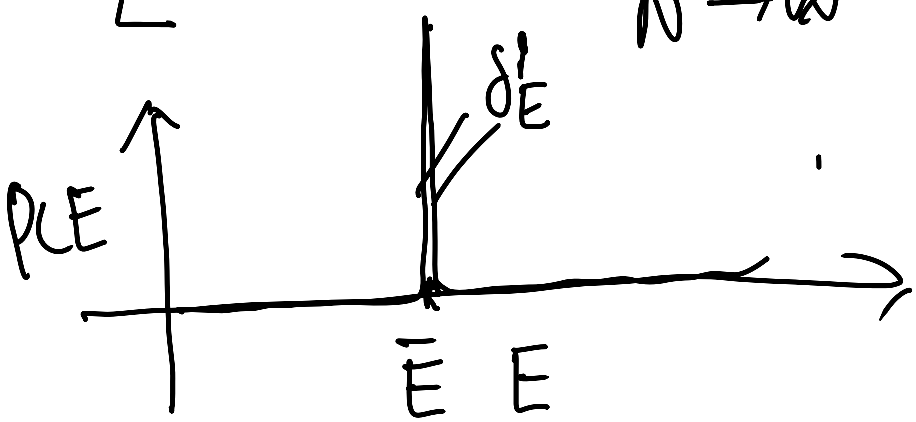
$$= k_B T^2 \cdot \left(\frac{\delta Q}{\partial T} \right)_{N,V} = \underbrace{k_B T^2}_{O(1)} \cdot C_V$$

$$\delta E \propto O(N^{1/2}) \, O(N)$$

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

$$N \rightarrow \infty$$

$$\delta E \rightarrow 0$$



μ, V, T : Grand Canonical Ensemble.

$$\frac{\delta_N}{N} = ?$$

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

$$= \frac{\beta}{\Xi} \sum_{N=0}^{\infty} N^2 e^{\beta\mu N} Q - \frac{\beta}{\Xi^2}\left(\sum_{N=0}^{\infty} N e^{\beta\mu N} Q\right)^2$$

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

$\downarrow$

$p, T, V \dots$ thermodynamics

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

$$d(E - TS + PV + \mu N) = 0$$

$$Vdp - SdT - Nd\mu = 0$$

const T:

$$V\,dp = N\,d\mu$$

$$\rightarrow \quad dp = \rho\, d\mu \qquad \overset{\text{fixed}}{(T)}$$

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

$$\rho(N,V) = N/V \qquad = \left(\frac{\partial \mu(\rho,T)}{\partial \rho}\right)_T\Bigg|_{\rho=\frac{N}{V}} \cdot \left(\frac{\partial \rho}{\partial N}\right)_V$$

$$= \left(\frac{\partial \mu(\rho,T)}{\partial \rho}\right)_T\Bigg|_{\rho=\frac{N}{V}} \cdot \frac{1}{V} \qquad (2)$$

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

$$= \underbrace{\left(\frac{\partial p(\rho,T)}{\partial \rho}\right)_T\Bigg|_{\rho=\frac{N}{V}}}\cdot \left(\frac{\partial \rho}{\partial V}\right)_N$$

$$= \left(\frac{\partial p(\rho,T)}{\partial \rho}\right)_T \Bigg|_{\rho=\frac{N}{V}} \cdot \left(-\frac{N}{V^2}\right)$$

$$= \left(\frac{\rho \cdot \partial \mu(\rho,T)}{\partial \rho}\right)_T \Bigg|_{\rho=\frac{N}{V}} \left(-\frac{N}{V^2}\right)$$

$$= \frac{N}{V} \cdot \left(\frac{\partial \mu(\rho,T)}{\partial \rho}\right)_T \Bigg|_{\rho=\frac{N}{V}} \left(-\frac{N}{V^2}\right) \quad ①$$

compare ① and ②

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

$$\Downarrow$$

$$\delta_N^2 = -k_B T \cdot \frac{N^2}{V^2} \cdot \left(\frac{\partial V}{\partial p}\right)_{N,T}$$

$$= k_B T \cdot \frac{N^2}{V} \underbrace{\left(-\frac{1}{V} \cdot \frac{\partial V}{\partial p}\right)_{N,T}}$$

κ_T isothermal compressibility.

$$= k_B T \cdot \frac{N^2}{V} \cdot \underbrace{\kappa_T}_{O(N)}$$

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

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

μ, V, T

$$\frac{\delta \rho}{\rho} = \frac{\delta \rho = \frac{\delta N}{V}}{\rho = \frac{N}{V}} = \frac{\delta N}{N}$$

N, P, T:

$$\Delta = \sum_V \sum_E \Omega e^{-\beta E} e^{-\beta P V}$$

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

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

$$\left(\frac{\delta V}{V}\right)^2 = -\frac{k_B T}{V^2}\cdot\left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{k_B T \chi_T}{V} \simeq O(N^{-1/2})$$

$$\bar{H} = \bar{E} + pV = \langle H_i \rangle = \langle E_i + pV_i \rangle$$

$$\left(\frac{\partial \bar{H}}{\partial \beta}\right)_{N,p} = \left(\frac{\partial \frac{1}{\Delta}\sum_{V_i}\sum_{E_i}(E_i+pV_i)e^{-\beta(E_i+pV_i)}}{\partial \beta}\right)_{N,p}$$

$$= -\left(\langle (E_i+pV_i)^2 \rangle - \langle E_i+pV_i \rangle^2\right)$$

$$\Rightarrow \delta_H^2 = k_B T^2 \cdot \left(\frac{\partial H}{\partial T}\right)_p = k_B T^2 \cdot \left(\frac{\delta Q}{\partial T}\right)_p = k_B T^2 \cdot C_p$$

$$dH = d(E+pV) = \overset{\delta Q}{\underline{SdT}} + \underbrace{Vdp}_{=0}$$

$$dH = \delta Q$$

$$N, V, T: \quad \delta_E^2 \sim k_B T^2 \cdot C_V$$

N, P, T: $\delta_E^2 \simeq$?

$$\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{N,P} = \frac{\partial \frac{1}{\Delta} \sum_{V_i} \sum_{E_i} \underset{\sim}{E_i}\, e^{-\beta P V_i} e^{-\beta E_i}}{\partial \beta}$$

$$= \frac{-\beta}{\Delta} \sum_{V_i} \sum_{E_i} E_i (E_i + P V_i) e^{-\beta(E_i + P V_i)}$$

$$+ \frac{\beta}{\Delta^2} \left(\sum_{V_i} \sum_{E_i} E_i e^{-\beta(E_i + P V_i)} \right) \times \left[\sum_{V_i} \sum_{E_i} (E_i + P V_i) e^{-\beta(E_i + P V_i)} \right]$$

$$= \underbrace{\langle E_i^2 \rangle - \langle E_i \rangle^2}_{\delta_E^2} + \underbrace{P \left(\langle E_i V_i \rangle - \langle E_i \rangle \langle V_i \rangle \right)}$$

Equavelency between ensembles:

$\mu, V, T \longleftrightarrow N, V, T$

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

$$t_N = \underbrace{\underline{e^{\beta\mu N}}\cdot \underline{Q(N,V,T)}}$$

$$= \underline{\sum_{N\geq 0}^{\infty} t_N} \qquad \mu < 0$$

t_N^*

Gaussian

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

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

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

$$\int_{-t'}^{t'} e^{-t^2} dt' = \sqrt{\pi}\cdot erf(t') \qquad \int_{-\infty}^{+\infty} e^{-\frac{(N-N^*)^2}{2\sigma_N^2}} \, dN$$

$t' \to \infty \quad erf(\infty) = 1$

$$= \ln t_N^* + \ln[(2\pi)^{1/2} \underline{\delta_N}] \qquad \delta_N \propto O(N^{1/2})$$

$$t_N^* = e^{\beta\mu N^*} Q(N^*, V, T) \qquad \frac{\delta_N}{N} \propto O(N^{-1/2})$$

$$= \ln Q(N^*, V, T) + \beta\mu N^* + \frac{1}{2}\ln[O(N)]$$

$$\ln Q(N^*, V, T) \to O(N) \qquad \beta\mu N^* \to O(N)$$

$$\approx \ln Q(N^*, V, T) + \beta\mu N^*$$

$$\beta PV = \ln Q(N^*, V, T) + \beta\mu N^*$$

$$N^* = \bar{N} \qquad \to \mu, V, T$$

$$\beta PV = \underbrace{\ln Q(\overset{(\mu,V,T)}{\bar{N}}, V, T)}_{\mu, V, T} + \beta\mu\bar{N}$$

$$\bar{N} \to \bar{N}(\mu, V, T)$$

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

$$pV = TS - E + \mu N$$

$$\beta pV = \beta(TS - E) + \beta\mu N$$

$$\beta pV = -\beta A + \beta\mu N$$

$$\beta \bar{p} V = \ln Q(N, V, T) + \beta\bar{\mu} N$$

$$N, V, T \rightarrow \bar{\mu}, \bar{p}$$

$$N = \bar{N}$$

$$\beta \bar{p} V = \ln Q(\bar{N}, V, T) + \beta\bar{\mu} \cdot \bar{N}$$

$$\mu \cdot \bar{N}(\mu, V, T) \quad)$$

$$\|$$

$$\bar{\mu} \cdot \bar{N}$$

$$(\bar{N}, V, T)$$

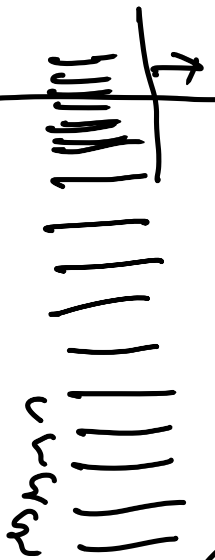
$N, \underline{V}, T$

$\bar{p}$

$N, \underline{p}, T$

$\bar{V}$

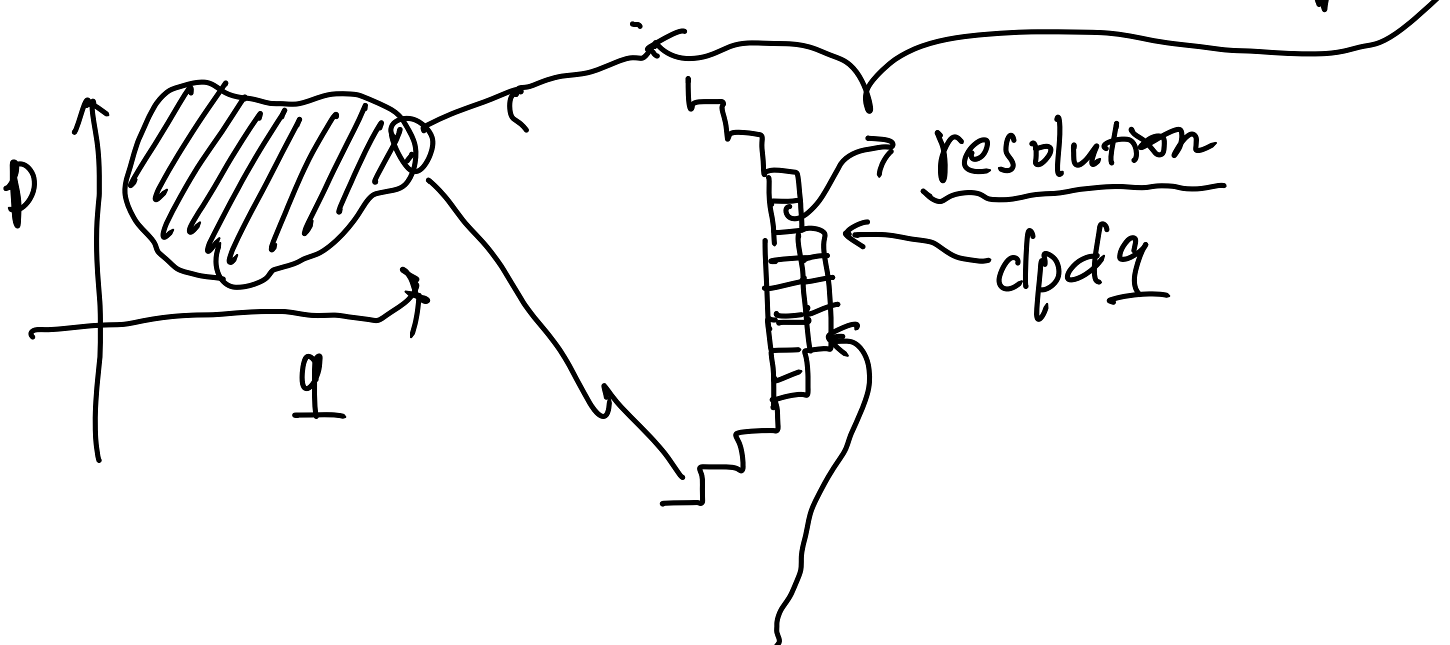
$$\bar{p} \cdot V_{(N,V,T)} = p \cdot \bar{V}_{(N,pT)}$$



$$\mathcal{H}\Psi_i = E_i \Psi_i$$

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

$$\underline{Q_c} \propto \iint e^{-\beta \mathcal{H}(q,p)} \underbrace{dp\,dq}$$



Heisenberg.

$$\underbrace{\Delta p \Delta q}_{} \geq \frac{\hbar}{4} \leftarrow \text{Plank}$$

$$Q_c \propto \hbar \cdot \sum_i \underbrace{e^{-\beta E_i}}_{Q}$$

$$Q \propto \frac{1}{\hbar} \iint e^{-\beta H(p,q)} \, dp \, dq$$

$$Q \propto \frac{1}{\hbar^n} \iint e^{-\beta H(p_{(n)}, q_{(n)})} \, dp_{(n)} \, dq_{(n)}$$

For N indistinguishable particles.

$$Q = \frac{1}{h^{3N} N!} \iint e^{-\beta H(\vec{p}_{(N)}, \vec{q}_{(N)})} \, d\vec{p}_{(N)} \, d\vec{q}_{(N)}$$

$$H(\vec{p}_{(N)}, \vec{q}_{(N)}) = U(\vec{q}_{(N)}) + K(\vec{p}_{(N)})$$

$$= \frac{1}{h^{3N} N!} \left(\int e^{-\beta U(\vec{q}_{(N)})} d\vec{q}_{(N)} \right) \underbrace{\left(\int e^{-\beta K(\vec{p}_{(N)})} d\vec{p}_{(N)} \right)}$$

$$K(\vec{p}_{(N)}) = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m_i} = \sum_{i=1}^{N} \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m_i}$$

$$\int_{-\infty}^{\infty} e^{-\beta \sum \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m_i}} dp_{1x} dp_{1y} dp_{1z} \cdots dp_{ix} d_{iy} d_{iz} \cdots dp_{Nx} dp_{Ny} dp_{Nz}$$

$$= \prod_{i=1}^{N} \left(\left(\underbrace{\int_{-\infty}^{\infty} e^{-\beta \frac{p_{ix}^2}{2m_i}} dp_{ix}} \right) \underbrace{\left(\int \cdots dp_{iy} \right)} \underbrace{\left(\int \cdots dp_{iz} \right)} \right)$$

$$= \left(\underbrace{\int_{-\infty}^{\infty} e^{-\beta \frac{t^2}{2m_i}} dt} \right)^{3N}$$

$$\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$$

$$\int$$

$$\sqrt{2\pi k_B T m_i}$$

$$Q = \frac{1}{h^{3N} \cdot N!} (2\pi k_B T m)^{\frac{3N}{2}} \cdot \int e^{-\beta U(\vec{q}_{(N)})} d\vec{q}_{(N)}$$

$$\Lambda = \frac{h}{\sqrt{2\pi k_B T m}}$$

$$Q = \frac{1}{\Lambda^{3N} N!} \boxed{\int e^{-\beta U(\vec{q}_{(N)})} d\vec{q}_{(N)}}$$

Z : configurational partition

A, B

m_A, m_B

N_A, N_B

$$Q_{A,B} = \frac{1}{\Lambda_A^{3N_A} \Lambda_B^{3N_B} N_A! N_B!} \cdot \int e^{-\beta U(\vec{q}^{A}_{(N)}, \vec{q}^{B}_{(N)})} d\vec{q}^{A}_{(N)} d\vec{q}^{B}_{(N)}$$

$$\Lambda_{A/B} = \frac{h}{\sqrt{2\pi k_B T m_{A/B}}}$$