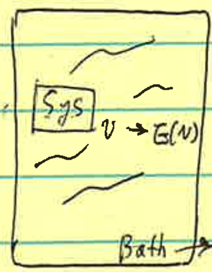
01/08/2024.

$\log \Omega$. $\quad$ rate $= \log \Omega$.

- $p(\nu) = e^{-NI(\rho, V, E)}$. $\qquad p(\nu) = \begin{cases} 1/\Omega(N, V, E) \\ 0 \end{cases}$

- Universe. (N_T, V_T, E_T). → Assumption: microcanonical postulate holds $\qquad$ (Ω counts states)



$$E_T = E(\nu) + E_B(\nu_B) \quad \text{must be satisfied.} \quad \text{—— } ⓪$$

$$p(\nu) = \sum_{\{\nu_B \mid E(\nu) + E_B(\nu_B) = E_T\}} p(\nu, \nu_B) \qquad p(\nu, \nu_B) = \frac{1}{\Omega(N_T, V_T, E_T)}$$

$$= \sum_{\nu_B;} 1/\Omega(N_T, V_T, E_T). \quad \text{—— } ①$$

→ Count as $\Omega_B(E_T - E(\nu), N_B, V_B)$

⇒ ① becomes,

$$p(\nu) = \frac{1}{\Omega_T} \Omega_B(\underbrace{E_T}_{\text{Big!}} - E(\nu), \ldots)$$

Since $E_T \gg E(\nu)$, use Taylor expansion,

$$\log p(\nu) \propto \log \Omega_B(E_T - E(\nu)) = \log \Omega_B E_T + \left(\frac{\partial \log \Omega_B(N_B, V_B, E_b)}{\partial E_b}\right)\{E_T - E(\nu)\}$$

$$+ \cancel{O((E_T - E(\nu))^2)} \to 0 \ldots$$

$$\Rightarrow \log p(\nu) \propto \underbrace{\left(\frac{-\partial \log \Omega_B}{\partial E_b}\right)_{N_B, V_B}}_{\text{property of bath} \equiv \beta} \cdot E(\nu)$$

$$\boxed{\therefore \ p(\nu) \propto e^{-\beta E(\nu)}} \quad \left(\beta = \frac{1}{k_B T}\right).$$

Boltzmann distribution.

Microcanonical Postulate → Boltzmann distribution.

$p(\nu) \propto ?$

$$p(E) = \sum_{\nu \mid E(\nu)=E} p(\nu) = \underbrace{\Omega(E)}_{\propto \omega^N} \cdot e^{-\beta E} \quad \propto \epsilon N$$

(N, V, E : Extensive : grow with system size
ω, v, ϵ : Intensive : not " " ")

$$\Rightarrow p(E) = e^{N(\underbrace{\log(\omega)}_{\text{Entropy ?}} - \beta\epsilon)}$$

$$-N\beta(\epsilon - \underbrace{k_B T \log \omega}_{T(k_B \log \omega)})$$

$S = k_B \log \omega^N$ (Ω)

$$e^{-N\beta(\underbrace{\epsilon - Ts}_{\text{Free energy } (a)})}$$

small s.

Note : $S = k_B \log \omega^N = k_B \ln \Omega = N \cdot k_B \cdot \log \omega \cdot = N \cdot s$

intensive property.

We derived $p(E) = e^{N(\log \omega - \beta\epsilon)} = e^{-N\beta(\epsilon - k_B T \log \omega)}$

$= e^{-N\beta(\epsilon - T k_B \cdot \log \omega)}$

$$\Rightarrow p(E) = e^{-N\beta(\epsilon - T \cdot s)}$$

s : entropy (intensive)

S : " (extensive)

01/10/2025.

- Recap

$\Omega(N,V,E)$ — Fix this: N,V; Relax this: E.

$E_T = \text{constant} \Rightarrow p(\nu) = \underbrace{e^{-\beta E(\nu)}}_{\text{statistical weight}}$ — microstate level

$$\Rightarrow p(E) = \sum_{\nu | E(\nu)=E} e^{-\beta E(\nu)} = e^{-\beta E}\,\Omega(E) \quad \text{——— ①}$$

- Entropy (S) –

$$S(N,V,E) = k_B \cdot \log \Omega(N,V,E) \quad : \text{extensive.} \quad \rightarrow \text{"Boltzman"} \quad \text{——— ②}$$

k-level: levels $0, \ldots, k-1$

$N = n_0 + n_1 + \cdots + n_{k-1}$

$E = \varepsilon_0 n_0 + \varepsilon_1 n_1 + \cdots + \varepsilon_{k-1} n_{k-1}$

$$\Omega(N,E) = \binom{N}{n_0}\binom{N-n_0}{n_1}\cdots\binom{n_{k-1}}{n_{k-1}} = \frac{N!}{n_0!\cdot n_1!\cdots n_{k-1}!} \quad \text{(possibilities)}$$

Using Sterling's approximation,

$\log N! \approx N \log N - N$ and (use $n_0 = p(n_0)\cdot N$)

$$\Rightarrow \log\Omega(N,E) = N\log N - N - \left(\sum_{i=0}^{k-1} p(n_i) N \log\left(p(n_i) N\right) - \underbrace{p(n_i) N}_{N}\right)$$

$$= N\log N - \left(N\sum_{i=0}^{k-1} p(n_i)\log(p(n_i))\right) - N\log N$$

$$= -N\cdot\sum_{i=0}^{k-1} p(n_i)\cdot\log(p(n_i)) \Rightarrow S = -Nk_B\sum_{i=0}^{k-1} p(n_i)\log(p(n_i)) \quad \text{——— ③}$$

↳ "Gibbs"

Canonical Ensemble

- $\boxed{\text{Fixing } N,V,T} \rightarrow \beta$

$$Z(\beta) = \sum_{\nu} e^{-\beta E(\nu)} = \sum_{E} \Omega(E)\cdot e^{-\beta E}$$

fixed!

$$p(\nu) = \frac{e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}}$$

$$\approx \int dE\ \Omega(E)\cdot e^{-\beta E} \quad : \text{"Laplace Transform of microcanonical partition function."}$$

$$= \int dE\ e^{-\beta[E - \beta^{-1}\log\Omega(E)]}$$

This is the partition function.

$$\Rightarrow Z(\beta) = \int dE \; e^{-\beta[E - \beta^{-1}\log \Omega(E)]}$$

$$= \int d\varepsilon \cdot e^{-\beta N[\underbrace{\varepsilon - \beta^{-1}\log w(\varepsilon)}_{= a(\varepsilon)}]}$$

$= a(\varepsilon)$ free energy (small ones contribute more).

$$\underbrace{\lim_{N\to\infty} \int d\varepsilon = e^{-\beta N a(\varepsilon_*)}}_{\text{Thermodynamical limit.}} \quad \text{where} \quad \varepsilon_* = \operatorname{argmin}\, a(\varepsilon).$$

How to get $\operatorname{argmin}\, a(\varepsilon) = \varepsilon^*$

$$\partial a(\varepsilon)/\partial\varepsilon = 0 \;\Rightarrow\; \underline{\beta = \frac{\partial \log w(\varepsilon)}{\partial \varepsilon}} \;\text{ at }\; \varepsilon = \varepsilon^* \quad \Leftrightarrow \quad \beta = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

This is Definition of Temperature $= 1/(k_B T)$

$$\boxed{\therefore\; \beta = \left(\partial S/\partial E\right)_{N,V} = 1/(k_B T)} \;\text{ is derived!}$$

$$Z(\beta) = e^{-\beta N a(\varepsilon^*)} = e^{-\beta[E_* - TS(E_*)]}$$

$\underline{A(N,V,T) = E - TS}$. : "Helmholtz Free Energy".

$$\Rightarrow Z(\beta) = e^{-\beta A(N,V,T)}$$

$$\Rightarrow \underbrace{-\beta^{-1}\log Z(\beta)}_{\text{Statistical quantity}} = \underbrace{A(N,V,T)}_{\text{Thermodynamics.}} \quad (\text{at } N\to\infty) \quad \text{———} \; ④$$

Take derivative of ④,

$$Z(\beta) = e^{-\beta E(N)}$$

Taking derivative,

$$-\frac{\partial \beta A}{\partial \beta} = -\frac{\partial \log Z(\beta)}{\partial \beta} = \frac{\partial \log \left(e^{-\beta E(\nu)} \Big/ 1 \right)}{\partial \beta}$$

$$= \frac{\sum_{\nu} E(\nu)\, e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}} = \sum_{\nu} E(\nu)\, p(\nu) = \langle E \rangle \quad \text{—— (5)}$$

One more derivative,

$$\frac{\partial^2 \log Z(\beta)}{\partial \beta^2} = \frac{\partial^2}{\partial \beta^2} \left(\log \sum_{\nu} e^{-\beta E(\nu)} \right) = \frac{\partial}{\partial \beta} \left(\frac{\sum_{\nu} E(\nu) \cdot e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}} \right)$$

$$= \underline{\frac{\sum_{\nu} E(\nu)^2 e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}}} - \underline{\left(\frac{\sum_{\nu} E(\nu)\, e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}} \right)^2}$$

$$= \langle E^2 \rangle - \langle E \rangle^2 = \mathrm{Var}(E) \quad \text{—————— (6)}$$

* $\log(Z(\beta))$: cumulant generation function. *

01/13/2024.

- Recap : $Z(\beta) = \sum_{\nu} e^{-\beta E(\nu)}$

↳ Canonical Partition Function (N, V, T)

$\Rightarrow p(\nu) = \dfrac{e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}}$ → probability of state ν.

Def) Moments of probability distribution. → Cumulants!

$\mu_n = \int x^n p(x)\, dx$ Ex) $Var(x) = \langle x^2 \rangle - \langle x \rangle^2 = \mu_2 - \mu_1^2$

- Cumulant Generating Function.

$g(\lambda) = \log \langle e^{\lambda x} \rangle$ w.r.t. x. $\Rightarrow dg/d\lambda = \dfrac{1}{\langle e^{\lambda x} \rangle} \cdot \langle x e^{\lambda x} \rangle$

① $dg/d\lambda \big|_{\lambda=0} = \langle x \rangle$: First cumulant

② $d^2g/d\lambda^2 \big|_{\lambda=0} = \langle x^2 \rangle - \langle x \rangle^2$: Second cumulant.

Now, take into $\log Z$.

$\Rightarrow \dfrac{d}{d(-\beta)} \log(Z(\beta)) = \dfrac{1}{Z(\beta)} \cdot \dfrac{d}{d(-\beta)} Z(\beta) = \dfrac{1}{Z(\beta)} \cdot \dfrac{d}{d(-\beta)} \left[\sum_{\nu} e^{-\beta E(\nu)} \right]$

$= \dfrac{1}{Z} \sum_{\nu} E(\nu) \cdot e^{-\beta E(\nu)} = \langle E \rangle$

$$\boxed{\therefore \dfrac{d}{d(-\beta)} \cdot \log(Z(\beta)) = \langle E \rangle}$$

$\Rightarrow \dfrac{d^2}{d(-\beta)^2} \cdot \log(Z(\beta)) = \dfrac{\partial}{\partial(-\beta)} = \dfrac{\left(\sum E(\nu) e^{-\beta E(\nu)}\right)}{\sum e^{-\beta E(\nu)}} = \langle E^2 \rangle - \langle E \rangle^2 = Var(E)$

$$\boxed{\therefore \dfrac{d^2}{d(-\beta)^2} \cdot \log(Z(\beta)) = Var(E)}$$

$\Rightarrow$ <u>$\log(Z(\beta))$ is a cumulant generating function.</u>

- $Z(\beta)$ related to thermodynamica properties. $(N \to \infty)$

$\approx\!> \boxed{\log Z(\beta) = -\beta A(N, V, T)}$ → Helmholtz. Free Energy.

Statistical — Thermodynamic.

⇒ "Free Energy" is "Cumulant generating function."

- Thermodynamics.

1st law) $dE = \bar{d}W + \bar{d}Q$ (d , $\bar{d}$ are different)

Differential. — Inexact differential.

→ Depends on pathway

$\int_{S_1}^{S_2} dE = \Delta E$

→ Path independent.

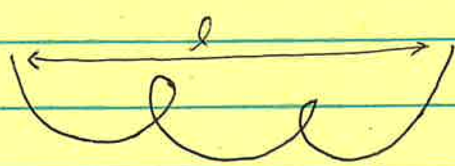
Recall , $\frac{d}{d(-\beta)} \log Z(\beta) = \langle E \rangle$, $\frac{d^2}{d(-\beta)^2} = \frac{d}{d(-\beta)} \langle E \rangle$, note: $\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$

⇒ $\frac{d}{d(-\beta)} \langle E \rangle$: energy change w.r.t temperature (T) : Heat capacity

⇒ $\frac{d\langle E \rangle}{dT} = +\frac{\partial \beta}{\partial T} \frac{\partial \langle E \rangle}{\partial \beta}$ ⇒ $\boxed{\underbrace{Var(E)}_{\text{Equil. condition}} = \underbrace{k_B T^2 C_V(T)}_{\text{Response}}}$

2nd law) Entropy of the universe is always increasing $\Delta S \geq 0$

↘ May be violated for "small" systems.



$\int_{l_1}^{l_2} f\, dl = \int_{l_1}^{l_2} \bar{d}W$

$W_{fast} > W_{slow}$ ∵ slow, at each time, less effort.

- Reversible Process.

$\Delta S = 0$ (i) 2^{nd} law (Clausius inequality) : $dS \geq \frac{đQ}{T}$

(ii) Adiabatic : $đQ = 0 \Rightarrow dE = dW$.

- Differentials.

$S(E, V, N)$

1) Total differential

$$dS = \left(\partial S/\partial E\right)_{V,N} dE + \left(\partial S/\partial V\right)_{E,N} dV + \left(\partial S/\partial N\right)_{E,V} dN$$

01/15/2024.

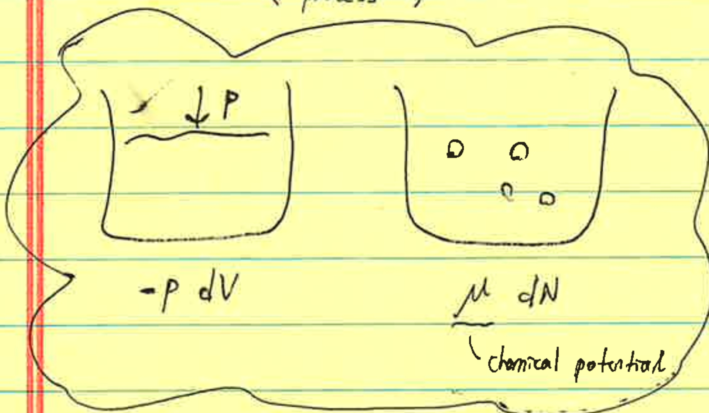
Recap

$dE = đW + đQ.$ 1st law

$\Delta S \geq 0$ (spontaneous process) 2nd law

Reversible $\Delta S = 0$ —— ①

Adiabatic $dE = đW_{rev} = dW = f dx.$ ②



total differential

$dE(S,V,N)$

$$= \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

$$\Rightarrow dE(S,V,N) = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}}_{=T} dS + \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{=-p} dV + \underbrace{\left(\frac{\partial E}{\partial N}\right)_{S,V}}_{=\mu} dN \quad \text{——} \; ③$$

$$dS(E, \underset{\sim}{x}) = \underbrace{\left(\frac{\partial S}{\partial E}\right)_{x}}_{=1/T} dE + \left(\frac{\partial S}{\partial \underset{\sim}{x}}\right)_E d\underset{\sim}{x} \quad \text{——} \; ④$$

(already known)

For reversible, $0 = \underbrace{\left(\frac{\partial S}{\partial E}\right)_x}_{=1/T} \underbrace{dW}_{= f dx} + \left(\frac{\partial S}{\partial x}\right)_E dx$

$$\Rightarrow \left(\frac{\partial S}{\partial x}\right)_E = -f/T \quad \text{——} \; ⑤$$

→ Entropic "Force." ~ penalty on Entropy.

③ becomes,

$dE = T dS - p dV + \mu dN$

Does this mean $\boxed{E = TS - pV + \mu N}$ Yes, but not always.

Note: S, V, N are extensive. $\Leftrightarrow$ $E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N)$ $(\lambda > 0)$

→ Homogeneous function of degree -1

Euler's theorem!

$E = TS - pV + \mu N \longrightarrow$ "Thermodynamic Potential"

$dE = TdS + SdT - pdV - Vdp + \mu dN - Nd\mu.$

$\Rightarrow \underbrace{SdT - Vdp + Nd\mu = 0}$ (Gibbs-Duhem eq.)

- Convert Thermodynamic Potential $\rightarrow$ Distinct Ensemble.

$E - \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}}_{=T} S$: Legendre Transformation. (remove dependence of S!)

$\Rightarrow A = E - TS$: Helmholtz Free Energy : we previously showed (N, V, T) from Canonical Partition Function

Let's check!

$dA = dE - TdS - SdT = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT.$

$\therefore$ dA depends only on N, V, T !

Gibb's Free Energy!

$G = E - TS - \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{=-p} \cdot V \Rightarrow G = E - TS + pV$, (N, P, T)

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

$= -SdT + \mu dN + VdP \rightarrow (N, P, T)$!

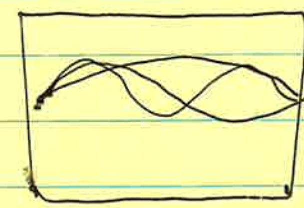
Stat. Mech. $\quad\quad$ Thermo.

$$Z(\beta) \quad \longleftrightarrow \quad e^{-\beta A}$$

Now, calculate $Z(\beta)$ for molecules.

$$Z(\beta) = \sum_{\nu} e^{-\beta E(\nu)}.$$

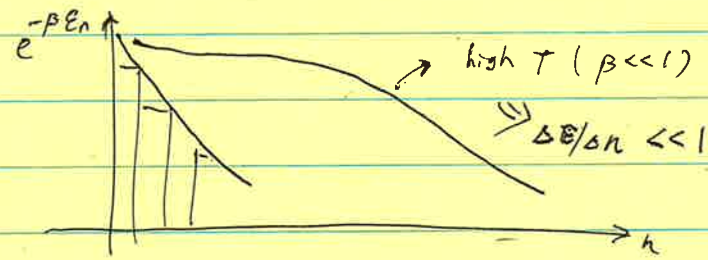
QM!



$$\varepsilon_n = \frac{n^2 h^2}{8ml^2} \quad \text{—— } (*)$$

Use $(*)$,

$$Z = \sum_{n=1}^{\infty} e^{-\frac{\beta n^2 h^2}{8ml^2}} \quad \text{—— ⑥}$$



⑥ can be approximated to $\approx \int_0^{\infty} e^{-\frac{\beta n^2 h^2}{8ml^2}} \cdot dn = \frac{\sqrt{2\pi m k_B T}}{h}$ (at $\beta \ll 1$)

$\Leftrightarrow \Delta\varepsilon_n/\Delta n \ll 1$

Now, 3D.

$$\varepsilon_n = \frac{h^2}{8m}\left((n_x/l_x)^2 + (n_y/l_y)^2 + (n_z/l_z)^2 \right)$$

$$\Rightarrow Z = \underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}}_{=\Lambda^{-3}} \underbrace{l_x l_y l_z}_{=V}$$

$$\Lambda = \underbrace{\left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}}$$

Thermal De Broglie Wavelength.

01/21/2025.

Recap : $\Delta G^{\ominus} = -k_B T \log K_{eq}$ ——— ①

$$K_{eq} = e^{-\Delta E_0/RT} \cdot \prod_{i,e\ \text{species}} \left(\frac{Z_{i,0}}{N_A}\right)^{\overset{\nearrow \text{stoichiometric coefficient}}{\nu_i}} \quad ——— ②$$

$Z_{i,0}^{\ominus}$ ($\ominus$ → standard state., i → species, 0 → zero-point)

		zero-point.
trans	$V^{\ominus}$	≈ 0
vib	/	$\hbar\omega/2$
rot	/	0
elec.	/	ε_0

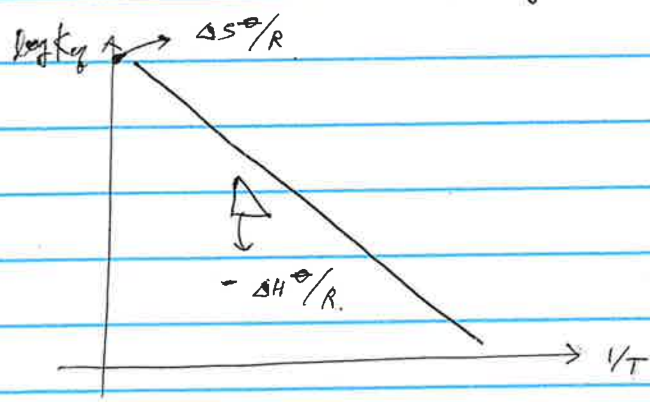
$\Delta G^{\ominus}$ = Enthalpy + Entropy.

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

$dG = -SdT + \underbrace{\mu dN - Vdp}_{\text{Enthalpy.}}.$

$G = E + pV$

$$\Rightarrow \Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \Rightarrow \log K_{eq} = -\frac{\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R} \quad — ①'$$



From ②,

$$\log K_{eq} = -\underbrace{\Delta E_0/(RT)}_{\text{Enthalpy}} + \underbrace{\sum_i \nu_i \log \frac{Z_{i,0}^{\ominus}}{N_A}}_{\text{Entropy}}$$

- Fluctuations in particle #

$$E_b + E(\nu) = E_{Total}$$

$$\Rightarrow \quad Z(\beta) = \sum_{\nu} e^{-\beta E(\nu)}$$

$$= \sum_{\{\nu | E(\nu) = E\}} \Omega(E)\, e^{-\beta E(\nu)} \approx \int dE\, \Omega(E)\, e^{-\beta E} = \tilde{\Omega}(E)$$

"Laplace Trans."

$$\approx \exp\left[-\beta \left(E - TS\right)\right] \quad (N \to \infty)$$

$$= e^{-\beta A}$$

$$E - \left(\frac{\partial E}{\partial S}\right)_{N,V} \cdot S \quad : \text{"Legendre Trans."}$$

Fix μ, T, V, $\quad p(\nu) \propto \exp\left(-k_B^{-1}\left[\left(\partial S/\partial E\right) E + \left(\partial S/\partial N\right) N\right]\right)$ we don't want N.

$$= \exp\left(-\beta E(\nu) + \beta \mu N(\nu)\right)$$

Grand Canonical pdf Ensemble.

$$\Xi = \sum_{\nu} e^{-\beta E(\nu) + \beta \mu N(\nu)} \rightarrow \text{Grand Canonical Partition Function.}$$

$\downarrow$ "Xi"

$$\left(\frac{\partial \log \Xi}{\partial (\beta\mu)}\right)_{T,V} = \frac{1}{\Xi}\left(\frac{\partial \Xi}{\partial (\beta\mu)}\right)_{T,V} = \frac{1}{\Xi} \cdot \frac{\partial}{\partial (\beta\mu)}\left\{\sum_{\nu} e^{-\beta E(\nu) + \beta\mu N(\nu)}\right\}$$

$$= \sum_{\nu} \frac{1}{\Xi} \cdot e^{-\beta E(\nu) + \beta\mu N(\nu)} \, N(\nu)$$

$$= \sum_{\nu} p(\nu)\, N(\nu) = \langle N \rangle$$

Response. Fluctuation!

Likewise, $\left(\frac{\partial^2 \log \Xi}{\partial (\beta\mu)^2}\right)_{T,V} = \langle N^2 \rangle - \langle N \rangle^2 = \left(\frac{\partial \langle N \rangle}{\partial (\beta\mu)}\right)_{T,V}$

⟨Laplace⟩ ⟨Legendre⟩

- Microcanonical $\Omega(N,V,E) = e^{S(E,V,N)/k_B}$
- Canonical $Z(\beta, V, N) = e^{-\beta A(N,V,T)}$
- Grand $\Xi(\beta, V, \mu) = e^{-\beta pV}$ $(*)$

$(*)$ $\Xi = \sum_{\nu} e^{-\beta E(\nu) + \beta\mu N(\nu)}$.

$$= \sum_{N} e^{\beta\mu N} \underbrace{\sum_{N(\nu)=N} e^{-\beta E(\nu)}}_{= Z(\beta) = e^{-\beta A}}$$

$(N, V, T$ fixed!$)$

$$= \sum_{N} e^{\beta\mu N - \beta A} = \sum e^{\beta pV}$$

Might as well, $E - (\partial E/\partial S)_{N,V} \cdot S = E - TS$. $(N,V,E) \to (N,V,T)$.

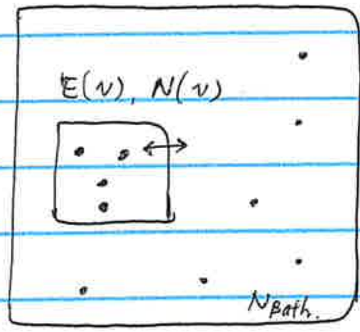
$A - (\partial A/\partial N)\cdot N = E - TS - \mu N$. $(N,V,T) \to (\mu,V,T)$

$= pV$.

$\to$ Landau potential

01/29/2025.

Recap.

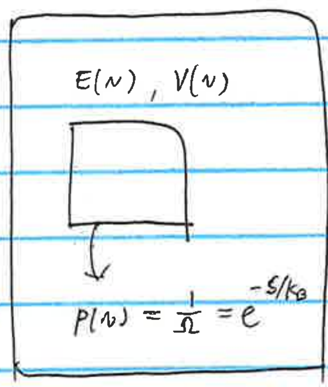


Grand - canonical Ensemble.

$$\Xi = \sum_{\nu} e^{-\beta E(\nu) + \beta\mu N(\nu)}.$$

$$\frac{\partial \log \Xi}{\partial(\beta\mu)} = \langle N \rangle, \quad \frac{\partial^2 \log \Xi}{\partial(\beta\mu)^2} = \langle N^2 \rangle - \langle N \rangle^2$$

$$= \left(\frac{\partial \langle N \rangle}{\partial(\beta\mu)} \right).$$ response!



$$p(\nu) \propto \exp\left[-\frac{1}{k_B}\left(\left(\frac{\partial S}{\partial E}\right) E(\nu) + \left(\frac{\partial S}{\partial V}\right) V(\nu) \right) \right]$$

$\Rightarrow$ Relaxing $E(\nu)$ and $V(\nu)$.

since, $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$

$$p(\nu) = \exp(-\beta E(\nu)) \cdot \exp(-\beta p \cdot V(\nu))$$

$$\underset{(N,P,T)}{\Delta} = \sum_{\nu} e^{-\beta E(\nu) - \beta p V(\nu)}.$$

isothermal, isobaric.

Microscopic

Macroscopic

$$\frac{\partial \log \Delta \beta p}{\partial(-\beta p)} = \langle V \rangle. \quad \frac{\partial^2 \log \Delta}{\partial(-\beta p)} = Var\langle V \rangle = \left(\frac{\partial \langle V \rangle}{\partial(-\beta P)} \right)$$

$\propto$ isothermal compressibility.

If $N \to \infty$, $Var(V) \downarrow 0$. $\to$ Hard to compress?

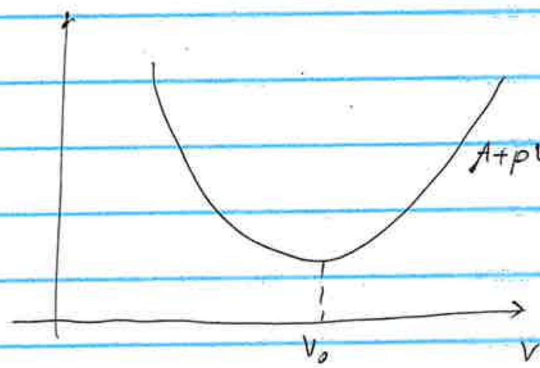
$$\Delta(N,p,T) = \sum_{\nu} e^{-\beta E(\nu) - \beta p V(\nu)}$$

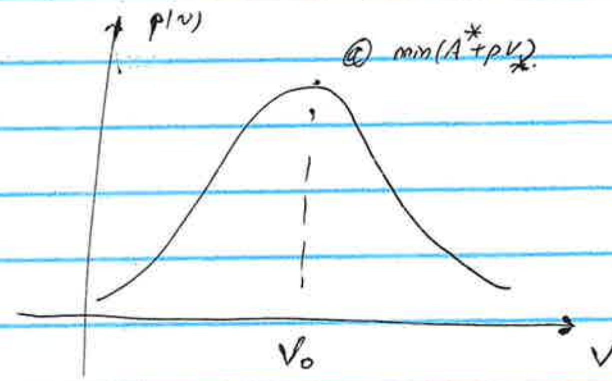
$$= \sum_{V} e^{-\beta p V} \underbrace{\sum_{V(\nu)=V} e^{-\beta E(\nu)}}_{N,V,T \Rightarrow Z(\cancel{\beta})}$$

$$= \underbrace{\sum_{V} e^{-\beta p V} Z(V)}_{\text{Laplace Trans.}} = \tilde{Z}(\beta p)$$

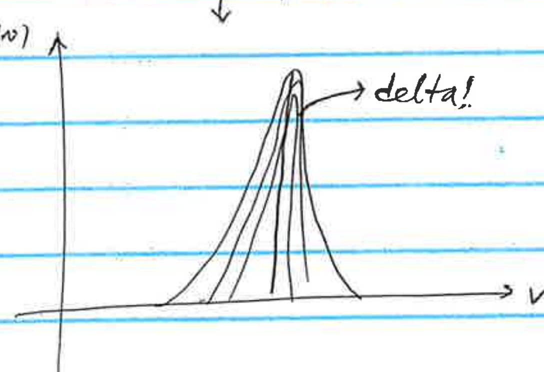
We know $Z = e^{-\beta A(N,V,T)}$

$$\Delta(N,pT) = \sum_{V} e^{-\beta \underbrace{(A+pV)}_{= G}} = \sum_{V} e^{-\beta G}$$





$\downarrow N \to \infty$



$$\therefore \Delta \approx e^{-\beta(A_* + pV_*)} = e^{-\beta G}$$

saddle point Laplace approx.

$\therefore G = -\beta^{-1} \log \Delta$.

$$\begin{tikzcd}
S(E,V,N) \arrow[r, "\text{Legendre}", "-\left(\frac{\partial S}{\partial E}\right)_{V,N} E"'] \arrow[d, "+pV"'] & A \arrow[d, "+pV"] \\
H(S,p,N) & G \arrow[l]
\end{tikzcd}$$

$$\begin{tikzcd}
e^{S/k_B} \arrow[r, "\text{Laplace}"] \arrow[dr] & e^{-\beta A} = Z \arrow[d] \\
& e^{-\beta G}
\end{tikzcd}$$

2

01/31/2025

Recap. $S(E,V,N) \longrightarrow A(N,V,T)$ $\qquad \Omega = e^{-S/k_B} \longrightarrow Z = e^{-\beta A}$

$\qquad\qquad\qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow$

$\phi(T,V,\mu) \longleftarrow G(N,P,T)$ $\qquad \Xi = e^{\beta PV} \longleftarrow \Delta = e^{-\beta G}$

- Realistic.. Quantum Particles.

$$E\psi = V\psi - \frac{h^2}{2m}\cdot \Delta\psi$$

Consider two particles.

$\psi(r_1, r_2)$ given. $\quad p(r_1,r_2) = \|\psi(r_1,r_2)\|^2$.

$\Rightarrow \psi(r_1,r_2) = e^{j\phi}\,\psi(r_2,r_1)$

$\phi = \pi$ ex) e^-, fermions, protons, neutrons.

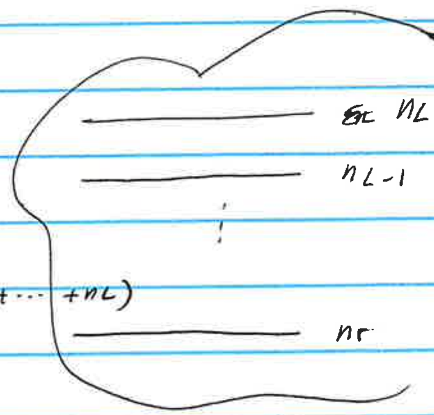
$\phi = 0$ ex) photons, Bosons, bound pair of fermion

Pauli exception principle

$$\psi_{Fermion}(r_1,r_2) = \frac{1}{\sqrt{2}}\left\{\psi_j(r_1)\psi_k(r_2) - \psi_j(r_2)\psi_k(r_1)\right\} = 0 \text{ if } r_1 = r_2$$

$$\psi_{Boson}(r_1,r_2) = \frac{1}{\sqrt{2}}\left\{\psi_j(r_1)\psi_k(r_2) + \psi_j(r_2)\psi_k(r_1)\right\} > 0 \text{ if } r_1 = r_2$$

Think about "how many" energy occupancy.



$$\Xi_{Fermion} = (\beta, \beta\mu) = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_L=0}^{1} \boxed{}$$

$$\boxed{} = e^{-\beta(n_1\varepsilon_1 + \cdots + n_L\varepsilon_L) + \beta\mu(n_1 + \cdots + n_L)}$$

$$\Rightarrow \Xi_{Fermion} = \sum\cdots\sum e^{-\beta\sum_{i=1}^{L}(\varepsilon_i - \mu)n_i}$$

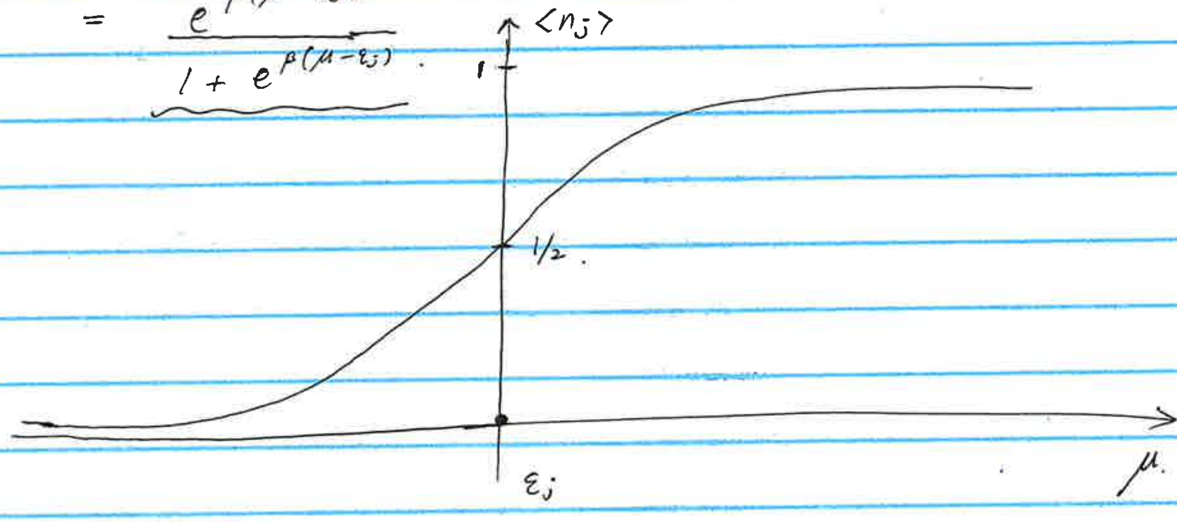
$$= \prod_{i=1}^{L}\left[1 + e^{-\beta(\varepsilon_i - \mu)}\right] \quad\text{———}\quad (*)$$

(*) gives grand canonical partition function.

$$\langle n_j \rangle = \frac{\partial \log \Xi}{\partial(-\beta(\varepsilon_j - \mu))} = \frac{\partial}{\partial(\beta(\mu - \varepsilon_j))} \log\left(\prod (11) \right).$$

$$= \frac{\partial}{\partial (11)} \sum \log \left(\quad \right) = \frac{\partial}{\partial(\beta(\mu-\varepsilon_j))} \left[\log \left(1 + e^{\beta(\mu - \varepsilon_j)} \right) \right].$$

$$= \frac{e^{\beta(\mu-\varepsilon_j)}}{1 + e^{\beta(\mu - \varepsilon_j)}}.$$



In Bosons.

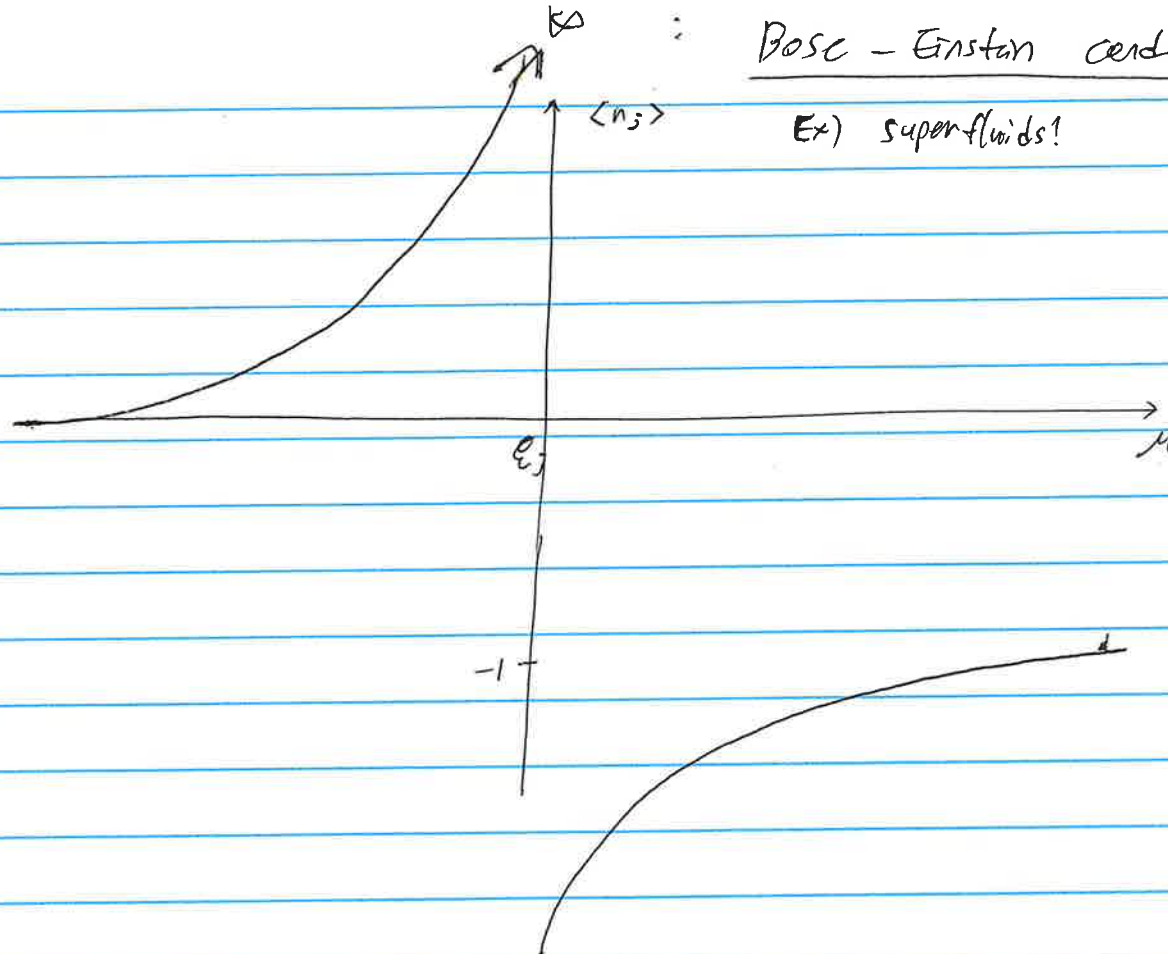
$$\Xi(\beta, \beta\mu) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_L=0}^{\infty} e^{-\beta(n_1\varepsilon_1 + \cdots + n_L\varepsilon_L) + \beta\mu(n_1 + \cdots + n_L)}.$$

$$= \sum_{i=1}^{L} \frac{1}{1 - e^{\beta(\mu - \varepsilon_i)}}$$

(Note $\sum_{n_i=0}^{\infty} e^{-(\mu - \varepsilon_i)n_i\beta} = \frac{1}{1 - e^{-(\mu - \varepsilon_i)\beta}}$)

$$\Rightarrow \frac{\partial \log \Xi}{\partial(\beta(\mu - \varepsilon_j))} = \langle n_j \rangle = \frac{\partial}{\partial(\beta(\mu-\varepsilon_j))} \left[\log \frac{1}{1 - e^{+\beta(\mu - \varepsilon_j)}} \right]$$

$$= \frac{e^{\beta(\mu - \varepsilon_j)}}{1 - e^{\beta(\mu - \varepsilon_j)}}$$



: Bose – Einstein condensation

Ex) superfluids!

02/03/2025.

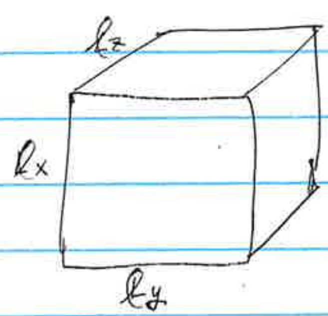
$\langle n_i \rangle = \; ?$

- Fermi' levels.

Metals "are" an ideal gas of Fermions.

$\downarrow$ Heat capacity metals can be explained with this model.

- Fermionic Energy Levels.



$l_x = l_y = l_z.$

$$\varepsilon = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right).$$

Define: $\vec{k} = \frac{\pi}{L}\cdot\left(n_x\,\hat{x} + n_y\,\hat{y} + n_z\,\hat{z}\right).$

$\searrow$ wave vectors.

$$\varepsilon(\vec{k}) = \frac{\hbar^2}{2m}\|\vec{k}\|_2^2.$$

$\rightarrow$ There is a degeneracy (with same $\|\vec{k}\|$).

$g(k) \propto \|k\|_2^2.$

Thus, $\langle E \rangle = \int \varepsilon\, F(\varepsilon)\cdot g(\varepsilon).\, d\varepsilon.$

02/05/2025.

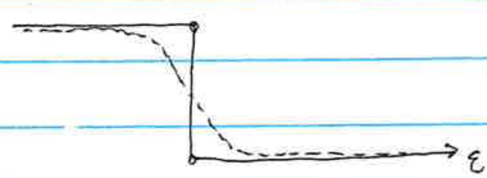
Ξ_{Boson} $\Xi_{Fermion}$.

$$\Xi_{Boson} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} - 1}$$ → it may diverge!

$$\Xi_{Fermion} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} + 1}$$

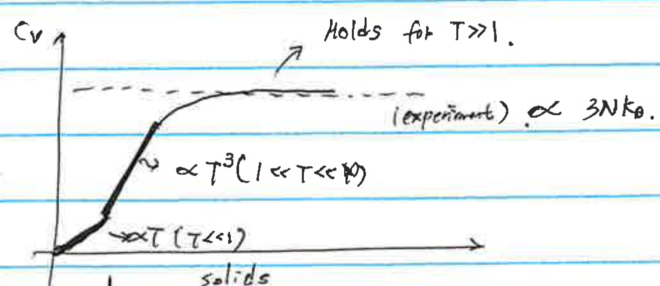
$$\langle E \rangle = \int_0^{\infty} \varepsilon \cdot g(\varepsilon) \cdot \left[F_0(\varepsilon) + \Delta F(\varepsilon, T) \right] d\varepsilon.$$

$F_0(\varepsilon)$



$\partial \langle E \rangle / \partial T$ = Heat Capacity.

* History : Dulong - Petit law.

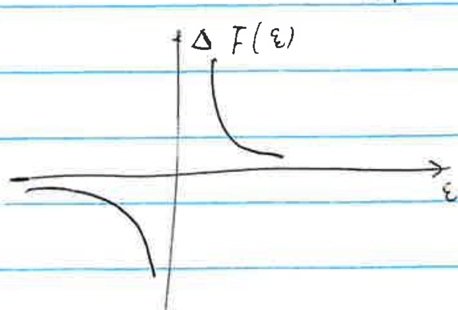


Equipartition Theorem!

→ Every harmonic oscillator contributes 3Nk_BT. !

Conclusion : Heat capacity is independent of T.

Now, how to get $\frac{\partial}{\partial T} \langle E \rangle$



$$\Rightarrow \langle E \rangle = \int_0^{\infty} \varepsilon \, g(\varepsilon) \, \Delta F(\varepsilon, T) \, d\varepsilon$$

Hence, $\langle E \rangle = \int_0^\infty \varepsilon\, g(\varepsilon) \cdot \Delta f(\varepsilon, T)\, d\varepsilon + \text{const.}$

$x = \beta(\varepsilon - \mu_0).$, $dx = \beta . d\varepsilon.$

$$\Rightarrow \langle E \rangle = \int_0^\infty (\mu_0 + k_B T x) . \Big[\underbrace{g(\mu_0) + g'(\mu_0) . k_B T x + \cdots}_{\text{all odd power of } T} \Big] \Delta f(\varepsilon, T)\, k_B T\, dx$$

$\equiv$ even powers of x goes to zero

$\because \Delta f(\varepsilon, T)$ is odd.

$$\therefore \langle E \rangle = A + BT^2 + CT^4 + \cdots$$

$$\Rightarrow C_V = \frac{\partial \langle E \rangle}{\partial T} = 2BT + 4CT^3 + \cdots$$

$\Rightarrow$ when $T \ll 1$, $C_V \propto T^1$

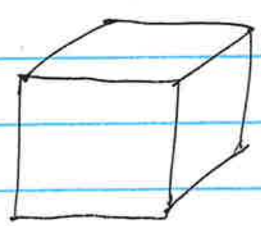
when $\langle n_j \rangle_{Boson} = \dfrac{1}{e^{\beta(\varepsilon_j - \mu)} - 1}$

$\langle n_j \rangle_{Fermion} = \dfrac{1}{e^{\beta(\varepsilon_j - \mu)} + 1}$

cannot distinguish when $\beta \ll 1$.

$\langle n_j \rangle_B \approx \langle n_j \rangle_F$

- Waves



e^{jkr} where $\vec{k} = \frac{\pi}{L}(n_x \hat{x} + n_y . \hat{y} + n_z . \hat{z})$.

$\downarrow$

plane wave basis.

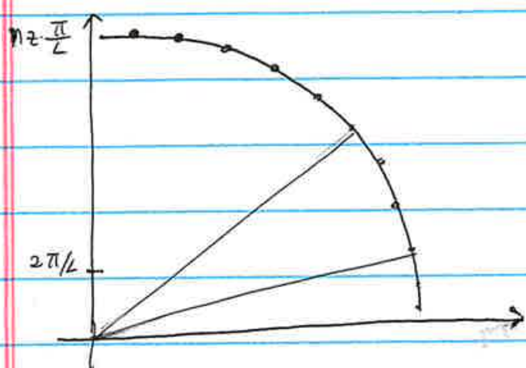
$\|\vec{k}\|_2$ norm $= k$

$$\Rightarrow g(k) = \frac{V}{2\pi^2} k^2$$

- Density of States.

$g(k).\,dk$ = # of $\vec{k}$ with magnitude $\|\vec{k}\| \in [k, k+dk]$

density   Volume.



(" How many modes / unit volume ")

$\times \; \frac{1}{8} \cdot$ (surf. area of sphere radius k)

Symmetry ! (positive axes only)

$$\Rightarrow g(k) = \frac{1}{\left(\frac{\pi}{L}\right)^3} \cdot \frac{4\pi k^2}{8} = \underline{\frac{V}{2\pi^2} \cdot k^2}$$

$$\Rightarrow \langle N \rangle = \int_0^\infty g(k)\, e^{-\beta E(k) + \beta\mu} = \frac{V}{2\pi^2} \cdot \int_0^\infty k^2\, e^{\beta\mu} \cdot e^{-\frac{\beta \hbar^2}{2m} k^2}$$

$$\therefore \langle N \rangle = V \cdot e^{\beta\mu} \cdot \Bigg(\underbrace{\frac{h}{2\pi m k_B T}}_{=\lambda_T}\Bigg)^{-3} = \frac{V}{(\lambda_T)^3}\, e^{\beta\mu}$$

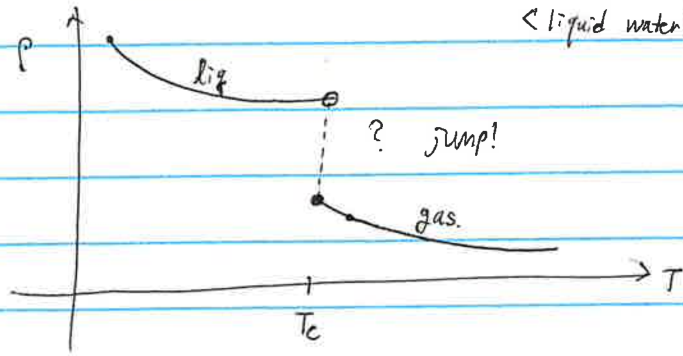
$$\therefore \frac{\langle N \rangle}{V} = \rho = e^{\beta\mu} / \Lambda_T^3$$

length scale.

ρ classical when $\frac{\langle N \rangle}{\Lambda_T^3} << 1$

02/07/2025

Recap $\rho_{classical}$ when $e^{\beta\mu}$.



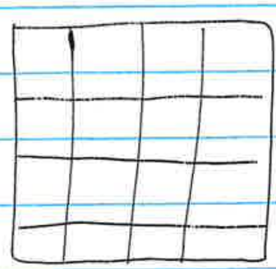
<liquid water>

- Mass partitioning between phases

$$Z_{liq} = \int_{liq} e^{-\beta\left(U(r_1 \sim r_N) + \frac{1}{2} p^T M^{-1} p\right)} dr^N dp^N$$

→ Contribution from momentum = Gaussian → out integral.

⇒ $\int_{liq} e^{-\beta(U(r_1 \sim r_N))}$ should be "non-analytic" for jump.



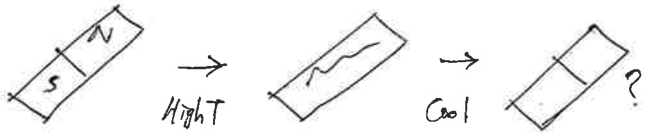
$\{ Z_{cell}(\beta) \}^N$

$-\beta A = N \log Z(\beta)$

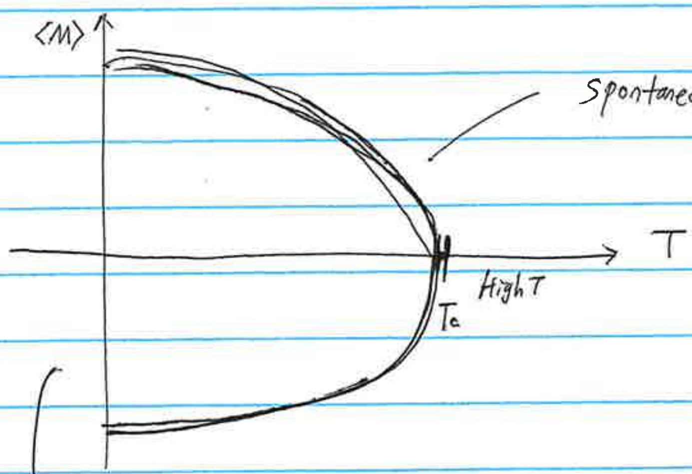
"Assumption : Cells are independent"

↳ Maybe not true ?

⇒ Modern Idea about phase Transitions diverging correlations.



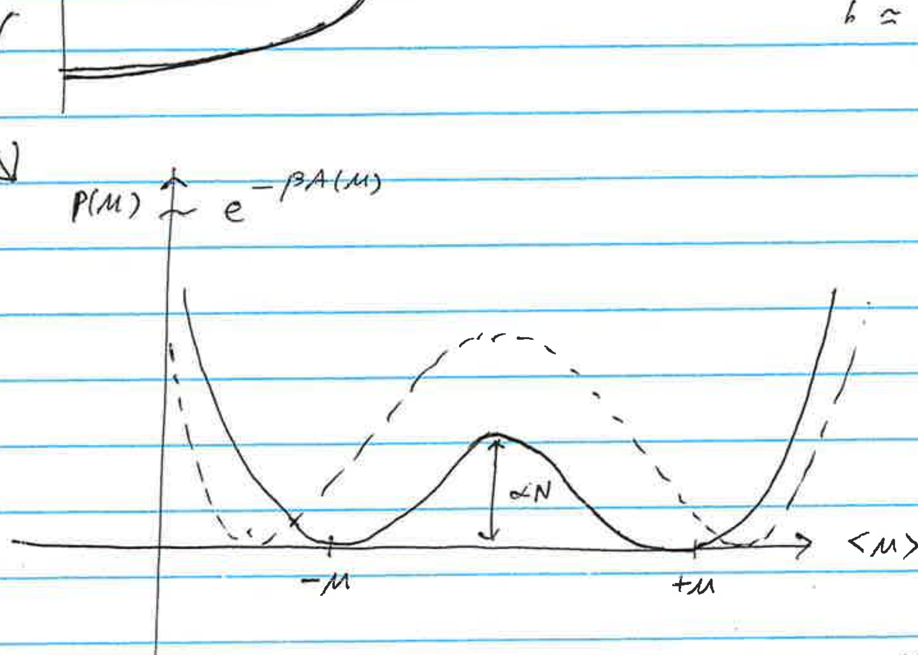
Magnets!



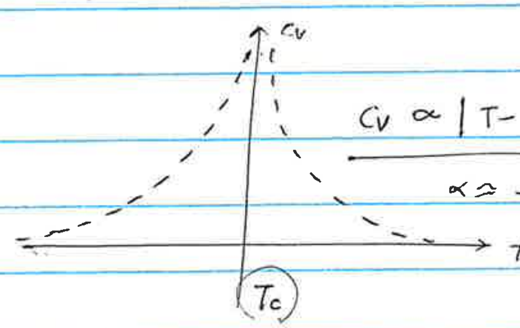
Spontaneous symmetry breaking.

$$\underline{\langle M\rangle \propto |T-T_c|^{b}}$$

$b \simeq 0.32$



$$\left|\frac{\partial M}{\partial T}\right|_{T_c} \gg 1 \qquad \underbrace{\left|\frac{\partial\langle E\rangle}{\partial T}\right|_{T_c}}_{=C_V} \gg 1$$



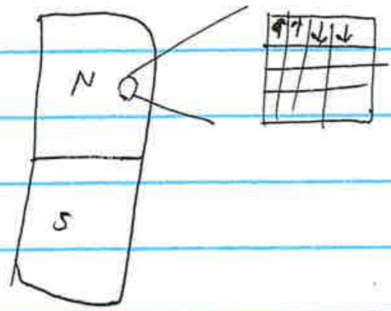
$$\underline{C_V \propto |T-T_c|^{\alpha}}$$

$\alpha \simeq -0.11$

Experiment : $\boxed{b_{mag} = b_{liq}}$: "Universality" "β"

Diverging lengthscales dominate phenomenology of phase transitions.

Independent of material properties, ...



$\{\sigma_i\}^N$

$E(\sigma_i) = -h_z \cdot \sigma_1$

$\{n_i\} = 0, 1$

What if they communicate?

$$E(\sigma_1, \sigma_2) = -h_z \cdot \sigma_1 - J \underbrace{f(\sigma_1, \sigma_2)}$$

$$= \sigma_1 \cdot \sigma_2 = \begin{cases} +1 & \text{aligned} \\ -1 & \text{not aligned.} \end{cases}$$

$$= -h_z \cdot \sigma_1 - J \sigma_1 \cdot \sigma_2 \qquad (J > 0)$$

$$Z(\beta) = \sum_{\sigma_1 = \pm 1} \sum_{\sigma_2 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \cdot \cancel{\exp\{\beta(h \sum_i \sigma_i + J \sigma_1 \sigma_2)\}}$$

(Ising Model)

$$e^{\beta h_z \sum_i \sigma_i + \beta J \underbrace{\sum_{j \in N(i)} \sigma_i \sigma_j}}$$

interaction term

not factorized.

02/10/2025

Recap : 2^{nd} order phase transition.

→ Have discontinuous jump in free energy.

→ Divergent fluctuation.

→ Susceptibility..

• Universality.

Near 2^{nd} order phase transitions

→ There exists universal "critical exponents" that $\boxed{\text{characterize divergence}}$

$$\left.\begin{array}{l} |\langle M\rangle| \propto |T-T_c|^{\beta} \\ |\rho-\rho_c| \propto |T-T_c|^{\beta} \end{array}\right\} \rightarrow \text{Can we predict } \beta\text{ ?} \rightarrow \text{Ising model}$$

∴ Fact : Microscopic detail is not necessary to describe critical phenomena.

• Ising model

$\sigma = \pm 1$

↑	↓	↑	↑
↓	↓	↑	↓
↑	↓	↑	↑
↑	↓	↓	↓

$$\mathcal{H}(\sigma_1 \sim \sigma_n) = -\sum_{i=1}^{N} h\cdot\sigma_i - J\underbrace{\sum_{j\in N(i)}}_{\text{neighbors.}} \sigma_i\sigma_j \quad (1)$$

$$\left(\underbrace{\{\sigma_i\}}_{\text{spins}} \rightarrow \underbrace{\{n_i\}}_{\text{occupancy}} \quad \{0,1\} = n_i \right)$$

(2)

$$\Rightarrow -\sum_{i,j\in N(i)} \varepsilon\cdot n_i n_j - \mu\cdot\sum_{i=1}^{N} n_i \rightarrow \text{How is this related to (1) ?}$$

Relate (1) and (2),

$$\underbrace{H = -\varepsilon \sum n_i n_j - \mu \cdot \sum n_i}_{\text{lattice gas}} \longleftrightarrow \underbrace{H = -\sum h\sigma_i - J \cdot \sum \sigma_i \sigma_j}_{\text{ising model}}$$

$$\Rightarrow Z_{ising}(\beta) = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_n = \pm 1} \cdot e^{+\beta h \sum \sigma_i} e^{+\beta J \sum \sigma_i \sigma_j}$$

- 1 Dimensional Ising Model.

Introduce $b_i = \sigma_i \sigma_{i+1} = \begin{Bmatrix} \pm 1 \\ \pm 1 \end{Bmatrix}$

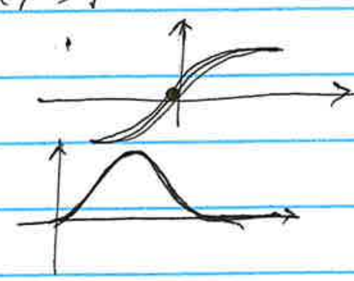
$\Rightarrow$ $\sigma_1, b_1, \cdots b_{N-1}$ recovers $\sigma_1 \sim \sigma_N$.

Assume no external field $(h=0)$,

$$Z(\beta) = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \exp\Big(\beta J \sum \underbrace{\sigma_i \sigma_{i+1}}_{= b_i}\Big)$$

$$= \sum_{\sigma_1} \left(e^{\beta J} + e^{-\beta J}\right) = 2 \cdot \left(e^{\beta J} + e^{-\beta J}\right)^{N-1}$$

$$= 2^N \cdot \{\cosh(\beta J)\}^{N-1}$$



$\Rightarrow$ $\partial \log Z / \partial \beta = NJ \tanh(\beta J)$.

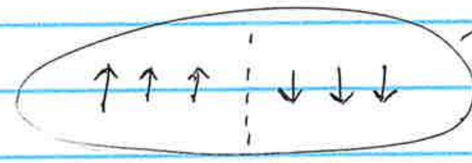
$\Rightarrow$ $\partial^2 \log Z / \partial \beta^2 = NJ^2 \left(1 - \tanh^2(\beta J)\right)$

$\therefore$ 1D $\rightarrow$ No phase transition.

• why no phase transition in 1D ?

→ Thermodynamics of "long range order"

$\Delta A = \Delta E - T\Delta S$



→ (*)

1) $\Delta E = -J - +J = -2J$

2) $T\Delta S = k_B T \cdot \log \underbrace{N}_{\text{choices to flip in } (*)}$

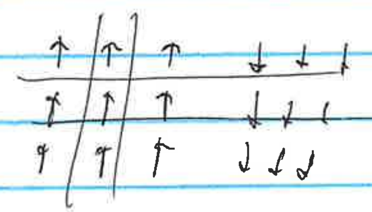
As $N \to \infty$, energetic penalty ↓

⇒ No phase transition ∵ energetic cost cannot compete with entropic benefit.

In 2D.

1) $\Delta E = 2J \cdot \sqrt{N}$

2) $T\Delta S = k_B T \cdot \log . \, 2\sqrt{N}$



As $N \to \infty$, $\Delta E \gg T\Delta S$

02/14/2025

- Detailed Balance

  $\sim \pi(\nu) \cdot P(\nu \to \nu') = \pi(\nu') \, P(\nu' \to \nu)$.

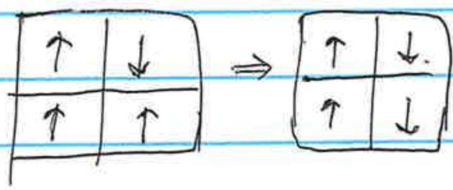
$$\Rightarrow \frac{\pi(\nu')}{\pi(\nu)} = \frac{P(\nu \to \nu')}{P(\nu' \to \nu)}$$

- Define proposal move. (Metropolis)

  $\nu_i \to \nu_{i+1}$.

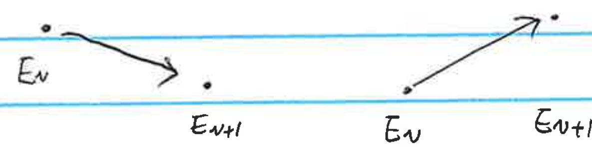
  1. select random, flip sign

  $P(\nu_i \to \nu_{i+1}) = 1/n$.



  2. Accept / Reject ↗ Metropolis!

  w/ prob $= \min[1, e^{-\beta(E(\nu_{i+1}) - E(\nu_i))}]$



Accept! Not sure $\sim e^{-\beta \Delta E}$

$$\frac{P(\nu_i \to \nu_{i+1})}{P(\nu_{i+1} \to \nu_i)} = \frac{\overset{1/n \text{ (state independent)}}{P_{gen}}(\nu_i \to \nu_{i+1})}{\underset{1/n}{P_{gen}}(\nu_{i+1} \to \nu_{i})} \cdot \frac{P_{acc}(\nu_i \to \nu_{i+1})}{P_{acc}(\nu_{i+1} \to \nu_i)}$$

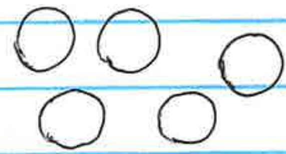
$$= \frac{\min[1, e^{-\beta \Delta E}]}{\min[1, e^{\beta \Delta E}]} = \begin{cases} \dfrac{e^{-\beta \Delta E}}{1} & \Delta E > 0 \\ \quad ||| & \\ \dfrac{1}{e^{\beta \Delta E}} & \Delta E < 0 \end{cases}$$

$$= e^{-\beta \Delta E} = \frac{e^{-\beta E_i}}{e^{-\beta E_{i+1}}} = \frac{\pi(\nu_i)}{\pi(\nu_{i+1})}$$

∴ Metropolis satisfies detailed balance.

Q) Detailed balance in continuous systems. → MCMC in liquid.

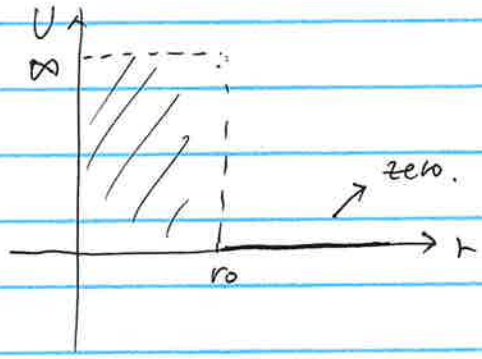
- Hard disk model



$V(r_1 \sim r_n)$ potential (interaction)

$= \sum_{i<j} u(r_{ij})$

$r_{ij} = \| \underset{\sim}{r_i} - \underset{\sim}{r_j} \|_2$.



① Choose particle random.

② Propose displacement $\Delta\vec{r} \sim N(0, \sigma^2)$

③ Check overlap and reject.

→ They repel each other → Higher pressure!

Define $n(r)$: # particles in radius (r).

$\Rightarrow g(r) = \frac{n(r)}{\#\text{ in ideal}}$ ≑ radial distribution function.

01/17/2025

Recap: $dE(S,V,N) = TdS - pdV + \mu dN$

- Gibbs-Duhem equation

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

→ Legendre transform.

1) $E - (\partial E/\partial S) S = E - TS = A$: Helmholtz free energy.

2) Gibbs ~~~

Construct $Z_{tras}(\beta)$: Translational only

$$= \sum_{n=1}^{\infty} e^{-\beta \varepsilon_{trans}^{(n)}} \approx \int_0^{\infty} e^{-\beta \varepsilon_{trans}^{(n)}} dn = V/\Lambda^3$$

At high temperature!

counting resolution.

$$\left(\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}\right)$$

- $$\varepsilon_{mol}^{(ijkl)} = \varepsilon_{trans}^{(i)} + \varepsilon_{vib}^{(j)} + \varepsilon_{rot}^{(j)} + \varepsilon_{elec}^{(k)} + \varepsilon_{nuclear}!$$

$$\Rightarrow Z_{mol}(\beta) = \sum_{i,j,k,l} e^{-\beta\left[\varepsilon_{trans}^{(i)} + \varepsilon_{vib}^{(j)} + \varepsilon_r^{(k)} + \varepsilon_e^{(l)}\right]}$$

$$= \underbrace{\sum_i e^{-\beta \varepsilon_t^{(i)}}}_{} \underbrace{\sum_j e^{-\beta \varepsilon_v^{(j)}}}_{} \underbrace{\sum_k e^{-\beta \varepsilon_r^{(k)}}}_{} \underbrace{\sum_l e^{-\beta \varepsilon_e^{(l)}}}_{}$$

$$= Z_{trans}(\beta) \; Z_v(\beta) \; Z_r(\beta) \; Z_e(\beta).$$

$$= V/\Lambda^3$$

Note : ε_{elec} is too large deviation

⇒ Cannot approximate into integral!

$$\frac{\partial \log\left(\frac{V}{\Lambda^3}\right)}{\partial V} = \frac{\Lambda^3}{V} \cdot \frac{1}{\Lambda^3} = \frac{1}{V}.$$

Rigid Rotor Model. (rotation !)

$$I = \mu r^2 \quad , \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\varepsilon_{rot}^{(l)} = \frac{\hbar^2}{2I} l(l+1) \quad , \quad B = \frac{\hbar^2}{2Ihc} = \frac{h}{8\pi^2 hc} \quad \text{(rotational constant)}$$

$$(l = 0, 1, \cdots)$$

$$z_{rot}(\beta) = \sum_{l=0}^{\infty} e^{-\beta B ch \cdot l(l+1)} g(l)$$

Can we do $\beta << 1$? Yes since $Bch\, l(l+1)$ not that abrupt change

$$\Rightarrow z_{rot}(\beta) \cong \int_0^\infty e^{-\beta ch \cdot B \cdot l(l+1)} dl \cdot g(l) \quad \text{where} \quad \Theta_{rot} = \frac{Bch}{k_B}.$$

$$\approx \int_0^\infty g(l)\, e^{-\frac{\Theta_{rot}}{T} l(l+1)} dl. \qquad g(l) : \text{degeneracy}.$$

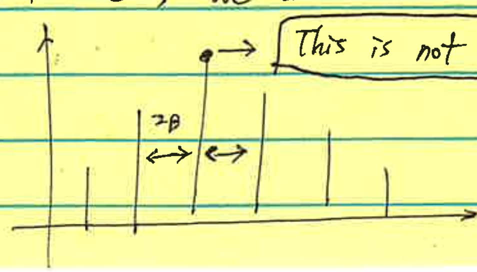
$$= \int_0^\infty (2l+1)\, e^{-\frac{\Theta_{rot}}{T} \cdot l(l+1)} dl = T/\Theta_{rot}$$

For hetero ~~male~~ nuclear.

Note : For Homonuclear Diatomic, $z_{rot}(\beta) = \frac{T}{2\Theta_{rot}}$ diatomic.

$$\boxed{\therefore\ z_{trns}(\beta) = V/\Lambda^3 \ , \ z_{rot}(\beta) = T/\Theta_{rot}.}$$

Ex) For CO, we do microwave spectroscopy.



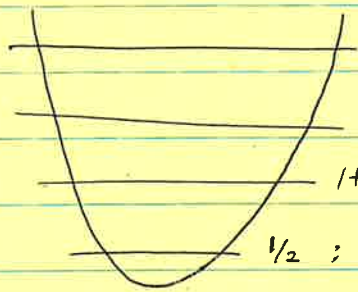
$\rightarrow$ This is not most prefered energy

$$p(l) \sim g(l)\, e^{-\frac{\Theta}{T} l(l+1)}$$

increase l .

Vibration!

- $$Z_{vib}(\beta) = \sum_n g_n \, e^{-\beta \varepsilon_{vib}^{(n)}}$$



$1 + 1/2$

$1/2$; zero point energy.

$$\varepsilon_{vib}^{(n)} = \hbar\omega\left(\frac{1}{2} + n\right)$$

no degeneracy!

$$Z_{vib}(\beta) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\frac{\hbar\omega}{2}} \cdot \frac{1}{1 - e^{-\beta\hbar\omega}}$$

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

- Sum them up

$$Z_{mol}(\beta) = Z_{trans}(\beta) \cdot Z_{rot}(\beta) \cdot Z_{vib}(\beta) \cdot Z_{elec}(\beta)$$

$$= \frac{V}{\Lambda^3} \cdot \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \cdot \frac{T}{\sigma\Theta_{rot}} \cdot Z_{elec}(\beta) \qquad \sigma = \begin{cases} 1 & \text{heteronuclear diat.} \\ 2 & \text{homonuclear. diato} \end{cases}$$

01/22/2024.

Recap.

		Energy	Appx.
$Z_{trans}(\beta) = V/\Lambda^3$		n^2	High T
$Z_{rot}(\beta) = \Theta_{rot}/\sigma T$	$\sigma = \begin{cases} 1 & \text{hetero dimer} \\ 2 & \text{Homo dimer} \end{cases}$	$\ell(\ell+1)$	High T
$Z_{vib}(\beta) = \dfrac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$			no approx.

- $Z_{elec}(\beta)$ and $Z_{nuclear}(\beta)$.

$$Z_{elec}(\beta) = \sum_{i=0}^{\infty} e^{-\beta\varepsilon_i} \cdot \underbrace{g_i}_{\text{degeneracy}}.$$

Ex) He. 20eV , $k_BT = 0.0257$

$$\Rightarrow g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1} \sim e^{-800} \ll 1$$

(But for nuclear excited state (first state)

$= 10^6 eV \gg k_BT$

$\Rightarrow$ degeneracy does contribute.

$$Z_{nuc}(\beta) = 2\underbrace{I}_{\text{nuclear quantum number}}+1$$

$$\Rightarrow \begin{cases} Z_{elec}(\beta) = 1 + g_1 e^{-\beta\varepsilon_1} & (k_BT \ll eV) \\ Z_{nuc}(\beta) = 2I+1 & (k_BT \ll 10^6 eV) \end{cases}$$

we stated,

$$\varepsilon_{mol}(i,j,k,\ell) = \varepsilon_{trans}(i) + \varepsilon_{rot}(j) + \varepsilon_{vib}(k) + \varepsilon_{elec}(\ell).$$

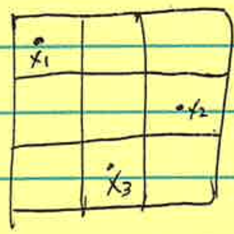
$$\underbrace{\sum_{ijk\ell} e^{-\beta\varepsilon(i,j,k,\ell)}}_{Z_{mol}(\beta)} = \underbrace{\sum_i e^{-\beta\varepsilon_{trans}(i)}}_{Z_{trans}(\beta)} \cdot \underbrace{\sum_j e^{-\beta\varepsilon_{rot}(j)}}_{Z_{rot}(\beta)} \cdot \underbrace{\sum_k e^{-\beta\varepsilon_{vib}(k)}}_{Z_{vib}(\beta)} \cdot \underbrace{\sum_\ell e^{-\beta\varepsilon_{elec}(\ell)}}_{Z_{elec}(\beta)}$$

$$\Rightarrow Z_{mol}(\beta) = Z_{trans} \cdot Z_{rot} \cdot Z_{vib} \cdot Z_{elec}.$$

- System of Particles.

1) Non-interacting

2) $T \approx 300K$.



$$E(x_1, x_2, \cdots, x_N) = \sum_{i=1}^{N} \varepsilon_{mol}(x_i)$$

$$Z(\beta) = \sum_{V} e^{-\beta E(x_1 - x_n)} \approx \int_V e^{-\beta E(x_1 \sim x_N)} dx_1 dx_2 \cdots dx_N$$

$$\Rightarrow Z(\beta) = \left(\int e^{-\beta \varepsilon_{mol}(x_1)} dx_1\right)\left(\int e^{-\beta \varepsilon_{mol}(x_2)} dx_2\right) \cdots \left(\int e^{-\beta \varepsilon_{mol}(x_N)} dx_N\right)$$

$$= \left(Z_{mol}(\beta)\right)^N$$

$\therefore$ partition function for N non-interacting particles is, (+ indistinguishable).

$$Z(\beta) = \underbrace{\left(\frac{1}{N!}\right)}_{\text{permutation.}} \cdot Z_{mol}^N(\beta)$$

- $$\langle E \rangle = \left(\frac{\partial \log Z(\beta)}{\partial(-\beta)}\right)_{N,V}$$

recall, $A(N,V,T) = -\beta^{-1} \log Z$

$dA = d(E - TS) = -SdT - pdV + \mu dN$

Note that $\partial/\partial(-\beta) = \frac{\partial(T)}{\partial(-\beta)} \frac{\partial}{\partial T}$

① $-p = \frac{dA}{dV} = -\frac{\partial}{\partial V}\Big)_{T,N} k_B T \log Z(\beta)$

$\Rightarrow p = k_B T N \cdot \underbrace{\frac{\partial \log(Z_{mol})}{\partial V}}$ → only "translational" is affected. (linear)

$= k_B T \cdot N \cdot \frac{\partial}{\partial V} \log V$

$\Rightarrow \underline{pV = N k_B T}$.

01/24/2025

Recap. $Z_{mol}(\beta) = \sim$

$= pV = Nk_BT \Rightarrow \underset{\sim\sim\sim}{\beta p = \rho}$

- Chemical equilibrium.

No net flux of material across chemical process.

$\Delta G = 0$ at equilibrium

$$\text{Recall, } dG(\vec{N}, p, T)\Big|_{p,T} = \sum_{i=1}^{k} \mu_i \, dN_i = 0 \qquad k \rightarrow \text{\# of species}$$

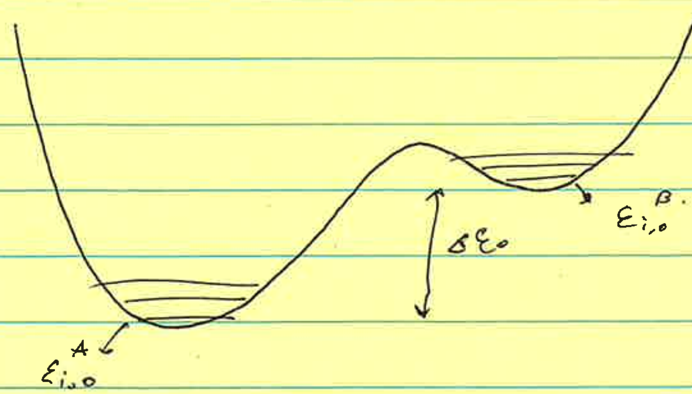
$$G = A + p \cdot V \quad \text{and} \quad A = -k_BT \log \frac{Z_{mol}^N}{N!}$$

Assume ideal gas ($pV = Nk_BT$)

$$G = -k_BT \log\left(\frac{Z_{mol}^N}{N!}\right) + Nk_BT \log(e)$$

$$= -Nk_BT \log(Z_{mol}) + (k_BT(N\log N - \cancel{N\log e})) + \cancel{Nk_BT \log e}$$

$$\therefore \underset{\sim\sim\sim\sim\sim\sim\sim\sim}{G = -Nk_BT \log\left(\frac{Z_{mol}}{N}\right)}.$$



① $\langle N_A \rangle = \dfrac{\sum_A e^{-\beta(\varepsilon_{i,0}^A - \Delta\varepsilon)}}{Z} \cdot N$

$= \dfrac{NZ_A}{Z} \cdot e^{\beta\Delta\varepsilon_0}$

② $\langle N_B \rangle = \dfrac{NZ_B}{Z}$

$$\Rightarrow \frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{Z_A}{Z_B} e^{\beta\Delta\varepsilon_0} = K_{eq}. \quad ?$$

$$dG = 0 = V dp \qquad (\text{Fix } N, T)$$

$$\Delta G = \int_{p_1}^{p_2} V dp = \int_{p_1}^{p_2} \frac{nRT}{p} dp = nRT \log(p_2/p_1).$$

$$G(p) - G^{\circ} = nRT \log(p/1\text{atm}). \quad — ③$$

Ex) $aA + bB \rightleftarrows cC + fF.$

$$\Delta G = \sum_{i \in \text{species}} \nu_i \Delta G_i = 0 \quad \Rightarrow 0 = \Delta G^{\ominus} + \sum nRT \log(p_i/p^{\ominus})^{\nu_i}$$

$$\Rightarrow -\Delta G^{\ominus} = \sum nRT \log(p_i/p_{\ominus})^{\nu_i} = nRT \log \underbrace{\left(\frac{\left(\frac{p_c}{p_\ominus}\right)^{1/c} \left(\frac{p_f}{p_\ominus}\right)^{1/f}}{\left(\frac{p_A}{p_\ominus}\right)^{1/a} \left(\frac{p_B}{p_\ominus}\right)^{1/b}} \right)}_{= K_p}.$$

Recall, $G_j^{\ominus} = -RT \cdot \log \frac{z_j^{\ominus}}{N_A}$ and using $\underline{\sum \nu_i \Delta G_i = 0}$.

$$\Rightarrow \quad -RT \log \left[\frac{(z_c/N_A)^c \cdot (z_f/N_A)^f}{(z_b/N_A)^b (z_a/N_A)^a} \right] = K_{eq}.$$

02/24/2025

- $\beta P = \rho + B(T)\rho^2 + \cdots$

$$B(T) \to 2\pi \int_0^\infty \{1 - \underbrace{g(r)}_{\text{Directly from experiments.}}\} \cdot r^2 dr$$

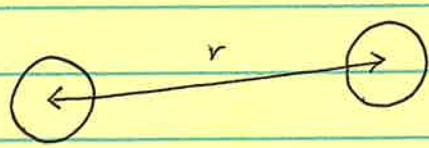
- MD simulation → sample from some ensemble.

$$\langle f \rangle = \frac{1}{N} \cdot \sum_{i=1}^{N} f(x_i) \quad , \quad \text{Need} : \frac{1}{T}\int_0^T f(x(t))dt \to \langle f \rangle$$

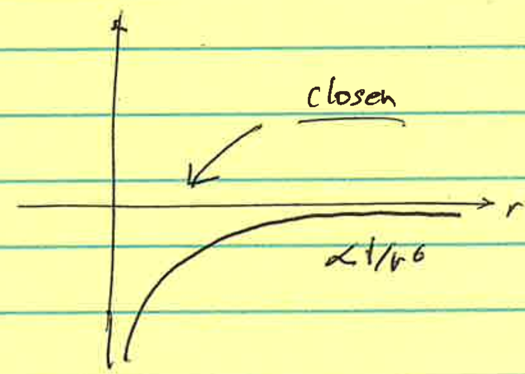
Ergodicity
"Time avg" = "Ensemble avg"

1) Initial conditions
2) Dynamics ~ Newtonian.
3) Compute observables.

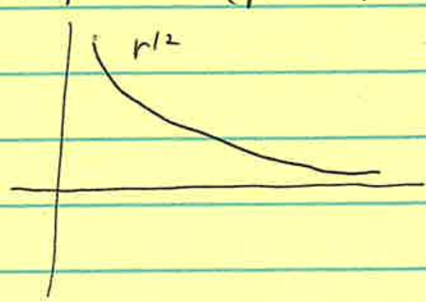
- Vander Waals.



dipole − dipole → perturbation r^6
r^3 $\qquad$ r^3



- Repulsion (pauli exclusion)



LJ potential : $U_{LJ}(r) = +4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

NVE.

$$H(x^N, p^N) = u(x^N) + p(x^N)$$

$$k(p^N) = \sum_{i=1}^{N} \frac{p_i^T p_i}{2m}.$$

$$p_i = m_i \dot{x}_i$$

$$\dot{x} = p_i / m_i$$

$$\boxed{\begin{aligned} \partial H/\partial p_i &= \dot{x}_i \\ \partial H/\partial x_i &= -\dot{p}_i \end{aligned}}$$

Check NVE

$$\left(\frac{dH}{dt}\right)_i = \frac{\partial H}{\partial p_i}\frac{dp_i}{dt} + \frac{\partial H}{\partial x_i}\frac{dx_i}{dt} \Rightarrow \underline{H = \text{conserved}}$$

$$= \dot{x}_i \dot{p}_i - \dot{p}_i \dot{x}_i = 0.$$

02/26/2025

- How to update

$$\Rightarrow x(t+\Delta t) = x(t) + \underbrace{\dot{x}(t)}_{= \frac{p}{m}} \Delta t + \frac{1}{2} \underbrace{\ddot{x}(t)}_{\frac{f}{m}} \Delta t^2 + o(\Delta t^3) + \cdots$$

- Velocity Verlet Algorithm. (N, V, E)

$$\begin{cases} p(t+\Delta t/2) = p(t) + \frac{f^{(x(t))}}{m} \left(\frac{\Delta t}{2}\right) \\ x(t+\Delta t) = x(t) + \dot{x}\ \Delta t = x + \frac{p(t+\Delta t/2)}{2} \cdot \Delta t \\ p(t+\Delta t) = p(\cancel{\Delta t} + \frac{\Delta t}{2} + \frac{\Delta t}{2}) = p(t) + \frac{\Delta t}{2}) + \frac{f(x(t+\Delta t))}{2m} \cdot \Delta t \end{cases}$$

↳ Symplectic (conserves energy → preserves volume).

- NVT → T is conserved. $Z \propto e^{-\beta \frac{p^2}{2m}}$

$\langle p_i^2/(2m) \rangle$: avg. kin. energy. $= \frac{1}{2} k_B T$

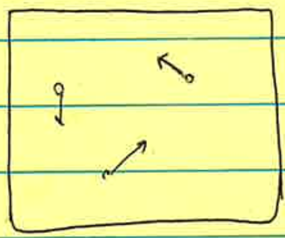
⇒ Average Kinetic Energy / degree of freedom $= \frac{1}{2} k_B T$.

- Classical equipartition of energy.

  Each quadratic DOF → $\frac{1}{2} k_B T$ avg energy.

$$\langle K \rangle = \frac{3}{2} N k_B T, \quad T_{eff} = \frac{2}{3 N k_B N} \sum_i p_i^T p_i / 2m$$

- Anderson Thermostat.



$P_{collision}(t) \propto \text{Poisson}(\gamma) = \gamma e^{-\gamma t}$

$\Rightarrow P_{collision}(\Delta t, \gamma) \cong \gamma$ (Taylor)

if $\text{rand}() < \gamma \Delta t$

$\rightarrow$ Resample velocities.

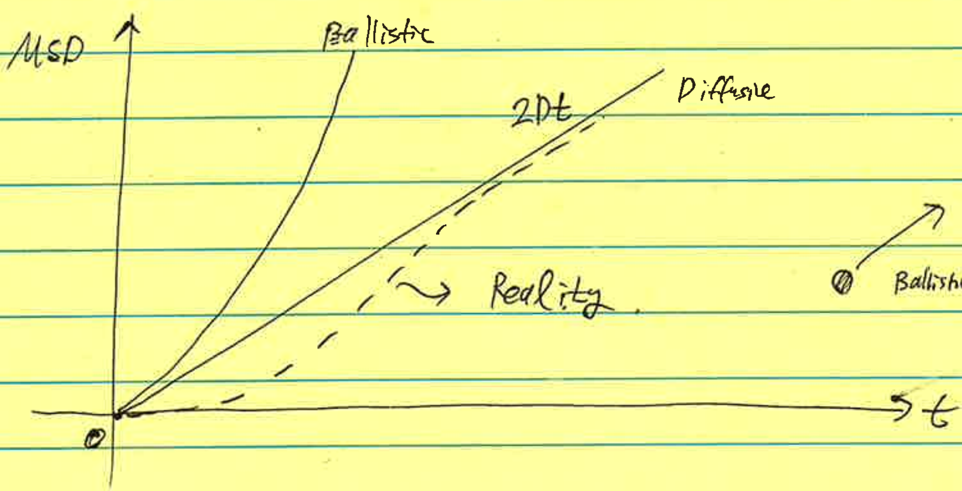
- $MSD(t) = \langle \| R(x(t)) - R(x(0)) \|^2 \rangle$

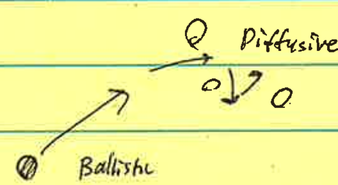
① Ballistic motions. $\underline{x = v \cdot \Delta t}$.

$MSD \propto t^2$

② Diffusive

$MSD \propto t$





02/28/2025.

Recap: Classical equipartition theorem.

$\langle K \rangle = \frac{3}{2} N k_B T$ each D.O.F. $\frac{1}{2} k_B T \times 3N \rightarrow \frac{3}{2} N k_B T$.

Molecular simulation: $T_{eff}(p^N) \Leftarrow$ Assign T to state. ✓

How? ⇒ Anderson thermostats

$P_{collision}(t), \gamma) = \gamma e^{-\gamma t}$ (every time collide with bath particle).

$P_{collision}() \approx \gamma \Delta t$

Goal: Expression for rate constant (γ) in ideal system.

"Encounter Limited" and this is a function of

typical particle "speeds"

$v = \|\vec{v}\| = (v_x^2 + v_y^2 + v_z^2)^{1/2}$

$p(\vec{v}_x) \propto \dfrac{\exp(-\beta m v_x^2/2)}{\sqrt{2\pi k_B T/m}}$ in 1D, $|\vec{v}| = v_x$

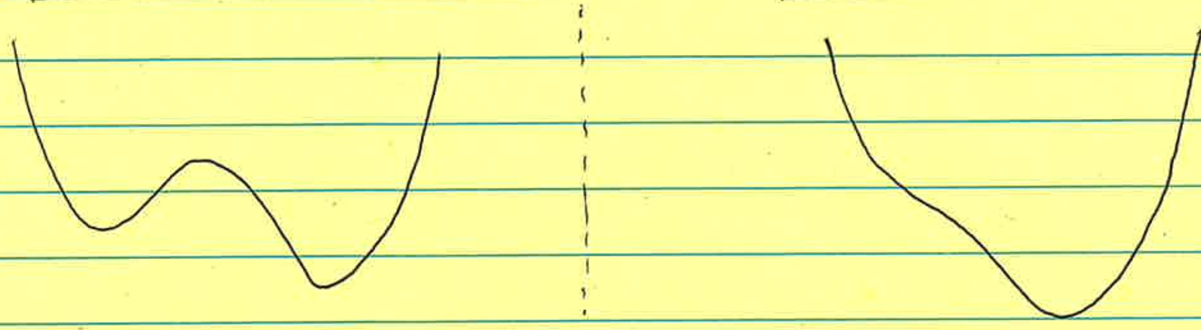
$$\Rightarrow p(v) = p(\|v\|^2 = v^2) \cdot (\# \text{ of states of } v)$$
$$= p(\|v\|^2 = v^2) \cdot 4\pi v^2 \, dv$$
$$= 4\pi v^2 \cdot dv \quad P(\vec{v})$$

$$\therefore \langle v \rangle = \int_0^\infty v \, p(v) \, dv = \sqrt{\frac{8 k_B T}{\pi m}} = V_{rms}$$

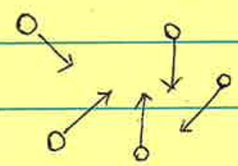
Ex) $V_{Lysozome} \cong 20$ m/s. → But not really...

→ Reactions & Diffusions.

Activated vs. Diffusion Limited.

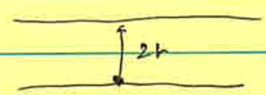


$$\underbrace{3-2+1}_{n} = ?$$



$$P(\text{collision in step } \Delta x) = \underbrace{\rho}_{\text{density!}} \cdot A \cdot \Delta x = \sigma \rho \Delta x$$

$n_{free}(x)$: # traveling x without collision.



$$A = \pi r^2 = \sigma$$

$$\frac{\partial}{\partial x} n_{free}(x) = -\sigma\rho \cdot n_{free}.$$

$$\Leftrightarrow \quad \Delta n_{free}(x) = -\sigma\rho\Delta x \cdot n_{free} \quad (\text{proof})$$

$$\Rightarrow \quad n_{free}(x) = n_0 e^{-\sigma\rho x}$$

Two at once!

$$P(\text{collision in time}) = \frac{1}{2} \sigma \cdot \langle v \rangle_{rel} \rho^2$$

$$\tau_{free} = \frac{\ell}{\langle v \rangle}$$

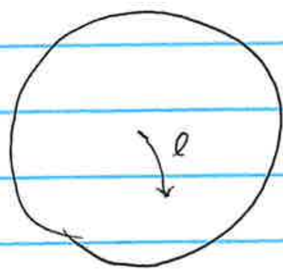
03/05/2025

Recap Flux : Fick's law : $J(x) = -D \nabla \rho(x)$.

+) Conservation of mass : $\partial \rho / \partial t = \partial_t \rho = D \nabla \cdot \nabla \rho(x,t) = D \Delta \rho$.

$$\rho(x,0) = \delta(x_0) \rightarrow \rho(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{(x-x_0)^2}{4Dt}\right).$$

- state - state solution



$\rho(\vec{x} = 0)$ for $\forall \vec{x}$ s.t $\|\vec{x}\| = \ell$. (B.C.)

At steady state, $D \Delta \rho = 0$.

By symmetry. $\Delta_r \rho = 0 \rightarrow \frac{\partial^2 \rho}{\partial r} = 0$.

$\rho(\ell) = 0$, $\rho(\infty) = \rho_{Bulk}$

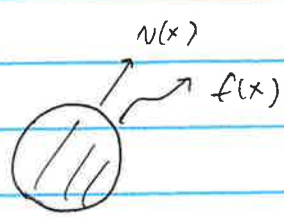
Guess : $\rho(r) = \left(1 - \ell/r\right) \rho_{Bulk}$.

↳ Check Laplacian for Midterm!

Net inward flux $J(\ell) = D \Delta \rho$. $=$ rate $\cdot$ (density)

- Stationary state $\rho(x) \sim e^{-\beta u(x)}$

$J(x) = \vec{v}(x)\, \rho(x)$



$\vec{v}(x) = \mu \vec{f}(x)$ $\Rightarrow$ $J = \mu \vec{f}(x) \cdot \rho(x)$

drag.

$\propto \mu \left(-\nabla_x u(x)\right) \rho(x)$

$$\Rightarrow J_{drag} = -\mu \frac{\partial}{\partial x} u(x) \cdot \rho(x).$$

$J_{diff} = -D \nabla_x \rho(x)$

At equilibrium, $J_{diff} + J_{drag} = 0$

$\Rightarrow \quad -D \frac{\partial}{\partial x} \rho(x) - \mu \frac{\partial}{\partial x} u(x) \rho(x) = 0$

$\Rightarrow \quad -D \partial_x \rho - \mu \partial_x u \; \rho = 0$

Note $\partial_x \rho \propto -\beta \partial_x u \; e^{-\beta u(x)} = \underline{-\beta \partial_x u \cdot \rho}$.

Plug in, $-D \cdot (-\beta \cancel{\partial_x u}) \cancel{\rho} - \mu \cancel{\partial_x u} \cancel{\rho} = 0$

$\Rightarrow \quad D\beta = \mu \quad \Rightarrow \quad \boxed{D = \mu k_B T \Leftrightarrow \mu = \beta D}$

Einstein's relation.

"only at equilibrium!"

$\boxed{\text{Stockes - Einstein : } D = \frac{k_B T}{6\pi \eta r}}$

Reynolds # : $\underset{\sim\sim\sim}{\frac{v \, l \cdot \rho}{\eta}}$

small vish $\sim 10^4$ $\quad \frac{10\,cm/s \;\; 10\,cm}{10^{-2}}$,

$\Downarrow$

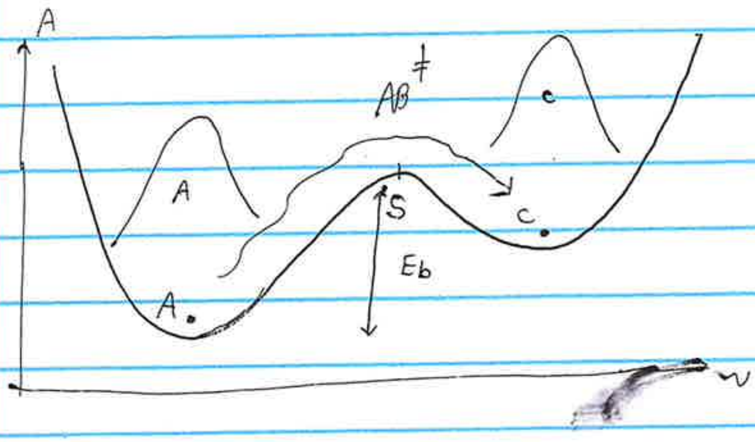
Bactera $\sim 10^{-5}$ $\quad \frac{10^{-3} \cdot 10^{-4} \cdot 1}{10^{-2}}$.

Low Re, applied force does not do aything!

03/07/2025

Recap : Steady state diffusion equation.

$$D = \mu k_B T = k_B T / \zeta$$



Can we derive K_a → rate

using stat. mech. + minimal assumptions.

$$k_{TST} \cong K_a$$

Assumptions

1) No dynamical recrossings.
2) Reaction coordinate separates r + p.
3) B.O. approx → all dynamics on single energy surface.
4) There exists equilibrium between A+B and $AB^\ddagger$

$$\frac{[AB^\ddagger]}{[A]\cdot[B]} = K_a = e^{-\beta\Delta G^\ddagger} \quad \text{and} \quad k\,[AB^\ddagger] = \omega^\ddagger [AB]$$

$$= \omega^\ddagger K_{eq}^\ddagger [A][B]$$

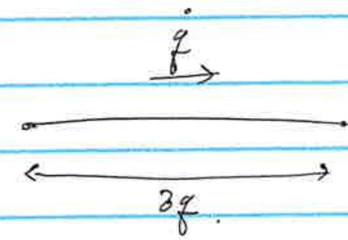
$$\frac{[AB^\ddagger]}{[A]\cdot[B]} = \frac{Z_{AB}}{Z_A Z_B}.$$

$$k_{TST} = \omega^\ddagger e^{-\beta\Delta G}$$

Attempt frequency.

$$Z_{AB}^{\ddagger} = \tilde{Z}_{AB}^{\ddagger} \cdot Z_{TST}(q)$$

$\downarrow$ not involving q.



$$\Rightarrow \quad Z_{TST}(q) = \frac{\delta q}{\Lambda_T}$$

(assume 1d small box)

$$\Lambda_T = \frac{h}{\sqrt{2\pi \mu_q k_B T}}$$

μ_q: artificial mass.

$$\Rightarrow \quad \boxed{\omega^{\ddagger} = \frac{1}{2} \frac{\langle |\dot{q}| \rangle}{\delta q}}$$

$$p(\dot{q}) \propto e^{-\beta\left(\mu_q \cdot \dot{q}^2/2\right)}$$

$$\Rightarrow \quad \langle |\dot{q}| \rangle = \frac{\int_{-\infty}^{\infty} |\dot{q}|\, e^{-\beta \mu_q \dot{q}^2/2}\, d\dot{q}}{\int_{-\infty}^{\infty} e^{-\beta \mu_q \dot{q}^2/2}\, d\dot{q}} = \frac{2}{\left(\sqrt{2\pi/\beta\mu}\right) \beta\mu}$$

$$\Rightarrow \quad k_{TST} = e^{-\beta \Delta G^{\ddagger}} \cdot \omega^{\ddagger} \quad Z_{TST}$$

$$= e^{-\beta \Delta G^{\ddagger}} \cdot \frac{\delta q}{\lambda_T} \quad \omega^{\ddagger}$$

$$\Rightarrow \quad k_{TST} = \frac{2}{\sqrt{2\pi}} \quad \cdots$$

$$= \underbrace{\left(\frac{k_B T}{h}\right) e^{-\beta \Delta G^{\ddagger}}}$$

$\hookrightarrow$ Eyring (1910 ~ 1930)

Review

03/12/2025.

① Canonical Ensemble

$$Z = \sum_{\nu} e^{-\beta E(\nu)} \longrightarrow A = -\beta^{-1} \log Z.$$

$$dA = s\,dT - p\,dV + \mu\,dN$$

$$\langle E \rangle = \frac{\partial}{\partial(-\beta)} \log Z$$

$$\text{var } E = \frac{\partial}{\partial(-\beta)^2} \log Z$$

② Molecular Partition Function

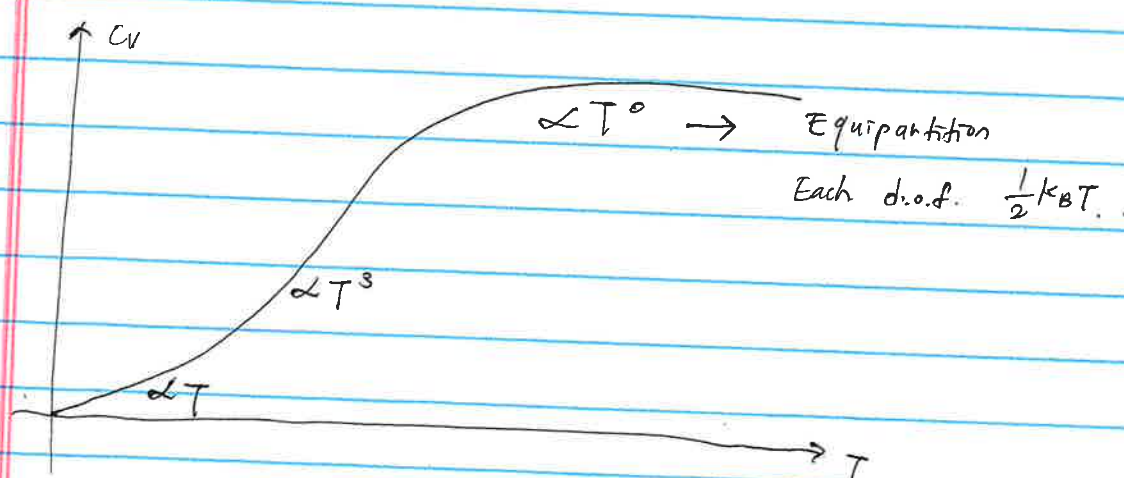
		Assmp.
Z_{trans}	$= V/\Lambda^3$	high T
Z_{rot}	$= T/\theta_{rot}$.	high T
Z_{vib}	$= e^{-\beta\hbar\omega}/(1-e^{-\beta\hbar\omega})$	harmonic.
Z_{elec}	$= g_0\, e^{-\beta\epsilon_{elec}^{(0)}}$	$k_BT \ll 1eV$
Z_{nucl}	$= 2I+1$	$k_BT \ll 10^5 eV.$

③ Quantum statistics

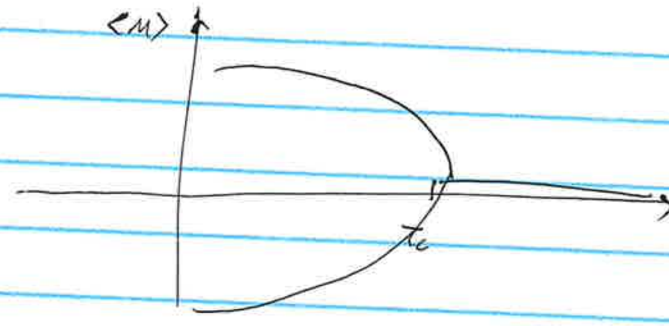
Fermion : $\psi(r_1,r_2) = -\psi(r_2,r_1)$ only single / occupancy

Boson : $\psi(r_1,r_2) = \psi(r_2,r_1)$ no constraint on occupancy.

④ Heat capacity

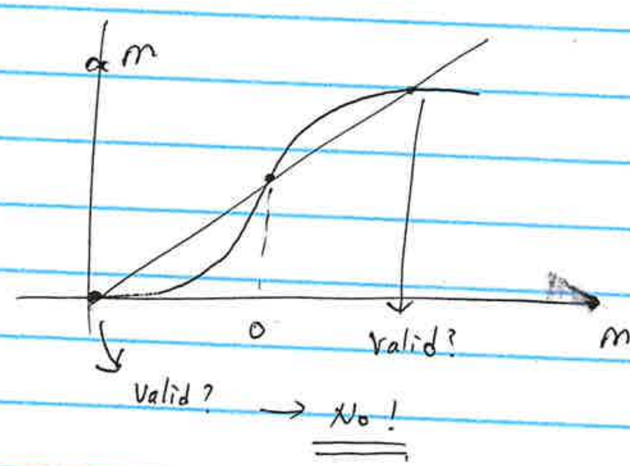


- Phase Transitions
  1) C_V diverges
  2) $\langle E \rangle$ singular
  3)



- Ising MFT. → predict m

  $m = \tanh(\beta h + \beta J z m)$



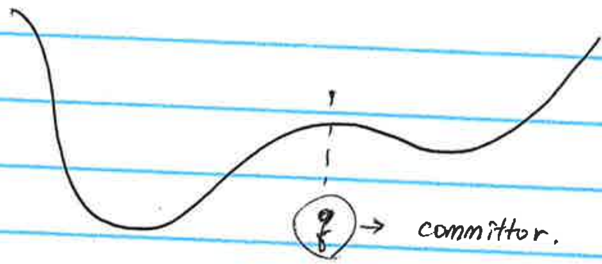
- Diffusion

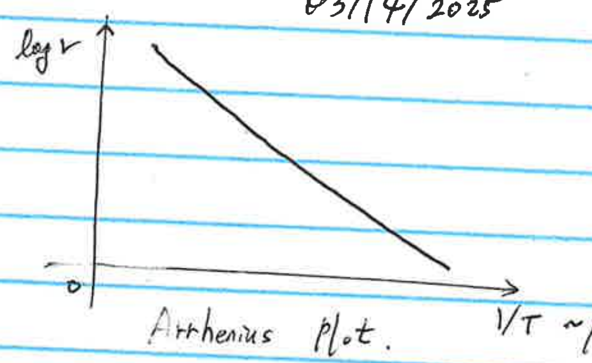
  $J = -D \cdot \partial\rho/\partial x$ (flux)

  $\partial_t \rho = D\, \partial\rho/\partial x = 0$.

03/14/2025

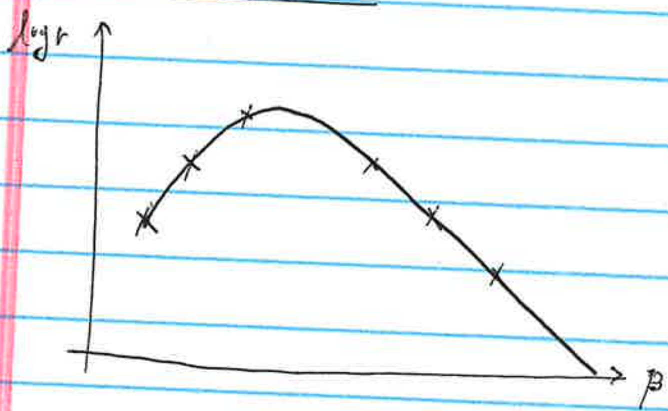
Recap





$$k_{TST} = \frac{k_B T}{h} e^{-\beta \Delta G^{\ddagger}}$$ (no dynamical recrossings).

- **Breakdown of TST.**



- **Dynamics of Reaction.** $A \rightleftarrows B$.

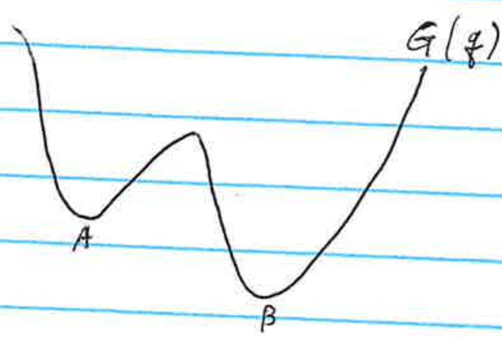
$$\frac{d[A]}{dt} = k_{BA}[B] - k_{AB}[A]$$

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt}$$

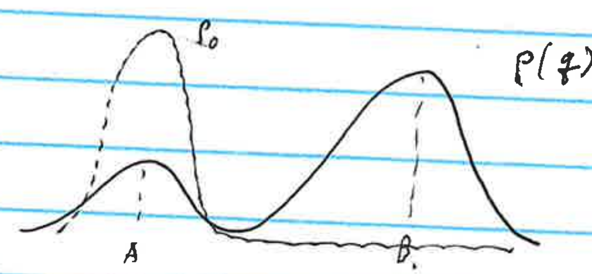
$\Rightarrow$ $[A](t) = [A](0) \cdot e^{-t/\tau}$, $\tau = (k_{AB} + k_{BA})^{-1}$

$[B](t) = [B](0) \sim$.

→ Start from non-eq initial condition.

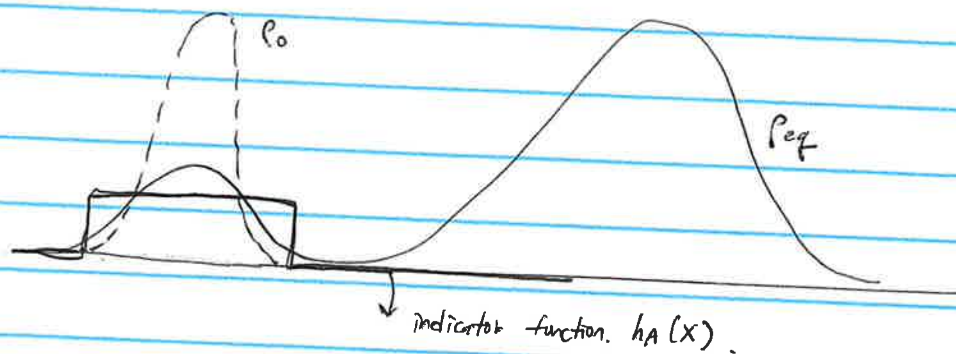


→



setting : ρ_0 is initial condition

How to create ρ_0 in A? → Use bias potential.



$$n_A(x) = \sum_i h_A(x_i) \to \langle n_A \rangle = \frac{1}{Z}\int n_A(x)\, e^{-\beta H(x)}\, dx$$

To polarize system into A, $Z^{-1}\int n_A(\cancel{x}_t)\cdot \exp\left(-\beta\left(H(x) - \varepsilon \cdot n_A(x_0)\right)\right) dx_0 = \overline{n_A}(t)$

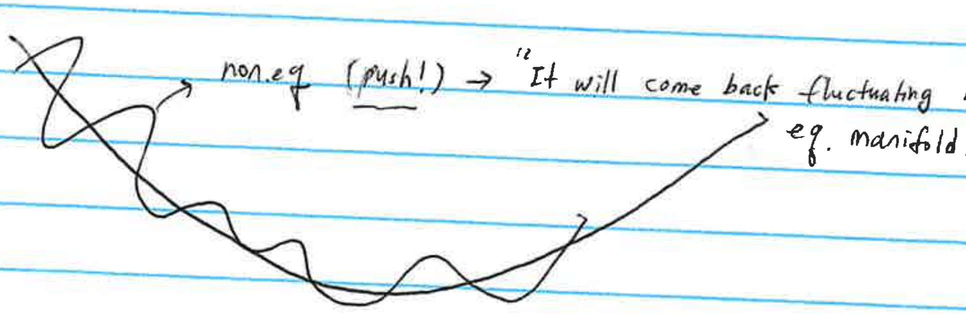
$$\Rightarrow Z^{-1}\int e^{-\beta H(x) + \beta\varepsilon n_A(x)}\, dx = \langle e^{\beta\varepsilon n_A}\rangle_{eq.}$$ (notice this!)

$$\Rightarrow \overline{n_A}(t) = Z^{-1}(\varepsilon)\int n_A(x_t)\cdot e^{-\beta H(x_0) + \beta\varepsilon n_A(x_0)}\, dx_0$$

$$= \frac{\langle n_A(x_t)\cdot e^{\beta\varepsilon n_A(x_0)}\rangle_{eq.}}{\langle e^{\beta\varepsilon n_A(x_0)}\rangle_{eq.}}$$

Non-eq property expressed with eq. property.

non.eq (push!) → "It will come back fluctuating but to eq. manifold"



⇒ Onsager's regression analysis.

- Linear Response ?

$$\begin{cases} \Delta c_A(t) = c_A(t) - \langle c_A \rangle \\ \Delta h_A(t) = n_A(t) - \langle n_A \rangle \end{cases}$$

$$\mathrm{Corr}(n_A) = \frac{\langle \Delta h_A(t)\, \Delta n_A(0) \rangle}{\langle \Delta h_A(0) \Delta n_A(0) \rangle} \sim e^{-t/\tau}.$$

$$\frac{\langle \Delta h_A(t) \cdot \Delta h_A(0) \rangle}{\langle \Delta h_A(0) \cdot \Delta h_A(0) \rangle} \rightarrow \text{Use TST to analyze this.}$$

At equilibrium, $\langle A(t)\ A(t') \rangle = \langle A(t-t')\, A(0) \rangle$

$= \langle A(0)\ A(t-t') \rangle$

→ "no directional time"

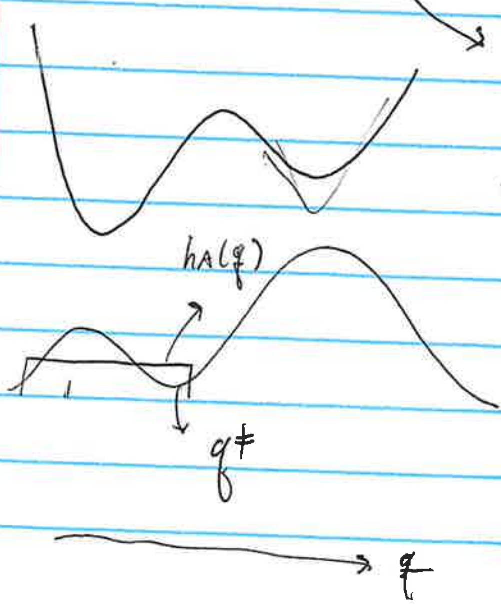
Time reversal symmetry ($\because$ no entropy change).

$$\frac{d}{dt} \langle h_A(0) \cdot h_A(t) \rangle = -\frac{d}{dt} \cdot \langle h_A(t) \cdot h_A(0) \rangle$$

Notice $\dot{h}_A(t) = \frac{\partial h_A}{\partial q} \cdot \dot{q}$

→ assume follows classical dynamics.

→ $\partial h_A / \partial q = -\delta(q - q^{\ddagger})$



$$\Rightarrow \boxed{\begin{aligned} \frac{d}{dt} \langle h_A(0) . h_A(t) \rangle &= -\langle \dot{h}_A(0)\, h_A(t) \rangle \\ &= -\langle \dot{q}(0)\, \delta(q - q^{\ddagger}) . h_A(t) \rangle \end{aligned}}$$

$$\frac{1}{h_A(0)\,h_A(0)} \cdot \frac{d}{dt}\langle h_A(0)\, h_A(t)\rangle = \frac{d}{dt}\cdot\left(e^{-t/\tau}\right) \cdot = -\frac{1}{\tau} e^{-t/\tau}$$

reaction rate.

prefactor!

$$\| $$

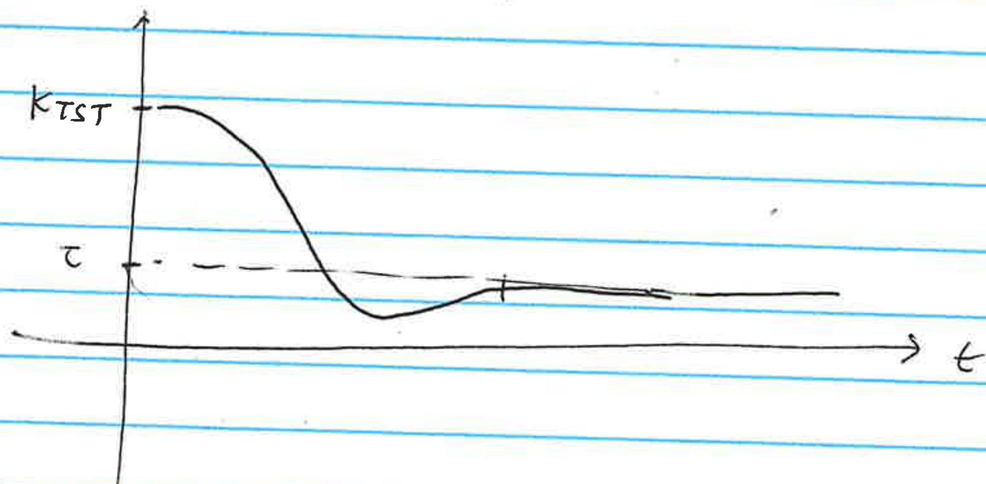
$$-\langle \dot{q}(0)\,\delta(q-q^{\ddagger}).\,h_A(t)\rangle_{eq}.$$

Recall $h_A(t) = 1 - h_B(t)$.

$$\Rightarrow \frac{\langle \dot{q}(0)\,\delta(q-q^{\ddagger}).\,h_B(t)\rangle}{\langle h_A\rangle} = \frac{1}{\tau} e^{-t/\tau} \quad \left(\because \langle h_A(0)\, h_A(0)\rangle = \langle h_A\rangle \text{ it's just } 1, 0 \right).$$

MATH.

$$\frac{\frac{1}{2}\langle |v|\rangle \langle \delta(q-q^{\ddagger})\rangle}{\langle h_A\rangle} = k_{BA}(t)$$



For TST make sense, relaxes fast and in equilibrium.