Statistical Mechanics ~ "The Golden Lecture"

Statistical Mechanics: Energy macroscopic properties for systems w/ many degrees of Freedom.

Composition (Molecules) →
Dynamical Rules (Hamiltonian) → (SM) → macroscopic properties

- Statistical Mechanics is inductive (rather than inductive)
- Statstical Mechanics is not N-body mechanics

The goal is to develope an intuitive understanding of what is happening.

Newtons Laws – reversible, deterministic
(we need initial conditions)

Statistical Mechanics – irreversible, fluctuation uncertainty
– both input and output are <u>incomplete</u>.
– Key is identify relavant input → useful output

ex) Ideal Gas

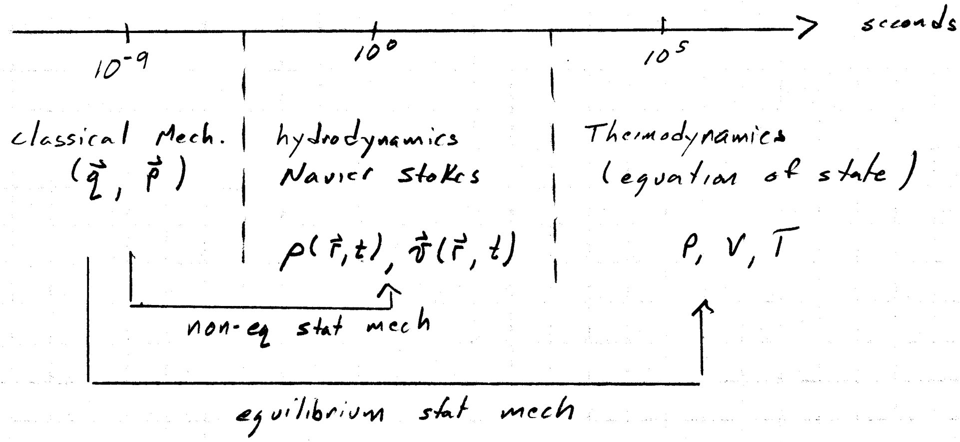
may choose inputs: V, T, P outputs: P, κ_T, C_V

κ_T: isothermal compressibility

ex) Magnetic

may choose inputs: H, T outputs: M, χ_m

• **Time Scale: Classical Gas**



Approach to Equilibrium:

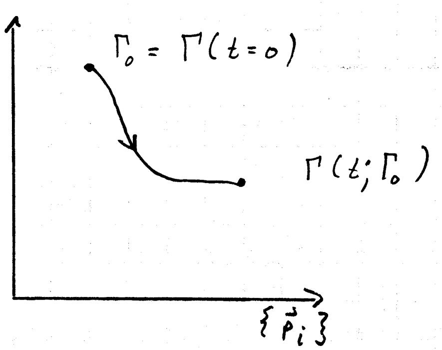
A. Phase space and Density Function

a) (classical mechanics) microstates

N distinguishable particles $\Gamma = \{\vec{q}_i, \vec{p}_i\}$ $i = 1, \dots, N$

(each particle has 6 coordinates, so Γ is $6N$ dimensional).

Phase Space



dynamics: $H(\vec{q}_i, \vec{p}_i)$

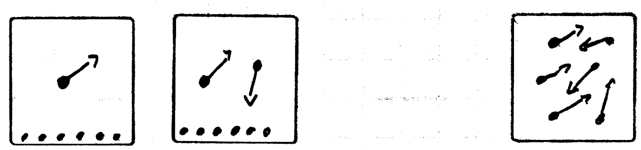
$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

path in phase space determined by H.

observable: $A(\{q_i, p_i\}) = A(\Gamma)$

b) Macroscopic state

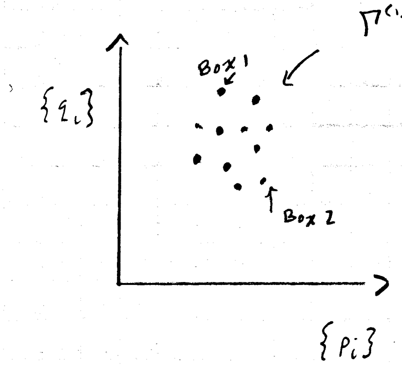
Ensemble $\equiv$ set of systems w/ same macroscopic constrainst (like E, N, V etc.) w/ different microscopic states.



each box w/same V, E, N but diff Γ_0

box 1 2 . . . M

c) Density Function



$\Gamma^{(1)}, \Gamma^{(2)}, \ldots, \Gamma^{(M)}$

$\Gamma^{(i)}$ $\equiv$ phase space pt. of i^{th} box (in 6M-D phase space)

Density function: $\rho(\Gamma) = \frac{1}{M} \sum_{i=1}^{M} \delta(\Gamma - \Gamma^{(i)})$

(similar to charge density in E&M: $\rho(\vec{r}) = \sum_{\alpha} e_{\alpha} \delta(\vec{r} - \vec{r}_{\alpha})$)

note: ρ is normalize $\left(\frac{1}{M}\right)$: $\int \rho(\Gamma)\, d\Gamma = 1$

$d\Gamma = dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}$

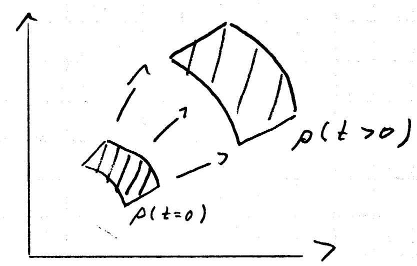
observables: $\langle A \rangle \equiv$ ensemble average

$= \frac{1}{M} \sum_{i=1}^{M} A(\Gamma^{(i)})$

$$\boxed{\langle A \rangle = \int d\Gamma \, A(\Gamma)\rho(\Gamma)}$$

evolution of system in time

$$\rho = \rho(\Gamma, t) = \frac{1}{M}\sum_{i=1}^{M} \delta(\Gamma - \Gamma^{(i)})$$



phase flow, expect incompressibility:

$$\vec{\nabla}_\Gamma \cdot \vec{v} = 0$$

proof: $\vec{v}(\Gamma) = \{ \dot{\vec{q}}_i , \dot{\vec{p}}_i \}$

$$\vec{\nabla}_\Gamma = \left\{ \frac{\partial}{\partial \vec{q}_i} , \frac{\partial}{\partial \vec{p}_i} \right\}$$

$$\vec{\nabla}_\Gamma \cdot \vec{v} = \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial}{\partial q_i}\left(\frac{\partial H}{\partial p_i}\right) + \frac{\partial}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right)$$

$$= 0 \quad \checkmark$$

Eq. of Motion for $\rho(\Gamma)$:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}_\Gamma \cdot (\rho \vec{v}) = 0 \quad (\text{conservation})$$

$$\frac{\partial \rho}{\partial t} + \underbrace{\cancel{(\vec{\nabla}_\Gamma \cdot \vec{v})}}_{0}\rho + \vec{v} \cdot \vec{\nabla}_\Gamma(\rho) = 0$$

incompressible

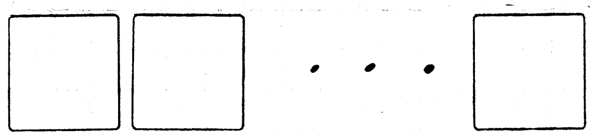
Piosson Bracket

$$\frac{\partial \rho}{\partial t} = -\sum_i \left(\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right) = -\{\rho, H\}$$

$$\boxed{\rho = -\{\rho, H\}}$$

"Liousville's Theorem"

Microcanonical Ensemble – (isolated system, fixed E, V, N)



$H_N(\Gamma)$ – hamiltonian for an N-body ensemble.

Multiple "copies" make up ensemble.

$H_N(\Gamma)$ - Hamiltonian; instead of following Mechanics (determined by H_N) simply write down the $\Gamma = \{\vec{r}_i, \vec{p}_i\}$ allowed by constraints:

1. $\vec{r}_i$ within volume
2. $H_N(\Gamma) = E$

(a) Density of states:

Let # of states (# of configurations $\{\vec{r}_i, \vec{p}_i\}$ for an energy between E and $E + \Delta E$ be

$$N(E) = \Omega(E)\,\Delta E$$

$$\Omega(E) \equiv \text{density of states} = \frac{N(E)}{\Delta E}$$

$$\boxed{\Omega(E) = \int \frac{d\Gamma}{h^{3N}}\, \delta(E - H_N(\Gamma))}$$

<u>Assertion</u>: $S(E) = k_B \ln\left(\dfrac{\Omega(E)}{N!}\right)$

$N!$ is Gibb's correction which compensates for overcounting due to particle label in H_N.

<u>need to show:</u>

1. S is extensive
2. S is non decreasing

(proof in Huang, chapter 6.2)

<u>example</u> : Ideal Gas:

box potential

$$H_N(\Gamma) = \sum_i \frac{p_i^2}{2m} + U_{ext}(\vec{r})$$

(collision provides the mechanism for equilibrium)

$$\Omega(E, V, N) = \int \frac{d\Gamma}{h^{3N}} \delta(E - H_N(\Gamma))$$

$$= \frac{1}{h^{3N}} \underbrace{\int d^3r_1 \cdots d^3r_N}_{V^N} \underbrace{\int d^3p_1 \cdots d^3p_N \, \delta\left(E - \sum_i \frac{p_i^2}{2m}\right)}_{\text{surface area of } 3N\text{-Dim sphere of radius } \sqrt{2mE}}$$

$$= \frac{V^N}{h^{3N}} A (2mE)^{\frac{3N}{2} - 1}$$

A is geometrical factor,

A_N = surface area of N-Dim unit sphere

$$A_1 = 2\pi, \quad A_2 = 4\pi \quad \cdots \quad A_N = \frac{2\pi^{N/2}}{\Gamma(N/2)}$$

Gamma Function

$$\boxed{\Omega(E, V, N) \overset{N \gg 1}{=} \frac{V^N}{h^{3N}} \frac{(2\pi)^{\frac{3N}{2}}}{\Gamma(3N/2)} (2mE)^{\frac{3N}{2}}}$$

note : drop -1 in exponent since $N \gg 1$.

Math Digression:

1. computation of A_N : consider $I = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_N \exp\left\{-\sum_i x_i^2\right\}$

$$I = \int d^d\vec{r}\, e^{-r^2} = \int dr\, A_d\, r^{d-1} e^{-r^2}; \quad y = r^2$$

$$= \frac{A_d}{2} \int_0^\infty dy\, e^{d/2-1} e^{-y}$$

$$= \frac{A_d}{2} \Gamma\left(\frac{d}{2}\right)$$

$$I = \left[\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2\, e^{-(x_1^2+x_2^2)} \right]^{d/2}$$

$$= \left[\int_0^r 2\pi r\, dr\, e^{-r^2} \right]^{d/2} = \pi^{d/2}, \quad d \text{ even only}$$

$$\Rightarrow \quad \frac{A_d}{2} \Gamma\left(\frac{d}{2}\right) = \pi^{d/2}$$

$$\boxed{A_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}}$$

2. $\Gamma(n+1) = \int_0^\infty dx\, x^n e^{-x}$, for integer n $\Gamma(n+1) = n\Gamma(n)$

$$\overset{n\to\infty}{=} \sqrt{2\pi n}\, n^n e^{-n} \left(1 + \frac{1}{12n} + \mathcal{O}\left(\frac{1}{n^2}\right)\right)$$

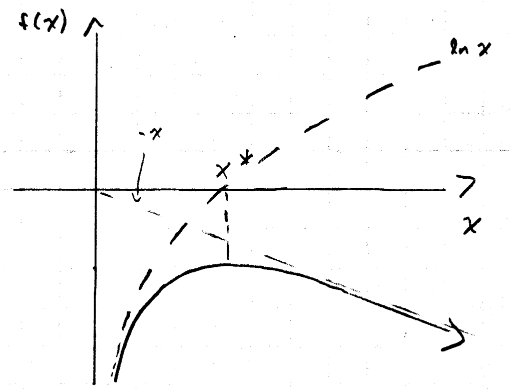
$$\boxed{\ln \Gamma(n+1) = \ln n! = n \ln n - n + \mathcal{O}(\ln n)}$$

Sterling's Formula

proof: (saddle point method)

write $\Gamma(n+1) = \int_0^\infty dx\, e^{f(x)}$

$$f(x) = n \ln x - x$$



$$f(x) = n \ln x - x$$

$$f'(x) = \frac{n}{x} - 1 = 0 \Rightarrow x^* = n$$

$$f''(x) = -\frac{n}{x^2} < 0 \Rightarrow f''(x^*) = -\frac{1}{n}$$

As coefficient of $f(x)$ is large $e^{f(x)}$ is <u>very</u> sharply peaked $\Rightarrow$ behaves as a delta function.

Expand $f(x)$ about x^*:

$$f(x) = f(x^*) + \underbrace{\cancel{f'(x^*)}}_{0}(x - x^*) + \frac{f''(x^*)}{2!}(x - x^*)^2 + \cdots$$

$$= n \ln n - n - \frac{(x-n)^2}{2n} + \frac{(x-n)^3}{3n^2} - \frac{(x-n)^4}{4n^3}$$

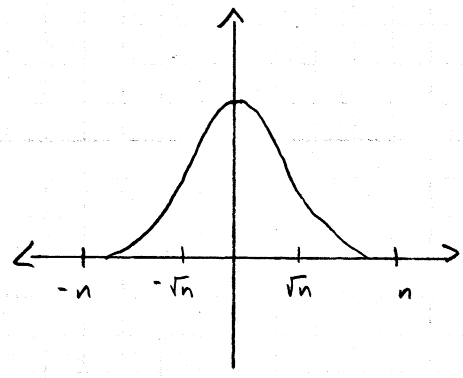
$$\Gamma(n+1) = e^{n \ln n - n} \int_0^\infty dx\, e^{-\frac{(x-n)^2}{2n} + \cdots}$$

$$= e^{n \ln n - n} \int_0^\infty dy \exp\left\{ -\frac{y^2}{2n} + \frac{y^3}{3n^2} - \frac{y^4}{4n^3} + \cdots \right\}$$

only significant near $-\sqrt{n} \le y \le \sqrt{n}$

when $y = \pm\sqrt{n}$, $\quad \frac{y^2}{2n} \sim O(1)$

$$\frac{y^3}{3n^2} \sim O(1/n)$$



$$e^{-\frac{y^2}{2n}} e^{(\quad)}$$

$$\cong e^{-\frac{y^2}{2n}}\left(1 + (\quad) + \cdots\right)$$

$\Rightarrow$ drop higher order terms in exp.

$$\Gamma(n+1) \cong \exp(n\ln n - n) \int_{-n \to -\infty}^{\infty} dy\, e^{-\frac{y^2}{2n}} \left[1 + \cancel{\frac{y^3}{3n^2}} - \frac{y^4}{4n^3}\right]$$

0 odd symmetry

extending to $-n \to -\infty$ doesn't cost us anything since $n \gg 1$
(there is no contribution due to smallness)

$$= \exp(n\ln n - n)\left[\sqrt{2\pi n} - \frac{\sqrt{n}}{4n}\int \frac{dy}{\sqrt{n}}\, e^{-\left(\frac{y^2}{2n}\right)}\left(\frac{y^4}{\sqrt{n}}\right)\right]$$

$\to \quad u = \frac{y}{\sqrt{n}}, \quad \int du\, e^{-u^2} u^4$

$$\boxed{\begin{aligned} \Gamma(n+1) &= \exp(n\ln n - n)\sqrt{2\pi n}\left(1 - \frac{1}{12n} + \cdots\right) \\ \ln \Gamma(n+1) &= n\ln n - n + \mathcal{O}(\ln n) \end{aligned}}$$

b) Partition Function: (you can fix E, V, N)

$$S = k_B \ln \left(\frac{\Omega(E)}{N!} \right)$$

$$\frac{\Omega(E)}{N!} = \frac{1}{N!} \int \frac{d\Gamma}{h^{3N}} \, \delta\left(E - \mathcal{H}_N(\Gamma)\right)$$

$$= \int \frac{ds}{2\pi} \cdot \frac{1}{N!} \underbrace{\int \frac{d\Gamma}{h^{3N}} \, e^{is\left(E - \mathcal{H}_N(\Gamma)\right)}}$$

Fourier Transform of δ-function

let $\alpha = is$

$$= \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \cdot \frac{1}{N!} \int \frac{d\Gamma}{h^{3N}} \, e^{\alpha\left(E - \mathcal{H}_N(\Gamma)\right)}$$

$H \rightarrow$ ground state: E_0

$$= \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} \, e^{\alpha(E - E_0)} \underbrace{\frac{1}{N!} \int \frac{d\Gamma}{h^{3N}} \, e^{-\alpha\overbrace{\left(\mathcal{H}_N(\Gamma) - E_0\right)}^{\text{positive}}}}$$

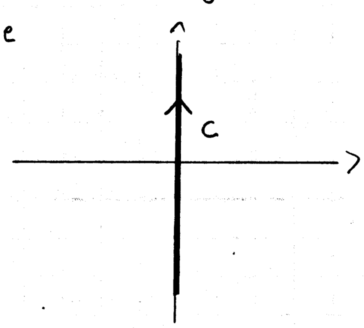
$\equiv Z_{N,V}(\alpha)$

i.e. partition function

- $Z(\alpha)$ analytic everywhere if $\mathrm{Re}\,\alpha > 0$

(each term in $\int d\Gamma$ is bounded)

α-plane



can view this expression as Laplace Transform

$$Z(\alpha) = \int_{E_0}^{\infty} dE' \left[\frac{\Omega(E')}{N!} \right] e^{-\alpha E'} \quad , \text{ Partition Function}$$

$\uparrow$

shift to zero.

For convenience set $E_0 = 0$,

$$\boxed{Z(\alpha) = \int \frac{d\Gamma}{N!\, h^{3N}} e^{-\alpha H_N(\Gamma)}} = \int \frac{dE'}{N!} \int \frac{d\Gamma}{h^{3N}} \delta(E - H_N(\Gamma)) e^{-\alpha E'}$$

c) Can we get directly from $Z(\alpha)$ to entropy?

$$\frac{\Omega(E)}{N!} = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i} e^{\alpha E} Z(\alpha) \qquad (E_0 = 0)$$

$$= \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi} \exp(g(\alpha))$$

Use (saddle point method):

behavior of $g(\alpha) = \alpha E + \ln Z(\alpha)$

$$\ln Z(\alpha) = \ln \int d\Gamma\, e^{-\alpha H_N(\Gamma)}$$

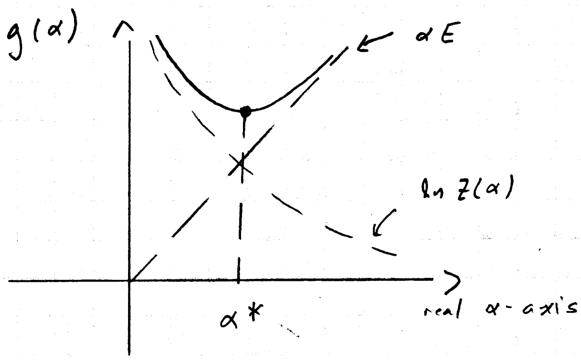
$$\frac{d}{d\alpha}(\ln Z(\alpha)) = \frac{1}{Z} \frac{dZ}{d\alpha}$$

$$= \frac{\int d\Gamma\, (-H_N(\Gamma))\, e^{-\alpha H_N(\Gamma)}}{\int d\Gamma\, e^{-\alpha H_N(\Gamma)}}$$

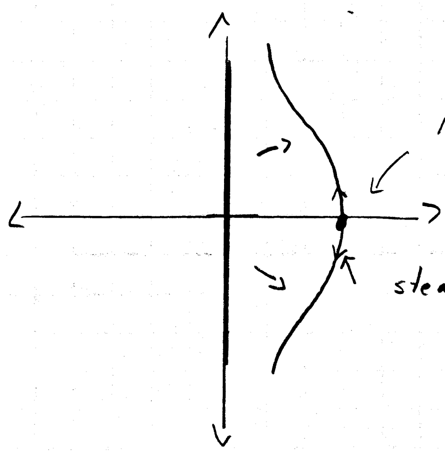
$$\equiv - \langle H_N \rangle_\alpha$$

$$\frac{d^2}{d\alpha^2} \ln Z = \frac{Z''}{Z} - \left(\frac{Z'}{Z}\right)^2 = \underbrace{\langle H_N^2 \rangle - \langle H_N \rangle^2}_{\text{variance}}$$

$$= \langle (H_N - \langle H_N \rangle)^2 \rangle \quad > 0$$



$$\lim_{Re\, \alpha \to \infty} (\ln Z) = \text{small const}$$



Push contour to saddle point

locally on contant phase contour

steapest desent path

$$g(\alpha) = \alpha E + \ln(Z(\alpha)) \qquad (\text{energy is extensive})$$

$$= \alpha N \mathcal{E} + N S(\alpha)$$

$$\boxed{\text{assumption : } \lim_{\substack{N \to \infty \\ V \to \infty}} \ln Z_{N,V}(\alpha) = N f\left(\alpha, \frac{N}{V}\right)}$$

at $\alpha \cong \alpha^*$, $g(\alpha) = g(\alpha^*) + g'(\alpha)(\alpha - \alpha^*) + \frac{g''(\alpha)}{2}(\alpha - \alpha^*)^2$

$$g'(\alpha) = 0 \to \mathcal{E} + f'(\alpha) = 0$$

$$g''(\alpha^*) = N f''(\alpha^*) > 0$$

$$\frac{\Omega(E)}{N!} = \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i}\, e^{g(\alpha)} \underset{\uparrow}{=} \int_{-i\infty}^{i\infty} \frac{dx}{2\pi i}\, e^{g(\alpha^*) + \frac{1}{2} x^2 g''}$$

$\alpha = \alpha^* + x$, shift contour

$$= e^{\alpha^* E + \ln Z(\alpha^*)} \underbrace{\int_{-\infty}^{\infty} \frac{dy}{2\pi}\, e^{-\frac{1}{2} y^2 g''(\alpha^*)}}_{\frac{1}{\sqrt{2\pi f''(N)}}}$$

subleading term

$$\frac{\Omega(E)}{N!} = \exp\left\{ \alpha^* E + \ln Z(\alpha^*) \right\}, \quad n \gg 1$$

$$\Rightarrow \frac{S(E)}{k_B} = \alpha^* E + \ln Z(\alpha^*), \quad E + f'(\alpha^*) = 0$$

$$\alpha^* \text{ from } E + \frac{\partial}{\partial \alpha} \ln Z(\alpha)\Big|_{\alpha^*} = 0$$

normally $\alpha^* \equiv \beta$:

$$\boxed{\begin{aligned} \frac{S(E)}{k_B} &= \beta(E)\, E + \ln Z(\beta(E)) \\ -\frac{\partial}{\partial \beta} \ln Z &= E \end{aligned}}$$

$$\left.\begin{aligned} \Rightarrow \frac{\Omega(E)}{N!} &= \int_{-i\infty}^{i\infty} \frac{d\alpha}{2\pi i}\, e^{\alpha E} Z_{N,V}(\alpha) \\ Z_{N,V}(\alpha) &= \int dE\, e^{-\alpha E} \frac{\Omega(E)}{N!} \end{aligned}\right\} \text{Laplace Transform pair}$$

$$= \frac{1}{N!} \int \frac{d\Gamma}{h^{3N}}\, e^{-\alpha H_N(\Gamma)}$$

$$= \sum_{\text{states}} e^{-\alpha E_s}$$

$$e^{\frac{S(E)}{k_B}} = \frac{\Omega(E)}{N!} = \int \frac{d\alpha}{2\pi i}\, e^{\alpha E + \ln Z(\alpha)}$$

saddle point : $\frac{\partial}{\partial E}\left(\alpha E + \ln Z(\alpha)\right)$

Equating exponents at saddle point α^*, ignore prefactor.

<u>Graphical relation between $S(E)$ and $\ln Z(\beta)$:</u>

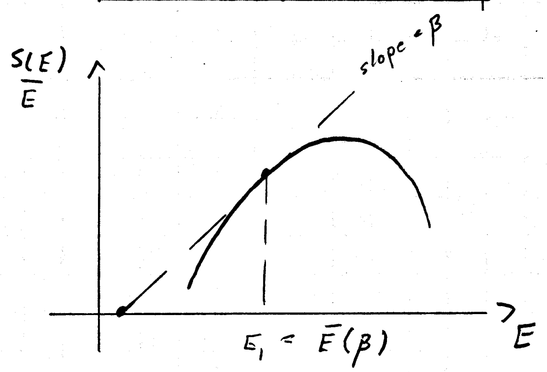
(1) $\frac{S(E)}{k_B} = \beta E + \ln Z$

(2) $-\frac{\partial}{\partial \beta} \ln Z = E$

slope @ E_1 : $\frac{1}{k_B}\frac{\partial S}{\partial E} = \beta + E\frac{\partial \beta}{\partial E} + \frac{\partial \beta}{\partial E}\frac{\partial}{\partial \beta}(\ln Z)$

but $E\frac{\partial \beta}{\partial E} = -\frac{\partial \beta}{\partial E}\frac{\partial}{\partial \beta}(\ln Z)$

$$\Rightarrow \boxed{\frac{1}{k_B}\frac{\partial S}{\partial E} = \beta}$$



$$S(E_1) = \beta(E_1 - x), \quad x = E_1 - \frac{S(E_1)}{\beta k_B}$$

$$\Rightarrow \boxed{x = -\frac{1}{\beta}\ln Z = F} \quad \text{(Helmholtz Free Energy)}$$

graphical Legendre Transformation

From <u>postulates</u>: $\frac{\partial S}{\partial E} = \frac{1}{T} = k_\beta \beta$

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

(concept of Temperature not well defined in macrocanical ensemble).

eq (1) becomes: $S = \frac{E}{T} + k_B \ln Z$

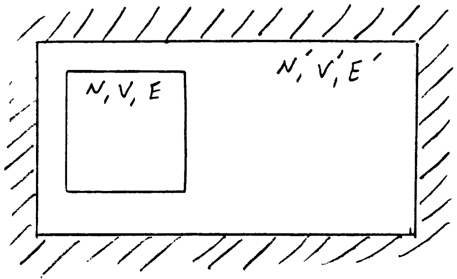
$$E - TS = - k_B T \ln Z$$

$$F = - k_\beta T \ln Z$$

"The golden Lecture" - Lecture 2

Canonical Ensemble:

A. Thermal Equilibrium (Heat Bath)



- Sample in thermal conctact w/ heat bath
- N, N', V, V' fixed
- E & E' can be exchanged

Total Energy, $\mathcal{E}_T = E + E' = \text{const}$

$$\left.\begin{array}{ll} \text{System:} & S(E, V, N) \\ \text{Reservoir:} & S'(E', V', N') \end{array}\right\} \quad S_T = S + S'$$

Let system and surroundings (reservoir) come to equilibrium:

$$\Delta S_T = \frac{\partial S}{\partial E} \Delta E + \frac{\partial S}{\partial E'} \Delta E' = 0$$

$$\Delta \mathcal{E}_T = 0 = \Delta E + \Delta E'$$

$$\Rightarrow \quad \boxed{\frac{\partial S}{\partial E} = \frac{\partial S'}{\partial E'}}$$

T is the easily measured quantity

$$\frac{1}{T} = \frac{1}{T'} \quad \text{or} \quad T = T'$$

Temperature is now a well defined quantity (T = Temp of Reservoir).

$$\boxed{\text{Canonical Ensemble: Fixed } T, V, N}$$

No longer need reservoir (multiple copies w/ same T, but different E).

- E is not fixed in canonical ensemble
- Probability sample has energy E:

$$P(E) = \text{const.} \, \frac{\Omega(E)}{N!} \, \frac{\Omega(\mathcal{E} - \overset{E'}{E})}{(N')!} \leftarrow \text{indistinguishable}$$

$$= \text{const.} \, \frac{\Omega(E)}{N!} \, e^{\frac{S'}{k_B}(\mathcal{E} - E)}$$

Require system << reservoir, $E \ll E' \simeq \mathcal{E}$

$$\Rightarrow \quad S'(\mathcal{E} - E) \cong S'(\mathcal{E}) - E\left(\frac{\partial S'}{\partial E}\right)_{N', V'} + \cdots$$

$$= S'(\mathcal{E}) - \frac{E}{T'}$$

$$= S'(\mathcal{E}) - \frac{E}{T} \qquad T = T' \text{ in eq.}$$

$$P(E) = \text{const.} \, \frac{\Omega(E)}{N!} \, \underbrace{e^{\frac{S'(\mathcal{E})}{k_B}}}_{\text{const}} {}^{- \frac{E}{k_B T}}$$

$$\Rightarrow \quad \boxed{P(E) = \text{const.} \, \underbrace{\frac{\Omega(E)}{N!}}_{\#\text{ of states w/ } E} \, \underbrace{e^{-\frac{E}{k_B T}}}_{\text{weighting factor}} \qquad \text{Boltzmann expression}}$$

<u>Normalization constant:</u>

$$\int dE \, P(E) = 1$$

$$\boxed{\frac{1}{\text{const}} = \int dE \, \frac{\Omega(E)}{N!} \, e^{-E/k_B T} = Z(\beta = 1/k_B T)}$$

$$\boxed{P(E) = \frac{1}{Z_{N,V}(\beta)} \frac{\Omega(E)}{N!} e^{-E\beta}}$$ familiar result

- not dependent on properties of reservoir except T.
- experimentally, Temp easier to control than E,

B. Observables in Canonical Ensemble:

$$\langle \mathcal{O} \rangle = \int dE\, \mathcal{O}\, P(E) = \frac{\int d\Gamma\, \mathcal{O}(\Gamma) e^{-\beta H_N(\Gamma)}}{\int d\Gamma\, e^{-\beta H_N(\Gamma)}}$$

using $\frac{\Omega(E)}{N!} = \int \frac{d\Gamma}{h^{3N} N!} \delta(E - H_N)$

ex) $$\bar{E}(T) = \langle H \rangle = \frac{\int d\Gamma\, H e^{-\beta H_N}}{\int d\Gamma\, e^{-\beta H_N}}$$

$$= -\frac{\partial}{\partial \beta} \ln \left\{ \int \frac{d\Gamma}{h^{3N} N!} e^{-\beta H} \right\}$$

constants for convenience

$= $ mean of $P(E)$

$$\Rightarrow \boxed{\bar{E}(T) = -\frac{\partial}{\partial \beta} \ln Z}$$

(similiar to $\frac{S(E)}{k_B} = \beta E + \ln Z$,

$\beta(E): -\frac{\partial}{\partial \beta} \ln Z = E$ from microcanonical

where E is fixed)

$$\frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial}{\partial \beta} \left\{ \frac{\int \frac{d\Gamma}{h^{3N} N!} \mathcal{H} e^{-\beta \mathcal{H}_N(\Gamma)}}{\int \frac{d\Gamma}{h^{3N} N!} e^{-\beta \mathcal{H}_N(\Gamma)}} \right\}$$

$$= \frac{\int d\Gamma\, \mathcal{H}^2 e^{-\beta \mathcal{H}}}{\int d\Gamma\, e^{-\beta \mathcal{H}}} - \left[\frac{\int d\Gamma\, \mathcal{H} e^{-\beta \mathcal{H}}}{\int d\Gamma\, e^{-\beta \mathcal{H}}} \right]^2$$

$$= \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \text{Variance of } P(E)$$

Specific Heat:

$$c_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_{N,V} = \left(\frac{\partial}{\partial T} \langle \mathcal{H} \rangle \right)_{N,V}$$

$$= \frac{\partial}{\partial \beta} \langle \mathcal{H} \rangle \cdot \frac{\partial \beta}{\partial T}$$

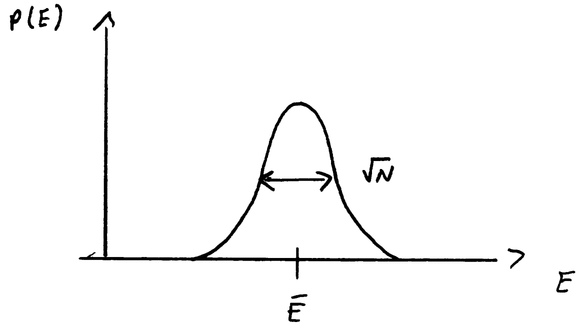
$$= \frac{1}{k_B T^2} \left(-\frac{\partial}{\partial \beta} \langle \mathcal{H} \rangle \right)$$

$$\Rightarrow \quad \langle \mathcal{H}^2 \rangle_T - \langle \mathcal{H} \rangle_T^2 = k_B T^2 c_V$$

- Relates fluctuations in E at a given T to response of E to change in T.
- Example of fluctuation - response relation
- $\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \langle (\mathcal{H} - \langle \mathcal{H} \rangle)^2 \rangle > 0$

  so $c_V > 0$ for a system in thermal equilibrium
- We know that c_V is <u>extensive</u> $\Rightarrow$ variance of distribution is extensive:

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 \sim N$$

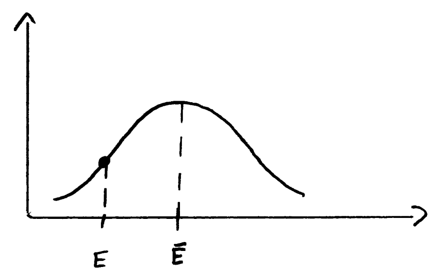


$$\frac{\sqrt{\text{Var}}}{\text{mean}} \rightarrow \frac{1}{\sqrt{N}} \rightarrow 0$$

$$P(E) \underset{N \to \infty}{\approx} \delta\left(E - \bar{E}(T)\right)$$

Energy Distribution :

$$P(E) \propto \frac{\Omega(E)}{N!} e^{-\beta E} = e^{\frac{S(E)}{k_B} - \beta E}$$



for $|E - \bar{E}| \ll \bar{E}$ (not at tail) Taylor Expansion

$$P(E) \propto e^{\frac{S(\bar{E})}{k_B} - \beta \bar{E}} \, e^{\left(\frac{1}{k_B}\frac{\partial S}{\partial E}\big|_{\bar{E}} - \beta\right)(E - \bar{E})} \, e^{\frac{1}{2k_B}\frac{\partial^2 S}{\partial E^2}\big|_{\bar{E}} (E-\bar{E})^2}$$

1. $\frac{1}{k_B T} - \beta = 0$

2. $\left.\frac{\partial^2 S}{\partial E^2}\right|_{\bar{E}(T)} = ?$

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial E}\right)_{\bar{E}(T)} = \frac{\partial E}{\partial T}\frac{\partial}{\partial E}\left(\frac{\partial S}{\partial E}\right)_{\bar{E}} = \frac{\partial \bar{E}}{\partial T}\left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}} = c_V \left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}}$$

$$\frac{\partial}{\partial T}\left(\frac{1}{T}\right) = -\frac{1}{T^2}$$

$$\Rightarrow \left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}(T)} = -\frac{1}{T^2 C_V}$$

So, $$P(E) \propto \exp\left\{-\frac{1}{2k_B T^2 C_V}(E-\bar{E})^2\right\}$$

$$= e^{-\frac{(E-\bar{E})^2}{2\,\mathrm{var}}}$$

normal distribution w/ $$\boxed{\begin{aligned} \mathrm{var} &= k_B T^2 C_V = \langle (H - \langle H\rangle)^2\rangle \\ \mathrm{mean} &= \bar{E}(T) \end{aligned}}$$

$$\left(\frac{\sqrt{\mathrm{var}}}{\mathrm{mean}}\right) = \frac{1}{\sqrt{N}} \to 0 \quad \text{as} \quad N \to \infty$$

<u>Partition Function:</u>

$$Z(\beta) = \int dE\, \frac{\Omega(E)}{N!}\, e^{-\beta E}$$

$$= e^{\frac{S(\bar{E})}{k_B} - \beta\bar{E}} \int dE\, e^{-\frac{(E-\bar{E})^2}{2k_B C_V T^2}}$$

$$\ln Z(\beta) = \underbrace{\frac{S(\bar{E})}{k_B} - \beta\bar{E}}_{\mathcal{O}(N)} + \ln \mathcal{O}(\sqrt{\mathrm{var}})$$

for large N:

$$\ln Z(\beta) = \frac{S(\bar{E})}{k_B} - \beta\bar{E}$$

Free Energy

$$\boxed{\begin{aligned} \bar{E} - TS &= -k_B T \ln Z = F(T,N,V) \\ \bar{E}(T) - TS(\bar{E}(T)) &= F(T,N,V) \end{aligned}}$$

In canonical ensemble, every follows from $F(T,N,V)$!!

$S(E,N,V)$ in canonical ensemble $\to$ replace E w/ $\bar{E}(T)$.

$$\Rightarrow \left(\frac{\partial^2 S}{\partial E^2}\right)_{\bar{E}(T)} = -\frac{1}{T^2 C_V}$$

So, $$P(E) \propto \exp\left\{-\frac{1}{2k_B T^2 C_V}(E-\bar{E})^2\right\}$$
$$= e^{-\frac{(E-\bar{E})^2}{2\,\mathrm{var}}}$$

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In canonical ensemble, every follows from $F(T,N,V)$!!

$S(E,N,V)$ in canonical ensemble $\to$ replace E w/ $\bar{E}(T)$.

$$dF = d\bar{E} - T\,dS - S\,dT$$

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

$$\left(d\bar{E} = -\bar{d}W + \bar{d}Q = -p\,dV + \mu\,dN + T\,dS \right)$$

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

<u>Isothermal</u> Process of a <u>closed</u> system $(dT = dN = 0)$:

$$dF = d\bar{E} - T\,dS$$

1^{st} and 2^{nd} Law: $\quad d\bar{E} = \bar{d}Q - \bar{d}W, \quad \bar{d}Q \le T\,dS$

$$\bar{d}W = \bar{d}Q - dE$$

$$\le T\,dS - (dF + T\,dS)$$

$$\boxed{dW \le -dF}$$

Max possible work done by system $= -dF$ (hence "Free" Energy) for isothermal process of a closed system.

if $dV = 0$, $\bar{d}W = 0 \Rightarrow dF \le 0$

Golden Lecture 3 ~ Grand Canonical Ensemble

1. Microcanonical (Isolated):

$$\Omega(E, V, N) = \frac{1}{N!}\int \frac{d\Gamma}{h^{3N}}\,\delta(E - H_N)$$

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

All Thermodynamic Properties follow from S.

2. Canonical Ensemble, relax fixed E;

$$Z(T, V, N) = \int d\Omega\ \Omega(E)e^{-\beta E}$$

$$e^{-\frac{F}{k_B T}} = \int dE\ e^{\frac{S(E)}{k_B} - \frac{E}{k_B T}}$$

@ saddle point $\quad F(T, V, N) = \bar{E} - TS(\bar{E})$

$$\left.\frac{\partial S}{\partial T}\right|_{\bar{E}} = \frac{1}{T}$$

need $\left.\dfrac{\partial^2 S}{\partial E^2}\right|_{\bar{E}} < 0 \Rightarrow c_V > 0$

or from $F(T) \to \dfrac{S(E)}{k} = \beta\bar{E} - \beta F(T)$, need $T(\bar{E})$

$$\frac{\partial}{\partial\beta}\ln Z = -\bar{E}(T)$$

3. relax both E, V:

$$Q(\beta, P, N) = \int dV\, e^{-\beta PV} Z(\beta, V, N)$$

$$e^{-\beta G} = \int dV\, e^{-\beta PV - \beta F}$$

using saddle point, at some $\bar{V}$:

$$P + \frac{\partial F}{\partial V}\Big|_{\bar{V}} = 0$$

$$G = P\bar{V} + F(\beta, \bar{V}(P), N)$$

require $\quad \frac{\partial^2 F}{\partial \bar{V}^2} > 0.$

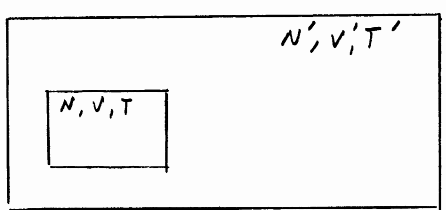
invert : $\quad$ from $\quad G(P) \to F(V)$

need $\quad P(\bar{V})$ from $\quad F(\bar{V}) = G(P(\bar{V})) - P(\bar{V})\bar{V}$

$$\bar{V}(p) = \frac{\partial}{\partial p}(\ln Q)$$

Grand Canonical Ensemble

Relax E, N from being fixed (open systems)



Exchange of particles w/ $N + N' = \text{const}$

$$\mathcal{Z}(\beta, V, \mu) = \sum_{n=0}^{\infty} e^{\beta\mu N} z(\beta, V, N)$$

z - transform (disrete version of Laplace Transform)

$\ln \mathcal{Z} \to$ Grand Potential obtained from Saddle point.

$$e^{\ln \mathcal{Z}} = \sum_N e^{\beta \mu N} e^{-\beta F}$$

$$\ln \mathcal{Z} = \beta \mu \bar{N} - \beta F(\bar{N})$$

$$\text{w/} \quad \beta \mu - \beta \frac{\partial F}{\partial N}\bigg|_{N=\bar{N}} = 0$$

$$\Rightarrow \quad \boxed{\mu = \frac{\partial F}{\partial N}\bigg|_{N=\bar{N}}} \quad \Rightarrow \quad \bar{N}(\mu) \text{ is saddle point}$$

so, $F(V, T, N) = -\frac{1}{\beta} \ln \mathcal{Z} + \mu \bar{N}(\mu)$ with $\mu(N)$

$$\boxed{\bar{N}(\mu) = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}}$$

<u>Grand Potential</u>:

$$\frac{\partial}{\partial V} \ln \mathcal{Z} = -\beta \left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$= \beta P$$

$$\Rightarrow \quad P = \frac{1}{\beta} \frac{\partial}{\partial V} \left(\log \mathcal{Z}\right)$$

but $\ln \mathcal{Z}$ is extensive so

$$\ln \mathcal{Z} = V f_n(\beta, \mu)$$

so, $\beta P = \frac{\partial}{\partial V} \ln \mathcal{Z} = f_n(\beta, \mu)$

$\Rightarrow \quad \ln \mathcal{Z}(\beta, V, \mu) = \beta P V \Rightarrow$ yields equation of state (between N, T, V, P)

Example: ideal Gas

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m}$$

$$Z_N = \frac{1}{h^{3N} N!} \int d\vec{r}_1 \cdots d\vec{r}_N \, d\vec{p}_1 \cdots d\vec{p}_N \, e^{-\beta \sum_i \frac{p_i^2}{2m}}$$

$$= \frac{V^N}{N!} \frac{1}{\lambda_T^{3N}}$$

where $$\lambda_T \equiv \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$\beta P V = \ln \mathcal{Z} = \frac{V e^{\beta\mu}}{\lambda_T^3}$$

need $$\bar{N}(\mu) = \frac{\sum_{N=0}^{\infty} N e^{-\beta\mu N} Z_N}{\sum_{N=0}^{\infty} e^{\beta\mu N} Z_N}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial\mu} \ln \mathcal{Z}$$

$$\bar{N}(\mu) = \frac{1}{\beta}\frac{\partial}{\partial\mu}\left(\frac{V e^{\beta\mu}}{\lambda_T^3}\right) = \frac{V e^{\beta\mu}}{\lambda_T^3}$$

so, $$\boxed{PV = \frac{N}{\beta} = k_B N T}$$

<u>Look at Second Derivative:</u>

Fluctuations in Grand Partition Ensemble

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\frac{\partial}{\partial\mu^2}(\ln \mathcal{Z}) = \frac{1}{\beta}\frac{\partial}{\partial\mu}\langle N\rangle$$

$$\mathrm{Var}(N) = -\frac{1}{\beta}\left\{ \underbrace{\frac{\langle N\rangle^2}{V}}_{\text{extensive}} \underbrace{\frac{\partial}{\partial\mu}\left(\frac{V}{\langle N\rangle}\right)}_{\text{intensive}} \right\}$$

$$\boxed{\frac{\mathrm{Var}(N)}{\langle N\rangle^2} \to 0 \quad \text{as} \quad N \to 0} \qquad (V = N v)$$

in thermodymic limit

for fixed β, V; $\left(\frac{\partial}{\partial\mu} \ln \mathcal{Z}\right)_{\beta, V} d\mu = \beta V dP$

$$\beta\langle N\rangle\, d\mu = \beta V dP$$

$$d\mu = \frac{V}{\langle N\rangle} dP$$

$$-\frac{\partial}{\partial\mu}\left(\frac{V}{\langle N\rangle}\right) = -\frac{\langle N\rangle}{V}\frac{\partial}{\partial p}\left(\frac{V}{\langle N\rangle}\right)$$

$$v \equiv \frac{V}{\langle N\rangle}$$

$$\Rightarrow \quad -\frac{1}{v}\frac{\partial v}{\partial p} = \kappa_T \quad \text{isothermally compressibility}$$

Golden Lecture 4 ~ Quantum Mechanical Ideal Gas

Assume QM ideal is noninteracting.

Consider a state:

$$|\psi\rangle = |n_1, n_2 \ldots, n_k, \ldots\rangle = |\{n_i\}\rangle$$

state label or occupation number

energy of state $i = \varepsilon_i$

$n_i = 0, 1, 2, \ldots, \infty$ (Boson)

$n_i = 0, 1$ (Fermions)

input into machinery of stat mech

apply fundamental postulate of stat mech:

$$E(\{n_i\}) = \sum_i \varepsilon_i n_i \quad , \quad n_i = \text{\# of states w/energy } \varepsilon_i$$

also have,

$$N = \sum_i n_i$$

Canonical partition function becomes:

$$Z(\beta, V, N) = \sum_{n_1}^{1,\infty} \sum_{n_2}^{1,\infty} \sum_{n_3}^{1,\infty} \cdots e^{-\beta E(\{n_i\})} \delta_{N, \sum_i n_i}$$

1 if Fermions
∞ if Bosons

$$= \sum_{\{n_i\}} e^{-\beta \sum_i \varepsilon_i n_i} \delta_{N, \sum_i n_i}$$

note: $\sum_{n_1}^{1,\infty} \sum_{n_2}^{1,\infty} \cdots \to \sum_{\{n_i\}}$ and there is no $\frac{1}{N!}$

$$= \sum_{\{n_i\}}{}' e^{-\beta \sum_i \varepsilon_i n_i}$$

where prime means $\sum_{\{n_i\}}$ with delta function constraint applied:

$$N - \sum_i n_i = 0$$

Consider Grand Partition Function:

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta \mu N} \; Z(\beta, V, N)$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{\{n_i\}}{}' \; e^{-\beta \sum_i \epsilon_i n_i}$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_i\}} e^{-\beta \sum_i \epsilon_i n_i + \beta \mu N} \; \delta_{N, \sum_i n_i}$$

delta kills sum over N:

$$= \sum_{\{n_i\}} \exp\left\{ -\beta \sum_i \epsilon_i n_i + \beta \mu \sum_i n_i \right\}$$

$$= \sum_{\{n_i\}} \exp\left\{ \sum_i \left(-\beta (\epsilon_i - \mu) n_i \right) \right\}$$

$$= \sum_{\{n_i\}} \prod_{i=1}^{\infty} \underbrace{\exp\left\{ -\beta(\epsilon_i - \mu) n_i \right\}}_{g_i(n_i)}$$

$$= \left(\sum_{n_1}^{1,\infty} \sum_{n_2}^{1,\infty} \sum_{n_3}^{1,\infty} \cdots \right) \prod_{i=1}^{\infty} g_i(n_i)$$

$$= \prod_{i=1}^{\infty} \left(\sum_{n_1}^{1,\infty} \sum_{n_2}^{1,\infty} \sum_{n_3}^{1,\infty} \cdots \right) g_i(n_i)$$

$$= \prod_{i=1}^{\infty} \sum_{n_i}^{1,\infty} g_i(n_i) = \prod_{i=1}^{\infty} \mathcal{Z}_i$$

example: fermions

$$\prod_{i=1}^{3} \sum_{n_i}^{1} g_i(n_i) = \left(g_1(0) + g_1(1) \right)\left(g_2(0) + g_2(1) \right)\left(g_3(0) + g_3(1) \right)$$

$$= g_1(0) g_2(0) g_3(0) + g_1(1) g_2(0) g_3(0) + \cdots$$

$$= \sum_{\{n_i\}} \prod_{i=1}^{3} g_i(n_i)$$

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

Fermions: $\sum_{n_i=0}^{1} e^{-\beta(\varepsilon_i - \mu)n_i} = 1 + e^{-\beta(\varepsilon_i - \mu)}$

so, $\sum_{n_i=0}^{1,\infty} e^{-\beta(\varepsilon_i - \mu)n_i} = \left[1 \mp e^{-\beta(\varepsilon_i - \mu)}\right]^{\mp 1}$

upper sign → Bosons

lower sign → Fermion

$$\mathcal{Z} = \prod_i \left[1 \mp e^{-\beta(\varepsilon_i - \mu)}\right]^{\mp 1}$$

$$\boxed{\ln \mathcal{Z} = \mp \sum_i \ln\left(1 \mp e^{-\beta(\varepsilon_i - \mu)}\right) = \beta PV} \quad (a)$$

Need $\mu(N)$ to get equation of state from (a).

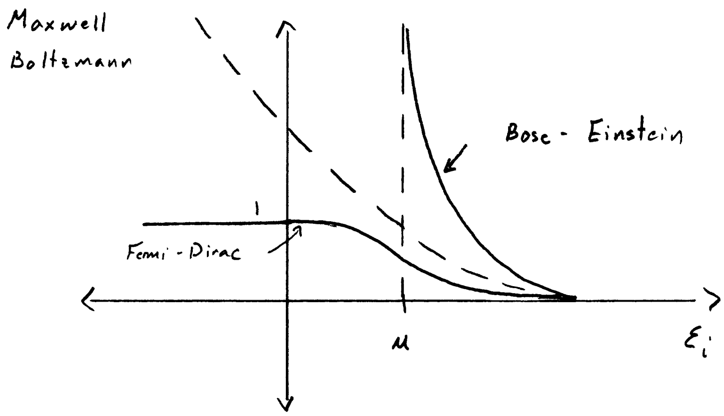
$$\mu(N): \quad \langle n_i \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln \underbrace{\left[1 \mp e^{-\beta(\varepsilon_i - \mu)}\right]^{\mp 1}}_{\mathcal{Z}_i}$$

$$\bar{N} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln \mathcal{Z} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\left(\sum_i \ln \mathcal{Z}_i\right) = \sum_i \langle n_i \rangle$$

$$\langle n_i \rangle = \pm \frac{1}{\beta}(\mp)\beta \frac{e^{-\beta(\varepsilon_i - \mu)}}{1 \mp e^{-\beta(\varepsilon_i - \mu)}}$$

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \mp 1}}$$

Quantum distribution function:



MB: large ε_i $\approx e^{-\beta \varepsilon_i}$

BE: $\varepsilon_i \to \mu \quad \to \quad \infty$

FD: $\varepsilon_i \to \mu \quad \to \quad \frac{1}{2}$

$$\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} \mp 1} \Rightarrow \mu(N)$$

pass to continuum limit:

$$\approx \int dE \, \mathcal{D}(E) \left[\frac{1}{e^{\beta(E-\mu)} \mp 1} \right]$$

where $\mathcal{D}(E) = \sum_i \delta(E - \varepsilon_i) \underset{\text{degeneracy}}{g(E)}$ is

the single particle density of state.

Consider ideal gas in box of size $L \times L \times L$ w/ periodic B.C.

$$\mathcal{E}_n = \frac{\hbar^2}{2m} K_n^2$$

$$K_x = \frac{2\pi}{L} n_x \ , \ \text{etc.} \qquad (\text{periodic B.C.})$$

$$\sum_i = \sum_{n_x} \sum_{n_y} \sum_{n_z} = \sum_{K_x} \sum_{K_y} \sum_{K_z} \left(\frac{L}{2\pi}\right)^3 \Delta K_x \, \Delta K_y \, \Delta K_z$$

note : $\Delta n_i = 1$,

$$\rightarrow \frac{V}{(2\pi)^3} \int d^3\vec{K}$$

$$\Omega(E) = \sum_{n_x} \sum_{n_y} \sum_{n_z} \delta\left(E - \mathcal{E}_{n_x n_y n_z}\right)$$

$$\simeq \frac{V}{(2\pi)^3} \int d^3\vec{K} \ \delta\left(E - \frac{\hbar^2 K^2}{2m}\right)$$

$$= \frac{V}{(2\pi)^3} 4\pi \int_0^\infty K^2 \, dK \ \delta\left(E - \frac{\hbar^2 K^2}{2m}\right)$$

recall $\delta\left[f(x) - f(x_0)\right] = \dfrac{1}{|f'(x_0)|} \delta(x - x_0)$.

let $y = K^2$, $dy = 2K\,dK = 2\sqrt{y}\,dK$

$$= \frac{V}{(2\pi)^3} \frac{4\pi}{\left(\frac{\hbar^2}{2m}\right)^{3/2}} \cdot \frac{1}{2} E^{1/2}$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

$$\langle N \rangle = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int dE \, \frac{E^{1/2}}{\left(f^{-1} e^{\beta E} \mp 1\right)} \qquad \text{fugacity, } f \equiv e^{\beta\mu}$$

$$= \frac{2}{\sqrt{\pi}} V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int dy \, \frac{y^{1/2}}{\left(f^{-1} e^{y} \mp 1\right)}$$

$$\lambda_T = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} \equiv \text{thermal De Broglie wavelength,}$$

$$\boxed{(1) \qquad \rho = \frac{\langle N \rangle}{V} = \lambda_T^{-3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y}}{f^{-1} e^y \mp 1}}$$

$$I_\pm(f) \equiv \frac{2}{\sqrt{\pi}} \int_0^y \frac{\sqrt{y}\, dy}{f^{-1} e^y \mp 1} \qquad \begin{array}{l} + \text{ Bosons} \\ - \text{ Fermions} \end{array}$$

Similarly

$$\boxed{(2) \qquad \beta P = \lambda_T^{-3} \frac{(\mp 2)}{\sqrt{\pi}} \int dy \sqrt{y}\, \ln\left(1 \mp f e^{-y}\right)}$$

$$J_\pm(f) = \frac{(\mp 2)}{\sqrt{\pi}} \int_0^\infty dy \sqrt{y}\, \ln\left(1 \mp f e^{-y}\right)$$

$$\frac{\partial J_\pm}{\partial f} = \frac{(\mp 2)}{\sqrt{\pi}} \int_0^\infty dy \sqrt{y} \left(\frac{1}{1 \mp f e^{-y}} \right) e^{-y}$$

$$= \frac{(\mp 2)}{\sqrt{\pi}} \int_0^\infty dy \frac{\sqrt{y}}{e^y \mp f}$$

$$f \frac{\partial J_\pm}{\partial f} = \frac{(\mp 2)}{\sqrt{\pi}} \int_0^\infty dy \frac{1}{f^{-1} e^y \mp 1} = I_\pm(f)$$

$$\boxed{(3) \qquad f \frac{\partial J_\pm(f)}{\partial f} = I_\pm(f)}$$

Use (1), (2) and (3) to elliminate f to get $\beta P(\rho)$: difficult in practice.