# 1. Probability 9/5 (목)

$P_a$ or $P(a)$ — represent the microstate either discrete or continuous

continuous: $P(x)dx$ → Probability density function

(*) Probability that we commonly encounter in Nature

- Gaussian $\quad P(x) = \dfrac{1}{\sqrt{2\pi}\,\sigma_0} \cdot e^{-\frac{(x-x_0)^2}{2\sigma_0^2}}$
- Poisson $\quad P_m(t) = \dfrac{t^m}{m!} e^{-t}$
- Binomial distribution $\quad B_N(m) = a^m b^{N-m} \cdot \dfrac{N!}{m!\,(N-m)!}$
- Lorentzian $\quad P(x) = \dfrac{\Gamma}{2\pi} \cdot \dfrac{1}{(x-x_0)^2 + (\Gamma/2)^2}$ ... bell shaped, long-tailed.
- Flat $\quad P(x) = \text{const}$

(*) Property

- $\displaystyle\int_{-\infty}^{\infty} dx\, P(x) = 1 \qquad \sum_a P_a = 1$ ... Normalisation
- The mean $\quad \bar{x} = \langle x \rangle = \int dx \cdot x P(x)$
- The mean square $\quad \langle x^2 \rangle = \int dx \cdot x^2 P(x)$
- Variance $= \langle x^2 \rangle - \langle x \rangle^2 \xrightarrow[\text{Standard deviation}]{} \sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

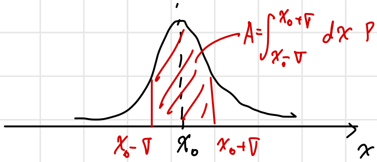
(*) Cumulative density function. (CDF)

$C(x) = \displaystyle\int_{-\infty}^{x} dx'\, P(x')$ ⟶ Monotonically increasing

$\Rightarrow P(a < x < b) = C(b) - C(a) = \displaystyle\int_a^b dx'\, P(x')$

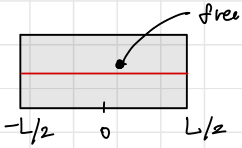
EX) $P(x) = \dfrac{1}{\sqrt{2\pi}\,\sigma_0} \cdot e^{-\frac{(x-x_0)^2}{2\sigma_0^2}}$ $\Rightarrow$ $\begin{cases} \langle x \rangle = \int dx\, x \cdot P(x) = x_0 \\ \langle x^2 \rangle = \sigma_0^2 + x_0^2 \end{cases}$

$\therefore \sigma = \sigma_0$




$A = \displaystyle\int_{x_0-\sigma}^{x_0+\sigma} dx\, P(x) = 0.68$ ⟶ True only for Gaussian. microstate.

⟷ (Counter ex)




free particle, assume flat prob : $P(x) = \dfrac{1}{L}$ → Maximally featureless

$\Rightarrow \sigma = 0.29L, \quad A = 0.58 \neq 0.68$.

(*) Increased, non-interacting particle numbers to $N$

- Suppose we are interested in correlated macroscopic quantities such as the center of mass
  - correlated: indirectly, somehow related.

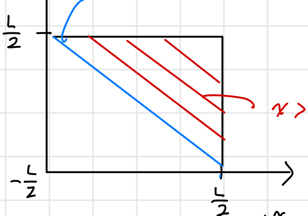
$$\equiv \frac{x_1 + x_2 + \cdots + x_N}{N}$$

- Two things happen: "Central Limit Theorem"
  ① As $N \to \infty$, precision increases as $\sigma/\sqrt{N}$
  ② $\lim_{N\to\infty} P_N(x) \longrightarrow$ Gaussian $P(x)$

cf) What is big enough number to be regard as infinity? even if $N = 3, 4 \cdots$ is sometimes enough

- Schematic diagram ($N=2$)

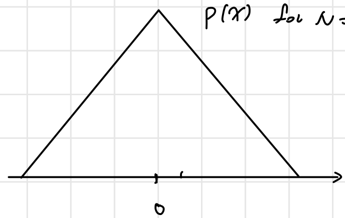
$x=0$ : Longest ($P$ maximized)



$x_1 + x_2 = 2x = \text{fixed}.$

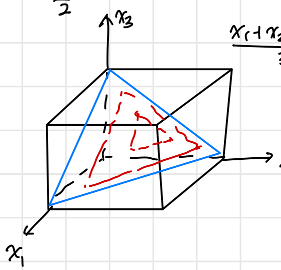
$x > 0$ ($x < 0$) : decreases linearly

$\Rightarrow$



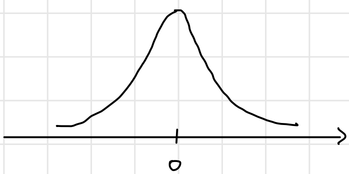
$P(x)$ for $N=2$

($N=3$)



$\frac{x_1 + x_2 + x_3}{3} = x$

$\Rightarrow$



(i) For $N$ particles, $\langle x \rangle_N = \int_{-L/2}^{L/2} dx_1 \cdots dx_N \, P(x_1) \cdots P(x_N) \left[ \frac{x_1 + x_2 + \cdots + x_N}{N} \right]$

$$= \frac{1}{N} \cdot \sum_{i=1}^{N} \underbrace{\int_{-L/2}^{L/2} dx_i \cdot P(x_i)\, x_i}_{\langle x \rangle} = \frac{1}{N} \cdot N \langle x \rangle = \langle x \rangle$$

(ii) $\langle x^2 \rangle_N = \int_{-L/2}^{L/2} dx_1 \cdots dx_N \, P(x_1) \cdots P(x_N) \left[ \frac{x_1 + x_2 + \cdots + x_N}{N} \right]^2$ (전개해서 정리)

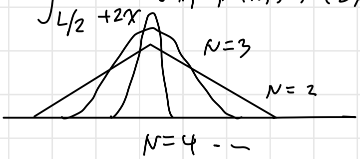
$$= \frac{1}{N^2} \cdot \left[ \sum_{i=1}^{N} \int_{-L/2}^{L/2} dx_i \cdot x_i^2 \, P(x_i) + \underbrace{\sum_{i \neq j}}_{?} \binom{N}{2} \int_{-L/2}^{L/2} dx_i \, dx_j \, P(x_i) P(x_j) \cdot 2 x_i x_j \right]$$

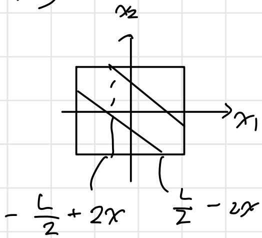
$$= \frac{1}{N^2} \left( N \langle x^2 \rangle + \frac{N(N-1)}{2} \times 2 \cdot \langle x^2 \rangle \right)$$

$\therefore \sigma_N = \sqrt{\langle x^2 \rangle_N - \langle x \rangle_N^2} \longrightarrow \frac{\sigma}{\sqrt{N}} \cdots$ ①

ex) $N=2$ $\quad P_2(x) = 2\int_{-L/2}^{L/2} dx_1\, p(x_1) \int_{-L/2}^{L/2} dx_2\, p(x_2)\cdot \delta(x_1+x_2-2x)$

$$= 2\int_{L/2+2x}^{L/2} dx_1\, p(x_1)\, p(2x-x_1) = \frac{2x-4x}{L^2} \quad (x>0)$$



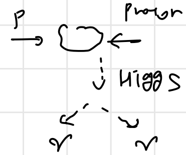

As $N\to\infty$, All detailed distribution information erased and ...

$$P_N(x) \longrightarrow \frac{1}{\sqrt{2\pi}\,\sigma_N} \exp\left(-\frac{(x-\langle x\rangle_N)^2}{2\,\sigma_N}\right)$$

$\langle x \rangle$

$\sigma/\sqrt{N}$

Due to C.L.T




(*) Poisson distribution

: When something happens discretely with small probability $\lambda$ for a continuous time $t$.

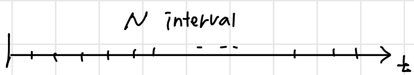
cf) dark matter $\lambda \sim 10^{-30\sim-50}$

ex) A block of $^{235}U$ containing $N \sim 10^{24}$ atoms (a mole)

each atom has a tiny probability for decaying $\lambda$.

$\Rightarrow dP = \lambda dt$

$\lambda$: decay rate $\quad \lambda^{235U} \sim 3\times 10^{-17}/\mathrm{sec}$




$\Delta t = \frac{t}{N} \xrightarrow[N\to\infty]{}$

$$\begin{cases} \text{If decay} \Rightarrow \lambda\cdot\Delta t = \lambda t/N \\ \text{If not decay} \Rightarrow 1-\lambda t/N \end{cases}$$

i) Prob of seeing no decay for time $t$ : $P_{\text{no decay}}(t) = \lim_{N\to\infty}\left(1-\frac{\lambda t}{N}\right)^N = e^{-\lambda t}$.

$\Rightarrow$ (Half time) $P_{\text{no decay}}(t_{1/2}) = \frac{1}{2} \therefore = e^{-\lambda t_{1/2}}$.

$\therefore\ t_{1/2} = \frac{\ln 2}{\lambda} \cong 0.7/\lambda$

cf) $e^{-\lambda t} = e^{-t/\tau}$

$\tau$ = lifetime $= 1/\lambda$.

ii) $P_{1\text{-decay}}(t) = \lim_{N\to\infty} \frac{\lambda t}{N}\left(1-\frac{\lambda t}{N}\right)^{N-1}\cdot N = -t\frac{\partial}{\partial t} P_{\text{no decay}}(t)$

$= \lambda t\, e^{-\lambda t}$

$P_{2\text{-decay}}(t) = \lim_{N\to\infty}\left(\frac{\lambda t}{N}\right)^2\left(1-\frac{\lambda t}{N}\right)^{N-2}\binom{N}{2} = \frac{1}{2}t^2\frac{\partial^2}{\partial t^2}P_{\text{no-decay}}(t) = \frac{1}{2}(\lambda t)^2 e^{-\lambda t}$.

$\vdots$

$$\boxed{P_{m\text{-decay}}(t) = \frac{(\lambda t)^m}{m!}\cdot e^{-\lambda t}}$$

... Poisson distribution

$\sum_{m=0}^{\infty} P_{m\text{-decay}}(t) = 1$ (Taylor expansion) $\rightarrow$ Normalized nicely.

$$\langle m \rangle = \sum_{m=0}^{\infty} m\, P_m(t) = \sum_{m=1}^{\infty} m \frac{(\lambda t)^m}{m!} e^{-\lambda t} = \sum_{m=1}^{\infty} \frac{(\lambda t)^{m-1}}{(m-1)!} e^{-\lambda t} \times \lambda t = \lambda t$$

$$\langle m^2 \rangle = \sum m^2 P_m(t) = (\lambda t)^2 + \lambda t. \qquad \therefore \sigma = \sqrt{\lambda t}. \qquad \langle m \rangle = \lambda t.$$

fractional error $\frac{\sigma}{\langle m \rangle} = \frac{1}{\sqrt{\lambda t}} \rightarrow 0$ as $t \rightarrow \infty$. (prediction)

Q. No-decay prob 과 m-decay prob 의 정확한 정의?

Due to the central limit theorem, Poisson distribution in the limit of large #
($m \sim O(10)$)

$$m = \lambda t(1+\delta) \qquad \delta = \frac{m - \langle m \rangle}{\langle m \rangle} \rightarrow 0$$

$$P_m(t) = \frac{(\lambda t)^m}{m!} e^{-\lambda t} \xrightarrow[m \to \infty]{} \frac{(\lambda t)^m e^{-\lambda t}}{\sqrt{2\pi m}\; m^m e^{-m}} \quad \text{(Stirling's formula)}$$

$\llcorner\; m = \lambda t(1+\delta)$

$$= \frac{e^{\lambda t \delta} (1+\delta)^{-\lambda t(1+\delta) - \frac{1}{2}}}{\sqrt{2\pi \lambda t}} \Leftarrow \ln(1+\delta)^{-\lambda t(1+\delta) - \frac{1}{2}} = -\left(\lambda t(1+\delta) + \tfrac{1}{2}\right)\left(\delta - \tfrac{1}{2}\delta^2 + \cdots\right)$$

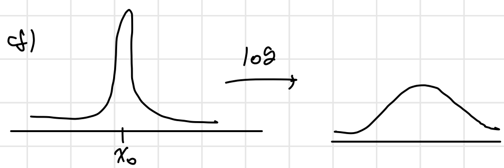
$$= -\left(\lambda t \delta + \tfrac{1}{2}\lambda t \delta^2 + \cdots\right)$$

$$\Rightarrow P_m(t) \simeq \frac{e^{-\frac{1}{2}\lambda t \delta^2}}{\sqrt{2\pi \lambda t}}. \qquad \left(\delta = \frac{m - \lambda t}{\lambda t}\right)$$

$$= \frac{1}{\sqrt{2\pi \lambda t}} \cdot e^{-\frac{(m-\lambda t)^2}{2\lambda t}} \qquad \left[\begin{array}{l} \langle m \rangle = \lambda t \\ \sigma = \sqrt{\lambda t} \end{array}\right.$$

Great! CLT works.

cf)

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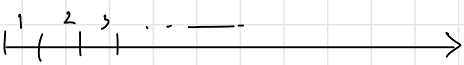
9/12 (목) Decay of the unstable particle $dP = \lambda\, dt$.

$$P_{\text{no-decay}}(t) = \lim_{N \to \infty} \left(1 - \frac{\lambda t}{N}\right)^N = e^{-\lambda t}$$

$$P_{\text{decay}} = 1 - e^{-\lambda t} \qquad \left(\because \lim_{N \to \infty} \sum_{i=1}^{N} \frac{\lambda t}{N} \left(1 - \frac{\lambda t}{N}\right)^{i-1} = 1 - e^{-\lambda t}\right)$$

$N_0$: number of particle at $t = 0$




particle array

$$\begin{cases} \text{decay} & 1-e^{-\lambda t} \\ \text{no-decay} & e^{-\lambda t} \end{cases}$$

$$P_N(t) = \binom{N_0}{N} \underbrace{\left(e^{-\lambda t}\right)}_{a}^{N} \left(\underbrace{1 - e^{-\lambda t}}_{b=1-a}\right)^{N_0 - N}$$

$$\langle N(t) \rangle = \sum_N N \cdot P_N(t) = N_0\, e^{-\lambda t}.$$

# Binomial distribution

$$\sum_{m=0}^{N} a^m b^{N-m} \binom{N}{m} = (a+b)^N \underset{\text{if } a+b=1}{=\!=\!=} 1$$

$\sum_{m=0}^{N} B_N(m)$

↳ properly normalized.

$a$ : prob of winning.

$$B_N(m) \xrightarrow[N\to\infty]{\text{CLM}} \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{(m-\langle m\rangle)^2}{2\sigma^2}}$$

① $\langle m \rangle = \sum_{m=0}^{N} m\, B_N(m) = \sum_{m=0}^{N} m \cdot a^m b^{N-m} \binom{N}{m}$

treat $a, b$ as independent variables

$$= a \cdot \frac{\partial}{\partial a}\left[\sum_{m=0}^{N} a^m b^{N-m} \binom{N}{m}\right] = a \frac{\partial}{\partial a}(a+b)^N$$

$$= Na(a+b)^{N-1} = Na$$

② $\langle m^2 \rangle = a^2 N(N-1) + Na$ (Same logic)

③ $\sigma = \sqrt{\langle m^2 \rangle - \langle m \rangle^2} = \sqrt{-a^2 N + Na}$

$= \sqrt{Na(1-a)} = \sqrt{Nab}$

(*) Random walk

$\langle \text{winning} \rangle = \langle m - (N-m) \rangle = \langle 2m - N \rangle = N(a-b)$

$\sigma_{\text{winning}} = 2\sqrt{Nab}$ $\quad a+b=1 \quad \leftarrow \mathrm{Var}(2m) = 2^2\sigma^2$

(*) For a fair game, $a = b = \frac{1}{2}$ : The situation falls into 1D unbiased equal step random walks

$\sigma = \sqrt{N}$ for $a = b = 1/2$

$= N^{\frac{1}{2}}$

(*) For an extremely unfair game. $(\because a \sim 0,\ b \sim 1)$ $\quad a \to 0 \quad b \to 1$

$a = \frac{\lambda t}{N} \to 0$

$N \cdot a = \lambda t = \text{fixed}.$

$$\lim_{N\to\infty} B_N(m) = \lim_{N\to\infty} \binom{N}{m} a^m b^{N-m} := \frac{(\lambda t)^m}{m!} e^{-\lambda t}. \to \text{Poisson}.$$

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Statistical Mechanics involves Sum or average of a series of fluctuations (Random steps)

$$S_N = \sum_{i=1}^{N} l_i \quad (l_i = \pm 1 \text{ in coin flip}) = \#\text{ heads} - \#\text{ tails}$$

Coin flip $\qquad \langle S_N \rangle = 0$

i) $N = 1$ $\quad S_1 = +1$ or $-1$ $\quad \langle S_1^2 \rangle = (+1)^2 \cdot \frac{1}{2} + (-1)^2 \frac{1}{2} = 1$

ii) $N = 2$ $\quad S_2 = +2, 0, -2$ $\quad \langle S_2^2 \rangle = 2^2 \cdot \frac{1}{4} + 0 \cdot \frac{1}{2} + (-2)^2 \cdot \frac{1}{4} = 2$

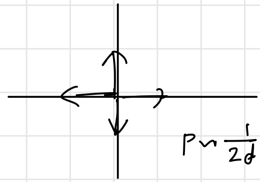
⋮

iii) $N$ $\quad \langle S_N^2 \rangle = \langle (S_{N-1} + l_N)^2 \rangle = \underbrace{\langle S_{N-1}^2 \rangle}_{= N-1 \text{ 이면}} + 1 = N$ $\quad$ (수학적귀납법)

$\therefore \langle S_N^2 \rangle = N.$ $\quad \sigma_S = \sqrt{\langle S_N^2 \rangle - \langle S_N \rangle^2} = \sqrt{N}.$

## 2D coin flip

$\vec{S_N} = \sum_{i=1}^{N} \vec{l_i}$



$P \sim \frac{1}{2d}$

$\langle \vec{S_1}^2 \rangle = 1 \cdot \frac{1}{4} \cdot 4 = 1.$

$\vdots$

$\langle \vec{S_N}^2 \rangle = \langle (\vec{S_{N-1}} + \vec{l_N})^2 \rangle = \langle \vec{S_{N-1}}^2 \rangle + 1 \quad (\because \langle (\vec{l_i} \cdot \vec{l_j}) \rangle = 0)$

$\therefore \langle \vec{S_N}^2 \rangle = N.$

$d \to N$ dim
이어도 확장가능

$\sigma_N$

$\sigma_N = \sqrt{N}$ for $|\vec{l}| = 1 \implies = \sqrt{N} \cdot L, \ |\vec{l}| = L$

$\Rightarrow$ Repeat many random walk; distribution of end points look like gaussian.

$\sigma_N = \sqrt{N} \cdot L$

Scale invariance

i) If $L \to \frac{L}{\alpha}$

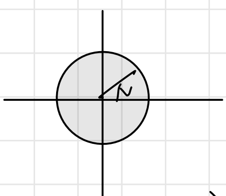
$I \longrightarrow I$

Zoom out by factor $\alpha$.

Then, $\sigma_N = \sqrt{N} \cdot L \longrightarrow \sqrt{N} \cdot \frac{L}{\alpha}$

ii) $L \to \frac{L}{\alpha}, \ N \to \alpha^2 \cdot N \Rightarrow \sigma_N = \sqrt{N} \cdot L \underset{\substack{\uparrow \\ \text{invar}}}{=} \sqrt{\alpha^2 N} \cdot \frac{L}{\alpha}$

# of steps to reach distance of $N$?

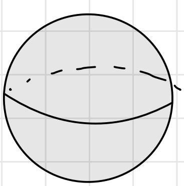


- We need $N^2$ steps to reach distance of $N$.
- Total # of points inside $N$-sized circle $\sim N^2$ $(N^2\pi)$

$\Rightarrow \dfrac{\text{steps to reach distance } N}{\text{steps inside area}} \sim \dfrac{N^2}{N^2} = 1$

$\to$ Drunk men come back to home.

⟨3D dim⟩



- Still need $N^2$ steps to reach distance $N$.
- total # of points inside $N$ sized sphere $\sim N^3$

$\dfrac{\text{steps to reach distance } N}{\text{steps inside area}} \sim \dfrac{N^2}{N^3} \sim \dfrac{1}{N} \to$ cannot go back home.

· Microscopically coin flip, poker game, drunkard's walk.

∴ Eventually same, $\sigma_N = \sqrt{N} \cdot L$ whose distribution follows Gaussian.

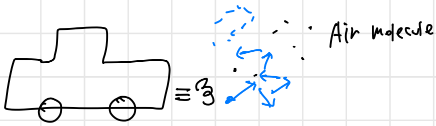
$N \to \infty$, Distance scale $\gg L$ $\longrightarrow$ Universality.

very important!

## ⟨ Diffusion ⟩

· Net spreading of particles due to random motion

· tells us how system of random walking particles approach equilibrium




Q. How far a particle "•" can travel in a given time $t$?

⇒ Classical mechanics fail.

- We can consider a collective motion of particles in a continuum limit. (or long distance limit)
- Introduce $\rho(x,t)$ as an evolving density of particles, or probability density.
- Consider $x(t)$ as particle's position at time $t$.

In time $\Delta t$, position changes by an increasement $\ell(t)$

$\ell(t)$ = random variable, and associated with the probability $\chi(\ell)$ for taking $\ell(t)$ step.

$$X(t+\Delta t) = x(t) + \ell(t)$$

$$\rho(x, t+\Delta t) = \int_{-\infty}^{\infty} d\ell \; \rho(x-\ell, t)\, \chi(\ell)$$

$$\rho(x,t) + \underbrace{\Delta t}_{\ll 1} \cdot \frac{\partial \rho}{\partial t} + \cdots \qquad \simeq \int_{-\infty}^{\infty} d\ell \cdot \Big(\rho(x,t) - \underbrace{\ell}_{\gg 1} \cdot \frac{\partial \rho}{\partial x} + \frac{1}{2}\ell^2 \frac{\partial^2 \rho}{\partial x^2} + \cdots \Big)\, \chi(\ell)$$

$\gg 1$ → fluctuation

eg) 1-D random walk
$\ell = \pm 1$
$\chi(\ell) = 1/2$

· Assumption: $\rho$ is slowly varying with respect to $\ell$, $\Delta t$

→ Macroscopic property $\rho$ is not that sensitive to the microscopic property

$$\Rightarrow \rho(x,t) + \Delta t \frac{\partial \rho}{\partial t} + \cdots = \rho(x,t) \underbrace{\int_{-\infty}^{\infty} d\ell \cdot \chi(\ell)}_{\to \text{Normalized},\ =1} - \frac{\partial \rho}{\partial x} \cancel{\int_{-\infty}^{\infty} d\ell \; \ell \cdot \chi(\ell)} + \frac{1}{2}\frac{\partial^2 \rho}{\partial x^2} \int d\ell \cdot \ell^2 \chi(\ell) + \cdots$$

mean of $\ell$, $= 0$.

$$\Rightarrow \Delta t \frac{\partial \rho}{\partial t} = \frac{a^2}{2}\frac{\partial^2 \rho}{\partial x^2} \Rightarrow \frac{\partial \rho}{\partial t} = \boxed{\frac{a^2}{2\Delta t}} \frac{\partial^2 \rho}{\partial x^2}$$

BMS, $a^2$.

$\equiv D$, diffusion constant. $= \dfrac{a^2}{2\Delta t}$.

$$\boxed{\frac{\partial \rho}{\partial t} = D \cdot \frac{\partial^2 \rho}{\partial x^2}}$$

... Diffusion equation.

Now, Let's solve!

(in k domain)

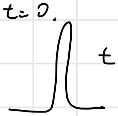
1) $\rho(x,t) = \tilde{\rho}_k(t) \cdot e^{ikx}$. $\rightarrow \dfrac{\partial \tilde{\rho}_k}{\partial t} = -D k^2 \tilde{\rho}_k(t)$ (By differs) $\therefore \tilde{\rho}_k(t) = \tilde{\rho}_k(0)\, e^{-Dk^2 t}$

$\rightarrow$ Plane wave solution.

$$\Rightarrow \rho(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, \tilde{\rho}_k(t)\, e^{ikx}$$

ex) Let particle is at $x$ at $t=0$.

$\rho(x, t=0) = \delta(x)$



$t=0 \xrightarrow{t}$

spread.

which we know in k domain,

$$\rho(x,t=0) = \delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{ikx} \quad (\Rightarrow \tilde{\rho}_k(0) = 1)$$

$\langle x \rangle = 0$.

$\sigma = \sqrt{2Dt}$.

$\propto \sqrt{t}$.

$$\rho(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\, e^{-Dk^2 t} e^{ikx} \quad (\because \tilde{\rho}_k(t) = 1 \cdot e^{-Dk^2 t})$$

$$= \frac{1}{\sqrt{4\pi D t}} \cdot e^{-\frac{x^2}{4Dt}}$$

... Green function method

$$\sigma = \sqrt{2 \cdot \frac{a^2}{2\Delta t} t} = a \cdot \sqrt{\frac{t}{\Delta t}} = \boxed{a\sqrt{N}}$$

... Random walk

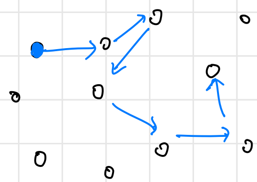
$N \equiv t/\Delta t$

Consistency.

cf) In Q.M. $e^{-\frac{i}{\hbar}Ht} \cdot e^{ikx}$.

$$\int dk\, e^{-Dt\left(k^2 - \frac{ix}{2Dt}\right)^2 + \frac{-x^2}{4Dt}}$$

$e^{-ax^2}$ $\quad$ $\sqrt{\frac{\pi}{a}}$ $\quad$ $\sqrt{\frac{\pi}{Dt}}$



- Average flying time
- Average Distance
- Average velocity ...

- Associate $\Delta t$ with collision time $\tau$

$a \left(= \sqrt{\langle l^2 \rangle}\right)$ with mean free path

$$D = \frac{a^2}{2\tau} = \frac{a}{2}\cdot\frac{a}{\tau} = \frac{a}{2}\bar{v}$$

(ex)

- $D = 10^{-9}\ m^2/s$ for typical molecule in water.

Let $\sigma = \sqrt{2Dt} \sim 1m \Rightarrow t \sim \dfrac{(1m)^2}{2D} \sim 10^9$ sec $\simeq 31$ yrs.

- Suppose particles in random walks are conserved.

If $\rho(x,t)$ is conserved, $\rho(x,t)$ should satisfy the continuity equation.

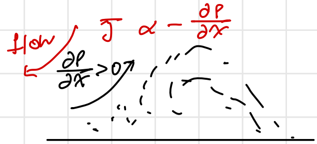
$$\Rightarrow \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}J = 0. \longrightarrow \frac{\partial \rho}{\partial t} + \nabla\cdot\vec{J} = 0.$$

$J$: current

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} = -\frac{\partial}{\partial x}\Big(\underbrace{-D\frac{\partial \rho}{\partial x}}_{\equiv J}\Big)$$ $\boxed{,\ J = -D\frac{\partial \rho}{\partial x}}$ … Fick's 1st law

$\xrightarrow{\text{one way}}$

$\xleftarrow{\text{Another approach}}$




· In presence of $F$, the particle responds by moving with the velocity $\underbrace{v = \gamma \cdot F}$ → causes the net drift by $\underline{v\Delta t}$

$\hookrightarrow$ Mobility $= \gamma \cdot F \cdot \Delta t$.

$\Rightarrow x(t+\Delta t) = x(t) + \gamma F \Delta t + l(t)$.

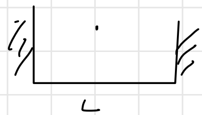
⇒ repeat similar step (2-1-2) with new term

we get $$\frac{\partial \rho}{\partial t} = -\gamma F\frac{\partial \rho}{\partial x} + D\frac{\partial^2 \rho}{\partial x^2} = -\frac{\partial}{\partial x}\Big(\underbrace{\gamma F \cdot \rho - D\frac{\partial \rho}{\partial x}}_{\equiv J}\Big)$$

• Example 1. Particle in the room.

a) No external force : $F = 0$, we are in equilibrium, $\left(\Rightarrow \frac{\partial \rho_*}{\partial t} = 0\right)$

$\Rightarrow \rho_* = \rho_0 + \cancel{B}^{\,0} \cdot x = \underbrace{\rho_0}_{\text{const}}$ evenly distributed throughout the room




$\rho(x) = \frac{1}{L}$

• Example 2. Gravity $F = mg$, In equilibrium

$$\Rightarrow 0 = \frac{\partial \rho_*}{\partial t} = \gamma mg\frac{\partial \rho_*}{\partial x} + D\frac{\partial^2 \rho_*}{\partial x^2}$$ $$\rho_*(x) = A\cdot e^{-\frac{\gamma}{D}mgx} + \cancel{B}^{\,0}$$

→ density of the air molecule.

$$\Rightarrow \rho_*(x) = A\cdot e^{-\frac{\gamma}{D}mgx} = A\cdot e^{-\frac{\gamma}{D}E} \propto e^{-E/k_BT} \quad \text{(from somewhere)}$$

$E = mgx$

$\Rightarrow \boxed{\frac{D}{\gamma} = k_BT}$

· Imagine a small diffusing particle in a diluted air (유도하자)

distance $\simeq \frac{1}{2}\left(\frac{F}{m}\right)(\Delta t)^2 = F\cdot\Delta t\left(\frac{\Delta t}{2m}\right)$ : net drift $= \gamma F \Delta t$.

$\frac{\Delta t}{2m} = \gamma$

$\Rightarrow \gamma = \dfrac{\Delta t}{2m}$. $\quad D = \dfrac{a^2}{2\Delta t} \quad \Rightarrow D \cdot \dfrac{2\Delta t}{a^2} = 1 \longrightarrow \gamma = D / m \left(\dfrac{a}{\Delta t}\right)^2 = \dfrac{D}{m\bar{v}^2}$

$\Rightarrow \dfrac{D}{2\gamma} = \dfrac{1}{2} m \bar{v}^2 = \dfrac{1}{2} k_B T.$ $\quad D/\gamma = \dfrac{a^2}{2\Delta t}\dfrac{2m}{\Delta t} = \underbrace{\left(\dfrac{a}{\Delta t}\right)^2}_{v} \cdot m = mv^2$

# Brownian motion

„Pollen

Random walk of a large particle due to stochastic collisions with smaller particles

collection of these small kicks causes visible macroscopic effect

$\Rightarrow$ Einstein used brownian motion to derive $N_A \sim 10^{24}$

· $m \cdot \dfrac{d^2\vec{x}}{dt^2} + \dfrac{1}{\gamma} \cdot \dfrac{d\vec{x}}{dt} = \vec{F}_{ext} + \vec{F}_B$ $\longrightarrow$ To measure $\gamma$ experimentally

$\gamma$ = drag coefficient, or mobility $\quad \vec{v} = \gamma \vec{F}$

· Once random $\gamma$ is known, remove $\vec{F}_{ext}$.

$\Rightarrow \langle \vec{x} \rangle = 0$. we compute $\sqrt{\langle \vec{x}^2 \rangle} = x_{RMS}$

$\dfrac{d(\vec{x})^2}{dt} = 2\vec{x} \cdot \dfrac{d\vec{x}}{dt} = 2\vec{x} \cdot \vec{v}$ ① $\quad$ where $m\dfrac{d\vec{v}}{dt} + \dfrac{1}{\gamma}\vec{v} = \vec{F}_B$. Again,

$\dfrac{d}{dt}(\vec{x} \cdot \vec{v}) = \dfrac{d\vec{x}}{dt} \cdot \vec{v} + \dfrac{d\vec{v}}{dt} \cdot \vec{x} = v^2 + \dfrac{1}{m}\left(-\dfrac{\vec{v}}{\gamma} + \vec{F}_B\right) \cdot \vec{x}$ $\quad$ then, take an average over molecular collisions

$\dfrac{d}{dt}\langle \vec{x} \cdot \vec{v} \rangle = \langle \vec{v}^2 \rangle - \dfrac{1}{m\gamma}\langle \vec{x} \cdot \vec{v} \rangle - \cancel{\dfrac{\langle \vec{x} \cdot \vec{v} \rangle}{m\gamma}} + \cancel{\dfrac{1}{m}\langle \vec{x} \cdot \vec{F}_B \rangle}$ $\quad$ 0 . ( Correlation X )

$\therefore \langle \vec{x} \cdot \vec{v} \rangle = m\gamma \langle \vec{v}^2 \rangle \left(1 - e^{-t/m\gamma}\right)$

If $t \gg m\gamma$. $\therefore \langle \vec{x} \cdot \vec{v} \rangle = m\gamma \langle \vec{v}^2 \rangle$. ① $\rightarrow \dfrac{d\langle \vec{x}^2 \rangle}{dt} = 2m\gamma \langle \vec{v}^2 \rangle$.

$\langle \vec{x}^2 \rangle = 2m\gamma \langle \vec{v}^2 \rangle t$.

$\Rightarrow x_{rms} = \sqrt{\langle \vec{v}^2 \rangle 2m\gamma t} = \sqrt{2Dt}$. $\quad D = \gamma \cdot \langle m\vec{v}^2 \rangle \quad D/\gamma = m \langle \vec{v}^2 \rangle$

$\dfrac{D}{2\gamma} = \dfrac{1}{2} m \langle \vec{v}^2 \rangle = \dfrac{3}{2} k_B T = \dfrac{3}{2}\dfrac{R}{N_A} T$.

$N_A \sim 10^{24}$

- Random walk → Diffusion → Equilibrium

at some point, the "macroscopic properties" of the system stop changing. ($\neq$ static)

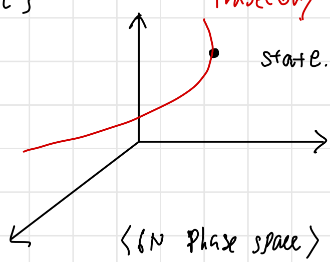
- From macroscopic point of views, the probability distribution of states does not change : or all possible states are "equally-likely"

"Phase space"

→ Imagine we have $N$ particles, with no internal degree of freedom

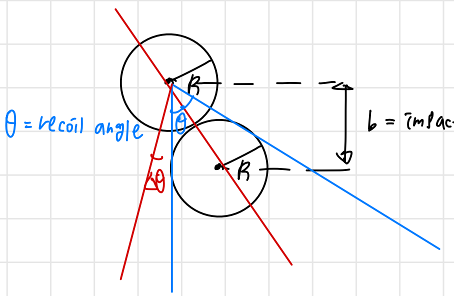
→ $\{\vec{q}_i(t), \vec{P}_i(t)\}$ $(i = 1, 2, \cdots, N)$ : $\{6N+1\}$ or $\{6N; t\}$

⇒ Getting exact trajectory is humanly impossible.

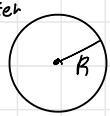



⟨6N Phase space⟩

## Chaos



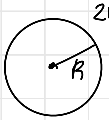

$$\frac{b}{2} = R\sin\left(\frac{\theta}{2}\right) \quad \cdots \text{ 1st collision}$$




$$\frac{b+\Delta b}{2} = R \cdot \sin\left(\frac{\theta+\Delta\theta}{2}\right)$$

$$\simeq R\sin\left(\frac{\theta}{2}\right) + R \cdot \frac{\Delta\theta}{2}\cos\frac{\theta}{2} + \cdots$$

2nd collision




$$\Rightarrow \Delta\theta \simeq \frac{\Delta b}{R\cos(\theta/2)} \sim \frac{\Delta b}{R} \quad \text{for } \cos\left(\frac{\theta}{2}\right) \sim O(1)$$

$$\therefore \Delta\theta \sim \frac{\Delta b}{R}$$

Now, let's generalise it;

$\Delta\theta_1 \simeq \frac{\Delta b_1}{R}$. $\qquad \Delta b_2 \simeq \ell\Delta\theta_1$ (Rough estimation)

$$\Rightarrow \Delta\theta_2 \simeq \frac{\Delta b_2}{R} \simeq \frac{\ell}{R}\Delta\theta_1$$

$\vdots$

N collisions

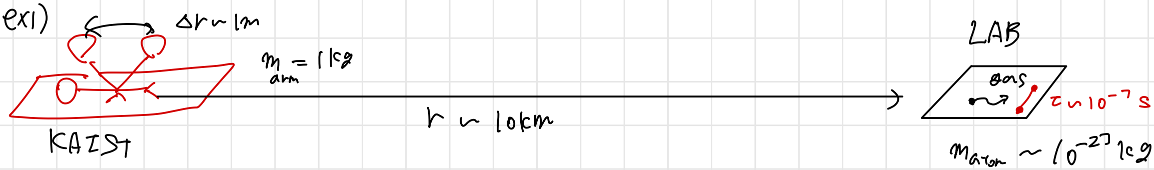
$$\boxed{\Delta\theta_N = \left(\frac{\ell}{R}\right)^{N+1}\Delta\theta_1 \qquad N \gg 1}$$

typically, $\ell \sim 10^{-7}\,m$, $R \sim 10^{-10}\,m$ ⇒ $\frac{\ell}{R} \sim 10^3$

$$\Rightarrow \boxed{\Delta\theta_N \sim 10^{3N}\Delta\theta_1}$$

Even if $\Delta\theta_1 \sim 10^{-3}$, after just 1 collision, $\Delta\theta_2$ is very huge.

ex1)




$$\Delta F = \frac{d}{dr} G\left(\frac{M_{atom} M_{arm}}{r^2}\right) \Delta r \cong 10^{-50} N$$

$$a = \frac{\Delta F}{m_{atom}} \cong \frac{10^{-50} N}{10^{-27} kg} \sim 10^{-23} m/s^2.$$

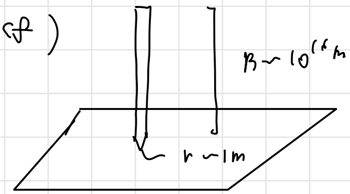
$\Delta b = a\tau^2 \simeq 10^{-41} m \ll B_{atom}$

$\Delta b_1 \sim 10^{-41} m.$

$\Delta\theta_1 \sim \frac{\Delta b_1}{B} \sim 10^{-31} m \quad (B_{atom} = 10^{-10} m)$

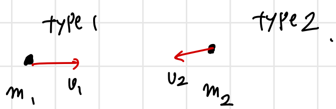
$\Delta\theta_N \sim 10^{3N} \Delta\theta_1 \quad N \sim 10.$

cf)




$\frac{r^2}{B^2} \sim 10^{-32}$

Maxwell's understanding of equilibrium




1) Randomly pick type 1 particle
2) 〃 2
3) Collide each other.

As long as $v_1, v_2$ random, $\langle \vec{v_1} \cdot \vec{v_2} \rangle = 0 \rightarrow \left\langle \frac{m_1 \vec{v_1}^2 - m_2 \vec{v_2}^2 - (m_2 - m_1)\vec{v_1}\cdot\vec{v_2}}{m_1 + m_2} \right\rangle = 0$

$\alpha \langle \cos\theta \rangle$

$(v_1, v_2) \longrightarrow (V_{cm}, V_{rel})$

$V_{cm} = \frac{m_1\vec{v_1} + m_2\vec{v_2}}{m_1 + m_2}$, $V_{rel} = \vec{v_1} - \vec{v_2}$

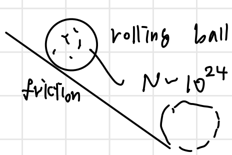
$(\because \langle \Delta\vec{v} \cdot \vec{v_{cm}} \rangle = 0)$

$$\boxed{\frac{1}{2}\langle m_1 \vec{v_1}^2 \rangle = \frac{1}{2}\langle m_2 \vec{v_2}^2 \rangle}$$

... Nontrivial result!!

For Quadratic mode $\longrightarrow \frac{3}{2} k_B T = \frac{E}{N}$ (Equipartition theorem)

• Illustrate example




1. $\underbrace{\left\langle \frac{P_{ball}^2}{2m_{ball}} \right\rangle}_{①} + N_{air} \underbrace{\left\langle \frac{P_{air}^2}{2m_{air}} \right\rangle}_{②} = E$

In equilibrium, ① = ②

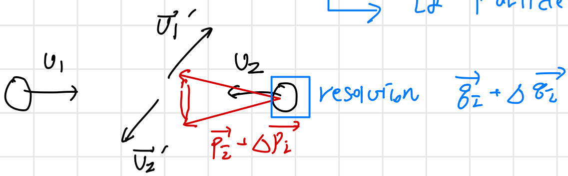
$\left\langle \frac{P_{ball}^2}{2m_{ball}} \right\rangle \sim E/N_{air} = 0.$

· Randomness of velocities of colliding particles is called "Molecular chaos" ( $\langle \vec{v_1} \cdot \vec{v_2} \rangle = 0$ )

· Suppose we have $N \sim 10^{24}$ particles $\Rightarrow$ $6N$ dim phase space

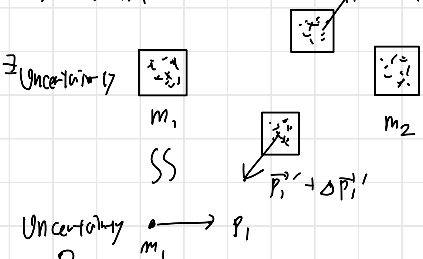
$$P(\vec{p_1}, \vec{q_1}, \cdots, \vec{p_N}, \vec{q_N}; t) = \prod_{i=1}^{N} P_1(\vec{q_i}, \vec{p_i}; t)$$

↳ If particles are independent.




$\Delta V \cong (\Delta P_i)^3 (\Delta q_i)^3$ for each

★ Represent a pointlike particle with a box.




$\simeq$ ←•

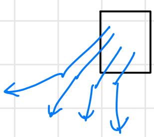
↓ approximation

= Coarse graining

Uncorrelated → Correlated.

$$\Delta\theta_N \sim \left(\frac{\ell}{R}\right)^N \cdot \Delta\theta_1 \sim 10^{3N} \Delta\theta_1$$

→ Erase the initial memory (After one-or-two collision)



(*) Boltzmann H-theorem

Introduce $P_a(t)$ ; prob of finding a state in "a"

and $T_{ab}$ ; transition rate for a turn into b.

$$\frac{dP_a(t)}{dt} = \sum_b P_b(t) T_{ba} - \sum_a P_a(t) T_{ab}$$

· Assume "the principle of detailed balance" : $T_{ab} = T_{ba}$

$$\Rightarrow \frac{dP_a(t)}{dt} = \sum_b T_{ab} \left( P_b(t) - P_a(t) \right)$$

① Suppose we have only 2 states ; $\frac{dP_a(t)}{dt} = T_{ab} [P_b(t) - P_a(t)]$

$\Rightarrow \lim_{t\to\infty} P_a(t) = \lim_{t\to\infty} P_b(t)$ (equilibrium)

② For $N$ states ; define the quantity $\mathcal{H}(t)$

: $H(t) = -\sum_a P_a(t) \ln P_a(t)$ where $\sum P_a(t) = 1$

$$\Rightarrow \frac{d\mathcal{H}(t)}{dt} = -\sum_a \frac{dP_a(t)}{dt} \ln P_a(t)$$

$$= \sum_a \sum_b T_{ab}\left(P_a(t) - P_b(t)\right) \ln P_a(t) \underset{\substack{a\to b \\ \text{half sum}}}{=} \frac{1}{2}\sum_a\sum_b T_{ab}\left[\underbrace{\ln P_a(t) - \ln P_b(t)}_{+,\,-}\right]\left(\underbrace{P_a(t) - P_b(t)}_{+,\,-}\right)$$

$\ln x$ is monotonic function in $x$.

$\geq 0$.

$$\boxed{\therefore \frac{dH}{dt} \geq 0}$$

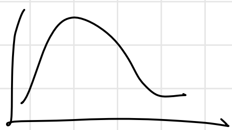
... Boltzmann's H-theorem

· Equilibrium is reached when $\frac{dH}{dt} = 0$ where prob for all states are same.

→ Not time-reversed invariant.

$dt \to -dt$ ?

Q. room temp Boltzmann distribution



→ 굴곡이?

The chaotic time evolution rapidly scramble whether knowledge we may have about the initial conditions of our system, leaving us effectively knowing only the conserved quantities eg) $E, \vec{P}, \vec{L}$ ...

(*) Micro canonical Ensemble

· Statistical ensemble of all possible states of our system that has an exactly specified total Energy $E$.

· Properties of it is obtained by averaging over the states with energy in a shell $(E, E+\delta E)$ and $\delta E \to 0$.

$$\langle O \rangle_E = \frac{\int_{E<H(P,Q)<E+\delta E} dP\,dQ\; O(P,Q)}{\int_{E<H<E+\delta E} dQ\,dP} \quad \text{and } \delta E \to 0.$$

↓

observable

$$= \frac{1}{\Omega(E)\,\delta E} \int_{E<H<E+\delta E} dP\,dQ\; O(P,Q)$$

· Focus on ideal gas (atoms with short-range interactions)

neglect ∀ interaction

· For ideal gas, all the energy in kinetic energy

· **Microcanonical Ensemble** : all points in the phase space are priori equally-likely

∴ the postulate of equal a priori probability.

## Configuration Space : Trivial assumption to nontrivial result.

· All the configurations are equally weighted.

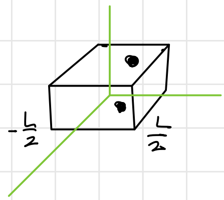
· For $N$ particles in a volume $V = L^3$

· Probability density : $\rho = \dfrac{1}{V^N}$

ex) 2 particles in a box. what is prob that 2 particles are found at $x>0$?

$\Rightarrow \rho = \dfrac{1}{(L^3)^2} = \dfrac{1}{L^6}$, the volume of phase space is

$$= \underbrace{L^2\left(\frac{L}{2}\right)}_{\text{Particle 1}} \times \underbrace{L^2\left(\frac{L}{2}\right)}_{2} = \frac{L^6}{4}$$

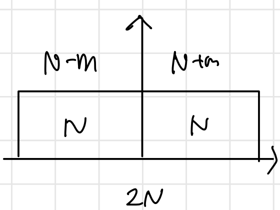



$\therefore P(x>0) = \rho \cdot \dfrac{L^6}{4} = \dfrac{1}{L^6} \cdot \dfrac{L^6}{4} = \dfrac{1}{4}$

| 1 | 2 |
|---|---|
| $x>0$ | $x>0$ |
| $x<0$ | $x<0$ |
| $x>0$ | $x<0$ |
| $x<0$ | $x>0$ |

$\frac{1}{4}$

· For given $2N$ non-interacting particles in a box. What is prob $P_m$ for finding $N+m$ particles in $x>0$?




· $\rho = \dfrac{1}{(L^3)^{2N}} = \dfrac{1}{L^{6N}}$

| $x<0$ | $x>0$ |
|---|---|
| $N-m$ | $N+m$ |

· Phase space $\underset{(N+m)}{(x>0)} = \left(\dfrac{L}{2}\cdot L^2\right)^{N+m} \times \left(\dfrac{L}{2}\times L^2\right)^{N-m} \times \dbinom{2N}{N+m}$

$$= \frac{(\chi^3)^{2N}}{(2)^{2N}} \binom{2N}{N+m}$$

$\therefore P_m = \rho \times$ (phase space for "$N+m$ particles at $x>0$")

$$= \frac{1}{2^{2N}} \cdot \binom{2N}{N+m} \longrightarrow \text{Non zero!}$$

$n! \sim \left(\frac{n}{e}\right)^n \sqrt{2\pi n} \longrightarrow$

$$= 2^{-2N} \cdot \frac{(2N)!}{(N+m)!\,(N-m)!} = \frac{2^{-2N} \cdot \left(\frac{2N}{e}\right)^{2N}}{\left(\frac{N+m}{e}\right)^{N+m}\left(\frac{N-m}{e}\right)^{N-m}} \cdot \sqrt{\frac{2\pi \times 2N}{(2\pi)^2 (N+m) \times (N-m)}}$$

$$= \sqrt{\frac{N}{\pi(N^2-m^2)}} \cdot \overbrace{\left(1-\frac{m^2}{N^2}\right)^{-N} \cdot \left(1+\frac{m}{N}\right)^{-m} \cdot \left(1-\frac{m}{N}\right)^{m}}^{①} \quad \text{when } \frac{|m|}{N} \ll 1$$

?

$$\approx \frac{1}{\sqrt{\pi N}} \cdot \left(e^{+\frac{m^2}{N^2}}\right)^N \left(e^{\frac{m}{N}}\right)^{-m} \left(e^{-\frac{m}{N}}\right)^m \simeq \boxed{\frac{1}{\sqrt{\pi N}} \cdot e^{-\frac{m^2}{N}}}$$

... Gaussian. ($\because$ C.L.T) in a large $N$ limit.

$$e^x = \lim_{n\to\infty}\left(1+\frac{x}{n}\right)^n \qquad \bar{m} \equiv \frac{m}{\sqrt{N}}$$

$$① = \left(1-\frac{\bar{m}^2}{N}\right)^{-N} \cdot \left(1+\frac{\bar{m}}{\sqrt{N}}\right)^{-\sqrt{N}\cdot\bar{m}} \cdot \left(1-\frac{\bar{m}}{\sqrt{N}}\right)^{\sqrt{N}\cdot\bar{m}}$$

- $\langle m \rangle = 0$
- $\sigma_m = \sqrt{\frac{N}{2}} \Rightarrow \frac{\sigma_m}{N} \propto \frac{1}{\sqrt{N}} \xrightarrow[N\sim 10^{24}]{} 10^{-12}$, negligible

⟨Momentum Space⟩ : total energy $E$

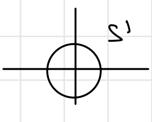
$$\Rightarrow E = \sum_{i=1}^{N} \frac{p_i^2}{2m} \xrightarrow[3D]{} \sum_{\alpha=1}^{3N} \frac{p_\alpha^2}{2m} \qquad (x^2+y^2+\cdots = R^2, \text{ constraint})$$

$$\longrightarrow p_1^2+\cdots+p_{3N}^2 = (\underbrace{\sqrt{2mE}}_{=B})^2 \longrightarrow \text{sphere in } 3N \text{ dim space}$$

$\longrightarrow$ $(3N-1)$ - sphere, $S^{3N-1}$

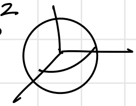
$$\int^R dp^d = \int^R dp \cdot p^{d-1} \underbrace{\int d\Omega_d}_{=\Omega_d} = \frac{R^d}{d} \cdot \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)} \rightarrow \text{volume}$$

$$= \Omega_d = \frac{(2\pi)^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2}\right)}$$



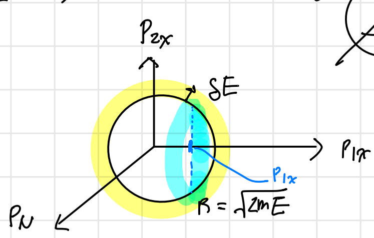

$$= \int_0^B dp \cdot p^{d-1} \frac{2\pi^{d/2}}{\Gamma(d/2)} = \frac{B^d \pi^{d/2}}{\Gamma\left(\frac{d}{2}+1\right)}$$

$S^2$



- Vol of $(\ell-1)$ sphere of radius $B$ ($\ell = 3N$)

$$= \mu\left(S^{\ell-1}_{B=\sqrt{2mE}}\right) = \frac{\pi^{\ell/2} B^\ell}{\left(\frac{\ell}{2}\right)!}$$



· Vol of phase space in $(E, E+\delta E)$ $= \dfrac{d\mu(S^{3N-1}_{\sqrt{2mE}})}{dE} \cdot \delta E$

$$= \frac{\pi^{\frac{3N}{2}} \cdot (3Nm)(2mE)^{\frac{3N}{2}-1}}{\left(\frac{3N}{2}\right)!} \cdot \delta E$$

$= \Omega(E)$

$$\rho = \frac{1}{\Omega(E)\,\delta E} = \frac{1}{\text{Vol}}$$

So, what is the prob density $\rho(P_{1x})$ that one particle has a momentum $P_{1x}$?

$$\rho(P_{1x}) = \frac{1}{\text{Vol of phase space of } E} \times (\text{Vol of phase space of } E \text{ with } P_{1x})$$

· Volume of the phase space of E with $P_{1x}$

$$= \left(\frac{d\mu\left(S^{3N-2}_{\sqrt{2mE - P_{1x}^2}}\right)}{dE}\right)\delta E \longrightarrow \rho(P_{1x}) = \frac{(3N-1)\, m\, \pi^{\frac{3N-1}{2}} \left(\frac{3N}{2}\right)!\, (2mE - P_{1x}^2)^{\frac{3N-1}{2}-1}}{3Nm\, \pi^{3N/2} \left(\frac{3N-1}{2}\right)!\, (2mE)^{\frac{3N}{2}-1}}$$

$$\rho(P_{1x}) = \frac{\text{Vol of P.S.(with E out } P_{1x})}{\text{Vol of P.S.}(E)}$$

$$\# \cdot e^{-\frac{P_{1x}^2}{2mE}\cdot\frac{3N}{2}} \longleftarrow \left( = \# \times \frac{\left(1 - \frac{P_{1x}^2}{2mE}\right)^{\frac{3N}{2}-1}}{\sqrt{2mE\left(1 - \frac{P_{1x}^2}{2mE}\right)}} \right.$$

$\rightarrow P_{1x} \ll 1$ 일 때만 dominant.

$$\boxed{\therefore \rho(P_{1x}) = \frac{1}{\sqrt{2\pi m\left(\frac{2E}{3N}\right)}}\, e^{-\underbrace{\frac{P_{1x}^2}{2m}}_{E_{km}} \cdot \underbrace{\frac{3N}{2E}}_{=\frac{1}{k_BT}}}}$$

$$P_{1x}^2 \longrightarrow P_{1x}^2 + P_{1y}^2 + P_{1z}^2 \quad : \rho(|\vec{P}|) = \frac{1}{\left[2\pi m\left(\frac{2E}{3N}\right)\right]^{\frac{3}{2}}} \cdot e^{-\frac{P^2}{2m}\cdot\frac{3N}{2E}}$$

$$\boxed{\int d^3\vec{P}\, \frac{\vec{P}^2}{2m}\, \rho(|\vec{P}|) = \left\langle \frac{\vec{P}^2}{2m} \right\rangle = \frac{E}{N}}$$

(*) Two subtle refinement

1) Dimension $[\Omega(E)] = ([\text{length}][\text{momentum}])^{3N}$ → Same dimension with Planck const h

· More importantly, there is always some measure for probability precision is limited by some intrinsic resolution $(\Delta q)^{3N}(\Delta P)^{3N}$

$(\Delta q)(\Delta P) \gtrsim h$

$$\Omega^{old}(E) \rightarrow \Omega^{new}(E) = \frac{\Omega^{old}(E)}{h^{3N}}$$

2) Distinguishable vs Indistinguishable

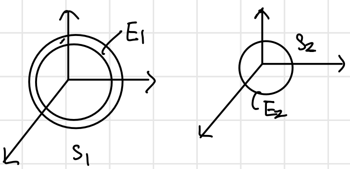
$\Rightarrow$ If particles are indistinguishable, $\Omega(E) \longrightarrow \dfrac{\Omega(E)}{N!}$

# Temperature

- Imagine we have two different types of particles, or gases, that can interact
- Question: How the energy of the system is distributed among two distinct gases in Equilibrium?

| Sub system 1 | Sub system 2 |
|---|---|
| $E_1$ | $E_2$ |
| $V_1, N_1$ | $V_2, N_2$ |

- We need to assure that two systems are **weakly connected (factorizable phase space)**




- A particular state of the whole system $(s_1, s_2)$

Each of those states has **equal weighting**

Then, what is the probability density for 1st subsystem has a particular state $s_1$?

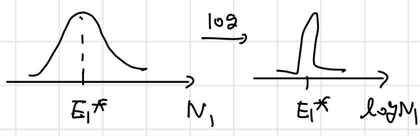
$\Rightarrow$ For $(s_1, s_2)$, $\rho(s_1) \propto \Omega_2(E_2 = E - E_1)$

Q. Prob density for subsystem 1 to have energy $E_1$?

$$P(E_1) \propto \Omega_1(E_1)\cdot\Omega_2(E-E_1) \longrightarrow P(E_1) = \frac{\Omega_1(E_1)\,\Omega_2(E-E_1)}{\Omega(E)}$$

where $\Omega(E) = \int dE_1\, \Omega_1(E_1)\, \Omega_2(E-E_1) = \frac{1}{\delta E}\cdot\int \prod_{i=1}^{N} d\vec{q}_i\, d\vec{p}_i \quad (E < \mathcal{H} < E + \delta E)$

We know $\Omega(E) \sim E^{\frac{3}{2}N}$, where $N \sim 10^{24}$. For large $N$




$\Rightarrow \Omega_1(E_1)\Omega_2(E-E_1) = E_1^{\frac{3}{2}N_1}\,(E-E_1)^{\frac{3}{2}N_2}$

$\Rightarrow \log\left(E_1^{\frac{3}{2}N_1}\,(E-E_1)^{\frac{3}{2}N_2}\right)$

$\sim \log\Omega_1(E_1^*)\,\log\Omega_2(E-E_1^*) + \frac{1}{2}\frac{d^2}{dE_1^2}\left[\log\Omega_1\Omega_2\right](E_1 - E_1^*)^2 + \cdots$ ($\because$ extremum)

$|\mathcal{I}_0^n = 0$

$\Rightarrow E_1^{\frac{3}{2}N_1}(E-E_1)^{\frac{3}{2}N_2} \sim \#\cdot\exp\left(-\frac{(E_1 - E_1^*)^2}{2\sigma^2}\right) \qquad \sigma = E_1^*\sqrt{\frac{2N_2}{3NN_1}} \sim \sqrt{N}$ ?

---

$\Rightarrow \frac{\sigma}{N} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$. In a large $N$ limit.

At the maximum, $\frac{d}{dE_1}\left[E_1^{\frac{3}{2}N_1}(E-E_1)^{\frac{3}{2}N_2}\right) = 0 \Rightarrow \frac{E_1^*}{N_1} = \frac{E_2^*}{N_2} = \frac{E}{N}$

$$\begin{cases} E_1^* = E\dfrac{N_1}{N_1+N_2} \\ E_2^* = E\dfrac{N_2}{N_1+N_2} \end{cases}$$

Generally, at the maximum,

$$\frac{\partial}{\partial E}P(E_1)\Big|_{max} = 0 = \frac{\Omega_1(E_1)\,\Omega_2(E-E_1)}{\Omega(E)}\left(\frac{1}{\Omega_1}\frac{\partial \Omega_1}{\partial E_1} - \frac{1}{\Omega_2}\frac{\partial \Omega_2}{\partial E_2}\right)$$

$$\Rightarrow \frac{\partial}{\partial E_1}\ln \Omega_1(E_1)\Big|_{E=E_1^*} = \frac{\partial}{\partial E_2}\ln \Omega_2(E_2)\Big|_{E=E_2^*} \longrightarrow \frac{1}{k_B T} = \frac{\partial}{\partial E}\ln \Omega(E)$$

$$\frac{1}{T} = \frac{\partial}{\partial E}\left[k_B \ln \Omega(E)\right] = \frac{\partial S}{\partial E} \quad \text{where } S_{eq} \equiv k_B \ln \Omega(E) \quad \ldots \text{Entropy}$$

- $S = S(E, V, N)$ can play a role of thermodynamic potential

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

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \Rightarrow P = T\cdot\frac{P}{T} = \left(\frac{\partial E}{\partial S}\right)_{V,N}\cdot\left(\frac{\partial S}{\partial V}\right)_{E,N} = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \quad (\mu = \text{chemical potential})$$

$$\left(\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1\right)$$

$$\text{So, } \mu = -T\cdot\left(-\frac{\mu}{T}\right) = -\left(\frac{\partial E}{\partial S}\right)_{V,N}\cdot\left(\frac{\partial S}{\partial N}\right)_{E,V} = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

→ What is the meaning of the fixing $S$ ? (등엔트로피 → 단열? )

(*) Ideal gas

$$\Omega(E) = \frac{V^N\left(\frac{3N}{2E}\right)\pi^{\frac{3}{2}N}(2mE)^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}$$

for large $N$, $\log N! = N\log N - N$.

$$\Rightarrow S_{eq}(E) = k_B \ln \Omega(E) = N k_B\left[\log V + \frac{3}{2}\log\frac{4\pi m E}{3N} + \frac{3}{2}\right] + \cdots$$

$$\to S(E) = N k_B\left(\log\frac{V}{N} + \frac{3}{2}\log\frac{4\pi m E}{3N h^2} + \frac{5}{2}\right) \quad \text{as } \Omega \to \frac{\Omega}{h^{3N} N!}$$

---

i) $$\frac{1}{T} = \frac{\partial S}{\partial E}\Big)_{V,N} = \frac{3}{2}N k_B\cdot\frac{1}{E} \qquad \therefore E = \frac{3}{2}N k_B T$$

ii) $$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right) = N k_B\cdot\frac{1}{V} \Rightarrow PV = N k_B T. \quad \ldots \text{Ideal gas law}$$

Definition of MicroCanonical Ensemble : All states are equally likely with $E$ = fixed.

$\exists\ \Omega(E) \longrightarrow \rho = \dfrac{1}{\Omega(E)}$

Energy becomes $\quad E = \sum_{\alpha=1}^{3N} \dfrac{p_\alpha^2}{2m} \quad$ (Non-relativistic)

$$\varepsilon = \sqrt{m^2c^4 + p^2c^2} \xrightarrow[c=1]{} \varepsilon = \sqrt{m^2+p^2} \simeq \begin{cases} m^2 + \dfrac{p^2}{2m} & \dfrac{p}{m} \ll 1 \\ p & p/m \gg 1 \end{cases}$$

relativistic ideal gas : $\quad E = (p_1 + \dots + p_N)\,c \qquad \dfrac{E}{N} = \dfrac{3}{2}k_BT$

$$\Omega^{rel}(E) \propto \int \prod_{i=1}^{N} \underbrace{d^3\vec{p}_i}_{=4\pi dp_i \cdot p_i^2}\, \delta(cp_1 + \dots + cp_N - E) = E^{3N}\int \prod 4\pi d\bar{p}_i\, \bar{p}_i^{\,2}\, \delta\big(E(c\bar{p}_1 + \dots + c\bar{p}_N - 1)\big)$$

$p_i = E\bar{p}_i$

$\frac{1}{E}\delta(x) = \delta(Ex)$

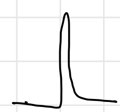
$$\simeq E^{3N-1}\ (\text{something out of } E) \propto E^{3N-1} \sim E^{3N} \quad (N \sim 10^{24})$$

$$S = k_B \ln \Omega^{rel}(E) \rightarrow \frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{d}{dE}\ln E^{3N} = 3N\cdot\frac{k_B}{E} \qquad \boxed{\therefore\ \frac{E}{N} = 3k_BT}$$

---

$$\rho(E) = \frac{\Omega_1(E_1)\,\Omega_2(E-E_1)}{\Omega(E)} = \frac{1}{\Omega(E)}\cdot\Big[\Omega_1(E_1) \times \Omega_2(E-E_1)\Big]$$

$$\propto E_1^{\frac{3N_1}{2}}\cdot(E-E_1)^{\frac{3N_2}{2}}$$



$$\boxed{\therefore\ \left.\frac{\partial \ln \Omega}{\partial E}\right|_{E_1} = \left.\frac{\partial \ln \Omega}{\partial E}\right|_{E_2}}$$

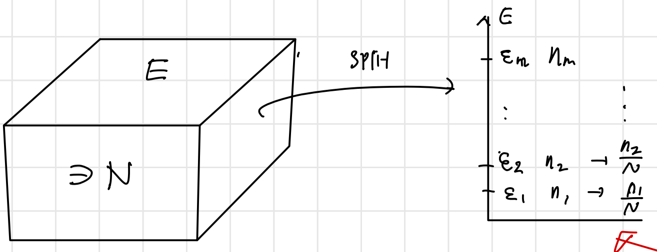
---

· Maximum Entropy as principle : To derive more useful properties.

$\Rightarrow$ The system is exponentially likely to be the state of Maximum entropy

$\therefore$ Principle of Maximum entropy.

Now, let's use this principle to derive Boltzmann factor.




· Particles $\exists$ m energy levels

$E = \sum_{i=1}^{m} \varepsilon_i n_i, \quad N = \sum_{i=1}^{m} n_i$

If we randomly pick a particle,

what is $P(\varepsilon_i) = ?$

• Now, restricting to only number of particles for now. $\Rightarrow \rho = \frac{1}{N}$

• Then imagine the splitting of $N$ into $m$ groups (Energy levels)

$\Rightarrow$ Total number of ways $\Omega = {}_N\Omega_{n_1} \times {}_{N-n_1}\Omega_{n_2} \times \cdots = \frac{N!}{n_1! n_2! \cdots n_m!}$

$\rightarrow \ln \Omega = N \ln N - N - \sum_{i=1}^{m} (n_i \ln n_i - n_i) = N \ln N - \sum n_i \ln n_i$

$\hookrightarrow \sum n_i$

$= -N \sum_{i=1}^{m} \frac{n_i}{N} \ln\left(\frac{n_i}{N}\right)$

Now, let $f_i = \frac{n_i}{N}$, $\sum_{i=1}^{m} f_i = 1$ (Probability)

$\Rightarrow \frac{\ln \Omega}{N} = -\sum_{i=1}^{m} f_i \ln f_i - \alpha \left( \sum f_i - 1 \right)$ (Lagrange multiplier)

Maximize this $\Rightarrow \frac{\partial}{\partial f_i}\left(\frac{\ln \Omega}{N}\right) = -(1 + \ln f_i) - \alpha = 0$ ($\because$ principle of maximum entropy)

$\therefore f_i = e^{-\alpha - 1}$

$1 = \sum f_i = \sum_{i=1}^{m} e^{-\alpha-1} = m e^{-\alpha - 1}$. $\Rightarrow f_i = \frac{1}{m} = \frac{1}{N} \times \frac{N}{m}$ ... ①

Now, Another situation constraint ($E$ isolated)

$\frac{\ln \Omega}{N} = -\sum f_i \ln f_i - \alpha \left(\sum f_i - 1\right) - \beta \left( \sum f_i \varepsilon_i - \bar{\varepsilon} \right) = 0$

$\left( \bar{\varepsilon} \equiv \frac{E}{N} = \sum \varepsilon_i \cdot \left(\frac{n_i}{N}\right) \right)$ $f_i$

$\Rightarrow \frac{\partial}{\partial f_i}\left(\frac{\ln \Omega}{N}\right) \Rightarrow f_i = e^{-1-\alpha} \cdot e^{-\beta \varepsilon_i}$

$\Rightarrow 1 = \sum f_i = e^{-1-\alpha} \underbrace{\sum_{i=1}^{m} e^{-\beta \varepsilon_i}}_{\equiv Z}$ $\Rightarrow f_i = \frac{e^{-\beta \varepsilon_i}}{Z} = P(\varepsilon_i)$

$\equiv Z$, partition function

• Entropy : the most influential concept to arise from statistical mechanics (Not included in Midterm)

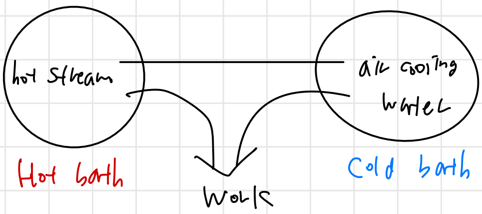
• It has various interpretations

ex) A measure of
- ① disorder
- ② Ignorance of systems
- ③ Irreversibility.

# 1) Entropy as a measure of irreversibility

· An original interpretation developed in 19th century where "heat" was the main form of energy.

ex) Steam Engine : transfer the fraction of the heat energy from hot stream into work, but some of the heat energy always end up wasted.




· A natural question would be like this.

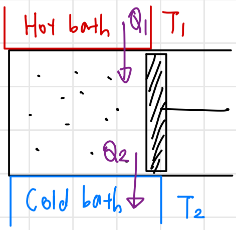
For given heat $Q_1$, drawn from heat steam, how much work $W$ can be done in principle?

⇒ What Sadi Carnot in 1820's was interested

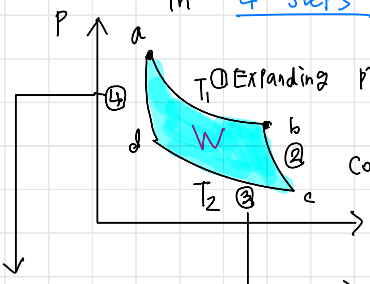
· Carnot's important observation was "There is a maximul efficiency depending only on temperature of steam (hot bath) and air (cold bath)" and he realised (in 1824) that the most efficient conversion should involve only in reversible process

↳ 게나 irreversible 과정 포함하면 max efficiency 도출 X.

(*) Carnot Engine.




· It was designed to move piston in and out in 4 steps




① Expanding piston, $T_1$ kept constant (Isothermal expansion)

→ Heat $Q_1$ flows in

② Cooling down, by adiabatic expansion

③ Compressing piston, $T_2$ kept constant (Isothermal compression)

→ Heat $Q_2$ flows out

④ Heated up, by adiabatic compression

⇒ Due to energy conservation, $W = Q_1 - Q_2$, Work $= \int_{\text{Carnot's cycle}} P\,dV$ $\left(\because = \int F\,dx\right)$

$\vec{F} \to \vec{A}$, $\vec{A}\,d\ell$.

· For ideal gas,
$$\begin{cases} pV = Nk_BT. \\ E = \frac{3}{2}Nk_BT = \frac{3}{2}pV \end{cases}$$

① $(a \to b)$ $\quad Q_1 = E_b - E_a + W_{ab} = \int_a^b p\,dV = \int_a^b \frac{Nk_BT}{V}\,dV = Nk_BT_1 \ln\left(\frac{V_b}{V_a}\right) > 0$

② $(b \to c)$ $\quad$ Work is done by internal energy : $W_{bc} = \frac{3}{2}Nk_B(T_1 - T_2) > 0$

③ $(c \to d)$ $\quad Q_2 = Nk_BT_2 \ln\left(\frac{V_c}{V_d}\right)$

④ $(d \to a)$ $\quad W_{ad} = \frac{3}{2}Nk_B(T_1 - T_2)$

positive work convention

$Q = \Delta E + W$.

흡입된 열 계에서 해준 일 계기준.

$\Rightarrow W_{net} = W_{ab} + \cancel{W_{bc}} - W_{dc} - \cancel{W_{ad}}$ 이제 V끼리 관계 찾자.

$\frac{Q_1}{T_1} = Nk_B \ln\left(\frac{V_b}{V_a}\right) \qquad \frac{Q_2}{T_2} = Nk_B \ln\left(\frac{V_c}{V_d}\right)$

Then, $\varepsilon = \frac{Q_1 - Q_2}{Q_1} \overset{?}{=} f(T_1, T_2)$

→ 무슨 조건이 필요한가?

$1 > 1 - \frac{T_2}{T_1} = \varepsilon = \frac{W}{Q_1}$ $\quad$ 100 $\quad$ 300

· 단열 이상기체 : $\underbrace{dW}_{p\,dV = Nk_BT\frac{dV}{V}} + \underbrace{dE}_{\frac{3}{2}Nk_B\,dT} = dQ = 0.$ $\qquad \frac{dV}{V} = -\frac{3}{2}\frac{dT}{T}$

$$\begin{cases} \left(\frac{V_c}{V_b}\right) = \left(\frac{T_1}{T_2}\right)^{\frac{3}{2}} \\ \left(\frac{V_d}{V_a}\right) = \left(\frac{T_1}{T_2}\right)^{\frac{3}{2}} \end{cases}$$

$$\boxed{\therefore \frac{Q_1}{T_1} = \frac{Q_2}{T_2}, \quad \varepsilon = \frac{T_1/T_2 - 1}{T_1/T_2} = \frac{T_1 - T_2}{T_1} < 1.}$$

$\frac{V_a}{V_b} = \frac{V_d}{V_c}$

---

· Later, Scientists decided to define the entropy change $(\Delta S)$ to the ratio of heat flows to temp.

$$\Delta S = \frac{Q}{T}.$$

First definition of entropy in troduced by Rudolf Clausius in 1865.

Clausius claimed that there are 2 sources of entropy increases.

→ Function of the state in that it is computed by collecting two states

① Irreversibility $\qquad$ ② Heat flow $\quad$ whose path is reversible $\to \Delta S = \int_{rev} \frac{dQ}{T}$

Solely determines the entropy difference for reversible process

$\Rightarrow$ In Carnot engine : $\Delta S_{tot} = \Delta S_{\substack{hot \\ bath}} + \Delta S_{\substack{cold \\ bath}} + \Delta S_{gas} = \frac{0}{T}.$

$$-\frac{Q_1}{T_1} \qquad \frac{Q_2}{T_2} \qquad 0$$

$= 0$

↳ Why? reversible!!!

For state A, B,

$A \to B$ : $S_B - S_A \geq 0$ by 2nd law of thermodynamics.

$B \to A$ : $S_A - S_B \geq 0$

2개 동시 만족 ⟺ reversible

$\Rightarrow S_B = S_A \qquad \therefore \Delta S_{Total} = 0$ for reversible.

$$\varepsilon = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$ : maximum eff.. why it is maximum?

· Better eff involves more heat flow from the hot bath

$$\Rightarrow \varepsilon_{new} = \frac{(Q_1 + \Delta) - Q_2}{Q_1 + \Delta} = \varepsilon + \frac{\Delta}{Q_1 + \Delta}\overset{\text{재배기}}{(1-\varepsilon)} > \varepsilon$$

$Q_2 = (1-\varepsilon)Q_1$

Then,

$$\Delta S^{new}_{total} = -\frac{Q_1 + \Delta}{T_1} + \frac{Q_2}{T_2} + \cancelto{0}{\Delta S_{gas}} = -\frac{\Delta}{T_1} < 0.$$

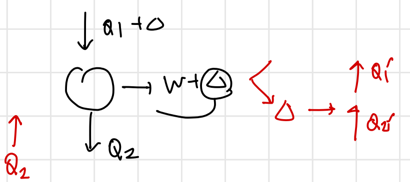
(Violates the 2nd law of thermodynamic)

$$W^{new} = (Q_1 + \Delta) - Q_2 = W + \Delta \quad (\text{more work})$$

⇒ we can use extra work for pulling $Q_2$ out of cold bath and putting $Q_1$ back to the hot bath

↳ 이걸 에어컨의 동력($Q_2$ 역방향 끌어내서 $Q_1$으로 빼기기)으로 사용하나(?)

⟶ The net effect is $(Q_1 + \Delta) - Q_1 = \underline{\Delta}$




Only this heat extracted from the hot bath and directly goes to work without being wasted

→ perpetual motion machine

" 불가능.... !! (적어도 여기선)

---

2) Entropy as a measure of disorder.

· In micro canonical ensemble approach, $S = k_B \ln \Omega$. (Function of $E, V, N$)

$E, V, N$ = constant   Boltzmann entropy

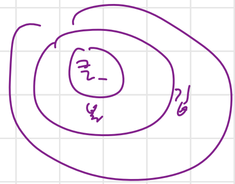
$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right)_{V,N} \qquad dQ = dE + \underbrace{dW}_{= PdV} \qquad \frac{1}{T} = \frac{\partial S}{\partial Q} \Rightarrow \Delta S = \int \frac{dQ}{T}$$

$\Rightarrow dQ = dE$

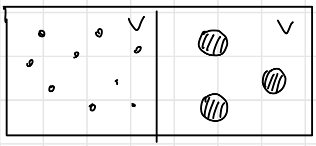
$$S = k_B \ln \Omega = -k_B \ln \frac{1}{\Omega} = -k_B \underbrace{\sum_i}_{\text{Sum of all the states} = \Omega} \cdot \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k_B \cdot \sum_i P_i \ln P_i$$

$$\boxed{\therefore\ S = -k_B \sum_i P_i \ln P_i}$$

... Gibbs entropy in 1878.



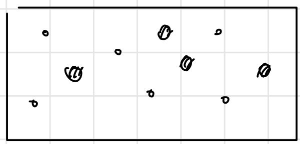
(*) Entropy of Mixing



$N/2$ $\quad$ $N/2$

$\xrightarrow{\text{Remove partition}}$

$\frac{N}{2} + \frac{N}{2}$ $\quad$ $2V$



"Free expansion" $\quad \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} k_B T = \text{const.}$

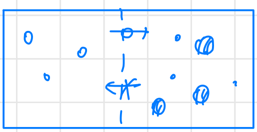
$$S_{\text{un-mixed}} = 2 \times \frac{N}{2} k_B \left( \ln V + \frac{3}{2} \ln \frac{4\pi m E}{3 \cdot \frac{N}{2}} + \frac{3}{2} \right) \qquad 0 = \Delta Q = \Delta \cancel{E} - \cancel{W} \quad (PV \propto T)$$

$$S_{\text{mixed}} = 2 \times \frac{N}{2} k_B \left( \ln 2V + \frac{3}{2} \ln \frac{4\pi m E}{3 \cdot \frac{N}{2}} + \frac{3}{2} \right)$$

$$\boxed{\Delta S = N k_B \ln 2}$$

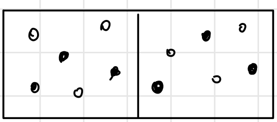
... Entropy of Mixing

cf)



Semi-permeable membrane → Pressure ↑ (스르륵) : Osmotic pressure (삼투압)

$\xrightarrow{\text{putting partition back}}$



$$S_{\text{after}} = 4 \times \frac{N}{4} k_B \left( \ln V + \frac{3}{2} \ln \frac{4\pi m E/2}{3\left(\frac{N}{4}\right)} + \frac{3}{2} \right)$$

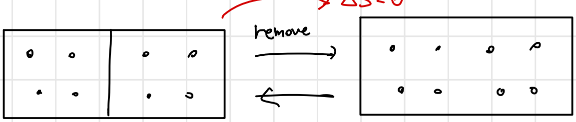
$\Delta S = -N k_B \ln 2$ decreased !

$\Delta S \overset{?}{=} 0$ ?

(직관) ⟷ (계산)

무엇이 맞나? Gibbs Paradox

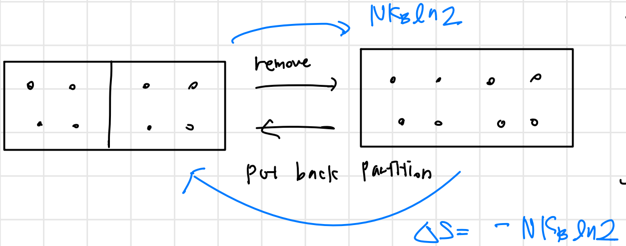
Let ○ = ●



remove ($\Delta S = 0$) →

← put back partition ($\Delta S = 0$)

직관적 예상.




실제 모순

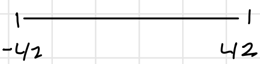
(해답) $\Omega \to \dfrac{\Omega}{N!}$ For identical particle, (Double counting 제거)

$$S(E) = Nk_B\left[\ln\frac{V}{N} + \frac{3}{2}\ln\frac{4\pi mE}{3N} + \frac{5}{2}\right] \longrightarrow \text{"}\Delta S = 0\text{"}$$

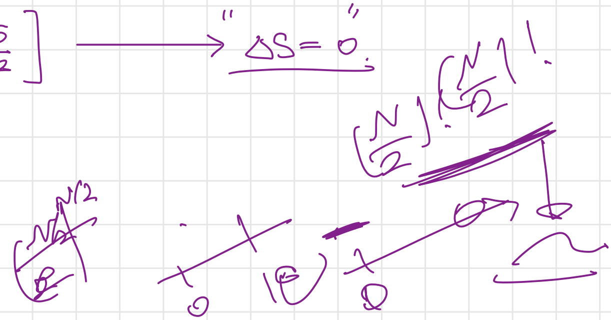
$+\cancel{\ln N}$

Acutally...

$P(m) \sim e^{-m}$




(4개 5개) (4개 3개)



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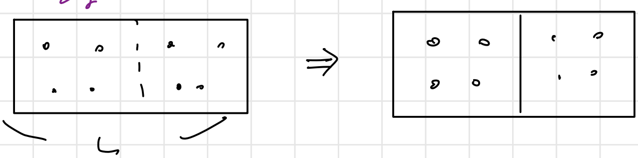
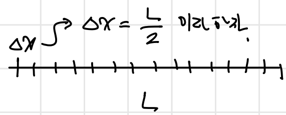
(*) Another intuitive understanding of $\Delta S = 0$ in 1D box

예)




• Uncertainty of measurement of position $= \Delta q = L/2$.

$\Rightarrow \Omega = \left(\dfrac{L}{\Delta q}\right)^N \underset{\Delta q = L/2}{=\!=} 2^N \Rightarrow S_{before} = k_B \ln 2^N = Nk_B \ln 2,$

$\Omega_{after} = 1 \qquad S_{after} = k_B \ln 1 = 0.$

$\Delta S = -Nk_B \ln 2 < 0.$ ???

$\xrightarrow[\text{사실}]{} \Omega_{after} = 1 \times \begin{pmatrix} N \\ N/2 \end{pmatrix} = \dfrac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \xrightarrow{\text{In large } N \text{ limit}} \sim 2^N.$

$S_{after} \simeq Nk_B \ln 2.$

## 3) Entropy as a measure of ignorance

The equil state of a system maximizes the entropy because we have lost all information about initial conditions except for conserved quantities

$\Rightarrow$ Maximizing entropy maximizes our ignorance about the details of the system

$$S(\Omega) = k_B \ln \Omega = -k_B \ln\Big(\underbrace{\tfrac{1}{\Omega}}_{\equiv P_i \text{ (In equilibrium)}}\Big) = -k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k_B \sum_i P_i \ln P_i$$

$$= -k_B \langle \ln P \rangle$$


$\xrightarrow[\text{For continuous case}]{}$ $S = -k_B \int \rho \ln \rho = -k_B \langle \ln \rho \rangle$

$$= -k_B \int_{E<H<E+\delta E} \rho(\vec{p}_i, \vec{q}_i) \ln \rho(\vec{p}_i, \vec{q}_i) \prod_{i=1}^{\Omega} dp_i \, dq_i$$

$\xrightarrow[k_B \text{는 불필요.}]{\text{살짝 수정}}$ information Entropy $S = -k_S \sum P_i \ln P_i = -\sum_i P_i \ln_2 P_i$

$k_S$: $\underline{\ \ } = \frac{1}{\ln 2}$

(shannon Entropy)

– measured in bits ($k_S \equiv \frac{1}{\ln 2}$)

– Shannon used this definition to put a "fundamental limit" on the amount that can be compressed

· $S_S$ is the unique function that satisfies 3 criteria

① Does not change if something with zero prob. is added.

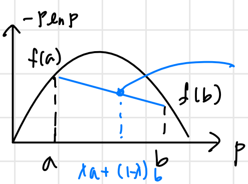
$P \ln P \to 0$ as $P \to 0$

② Entropy is maximum for equal probability

– Suppose we have $\Omega$ possible states with $\sum_{i=1}^{\Omega} P_i = 1$

$$S_{max}\left(\tfrac{1}{\Omega}, \cdots, \tfrac{1}{\Omega}\right) \geq S(P_1, \cdots, P_\Omega)$$

$f(P) = -P \ln P$ concave




$0 \leq \lambda \leq 1$

$\lambda f(a) + (1-\lambda) f(b)$

$f(\lambda a + (1-\lambda) b) \geq \lambda f(a) + (1-\lambda) f(b)$

generalize to $\Omega$ state

$$f\left(\frac{1}{\Omega}\sum_k p_k\right) \geq \frac{1}{\Omega}\sum_k f(p_k)$$

$$S(p_1, \cdots, p_\Omega) = -k_B \sum_{k=1}^{\Omega} p_k \ln p_k = k_B \sum f(p_k) \leq k_B \Omega\, f\Big(\frac{1}{\Omega}\underbrace{\sum p_k}_{=1}\Big)$$

$$= -k_B\, \Omega \cdot \frac{1}{\Omega} \ln \frac{1}{\Omega}$$

$$= S\left(\frac{1}{\Omega}, \cdots, \frac{1}{\Omega}\right)$$

③ Entropy change for conditional probabilities

ex) You're looking for keys and you're asking your roommate for her advice

$\Omega$ possible sites, called $A_k$ with prob $p_k$

$= \ln \Omega$ $\ell$?

To reduce your ignorance, you ask your roommate where she saw the keys last time

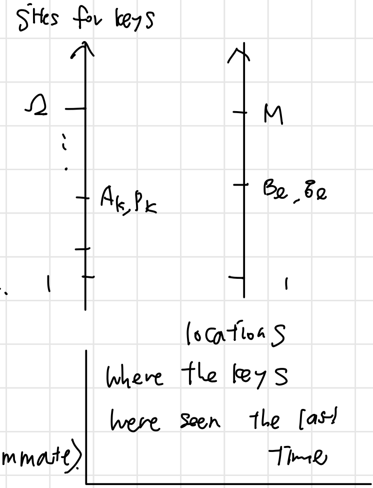
$\Rightarrow$ M possible locations, called $B_\ell$ with $\varrho_\ell$ 그녀의 확률

- $r_{k\ell} = P(A_k \text{ and } B_\ell)$ M possible locations
  - $\Omega$ possible site
- $C_{k\ell} = P(A_k | B_\ell) = \dfrac{P(A_k \text{ and } B_\ell)}{P(B_\ell)} = \dfrac{r_{k\ell}}{\varrho_\ell}$ , $\sum_k C_{k\ell} = 1$

Before your investigation :

$S(p_1, \cdots, p_\Omega)$ = your ignorance about the site
$= S(A)$ of keys

$S(\varrho_1, \cdots, \varrho_M)$ = ignorance about the location
$= S(B)$ the keys were seen the last time.




$S(AB) = S(r_{11}, r_{12}, \cdots, r_{1M}, r_{21}, \cdots, r_{\Omega M})$ ; joint ignorance
(전체 총 무지)

< After investigation, you have answer from your roommate >
$\Rightarrow B_\ell, \varrho_\ell$

$C_{k\ell} = P(A_k | B_\ell)$
↳ answer from your roommate

$S(A|B_\ell) = S(C_{1\ell}, \cdots, C_{\Omega\ell})$ fixed (새롭게 바뀐 총 무지)

· Introduce expected ignorance as a measurement of how useful your question is.

$$\Rightarrow \boxed{\langle S(A|B_\ell)\rangle = \underline{\sum_\ell S(A|B_\ell)\, g_\ell} \;\underset{\text{claim}}{=\!=}\; S(AB) - S(B)}$$

→ 질문이 얼마나 유용했나?

• More intuition on Shannon entropy

· To understand how compression works, quick review

original ASCII ⇒ 7 bits $2^7 = 128$ different patters (or 127)

$e = 101$, $\& = 38$, $f = 102$

Extended ASCII ⇒ $\overset{\text{1 byte}}{\overline{\text{8 bits}}}$ $2^8 = 256$ different patterns

$\ddot{a} = 228$, $\mathring{a} = 229$ $\acute{e} = 233$

Toy example

DNA sequence ⇒ DNA fragment

| | Guanine | Cytosine | Adenine | Thymine |
|---|---|---|---|---|
| | G | C | A | T |
| | | | ⇒ 4 patterns | |
| | 00 | 01 | 10 | 11 |
| | | | (2 digits) | |
| (Probability) | 25% | 25% | 25% | 25% |

(∵ 정보 X, 특정 염기 선호 이유 X)

1 0 0 1 1 1 0 0 ... ) encode ) decode

A C T G

(Average bits we used)

$$= \frac{1}{4}\times 2 + \frac{1}{4}\times 2 + \frac{1}{4}\times 2 + \frac{1}{4}\times 2 = \underline{2 \text{ bits}}$$

└ Maximum for $P_i = \frac{1}{2^2}$.

$-\ln_2 2^{-2} = \log_2 2^2$ $= -\sum_{i=1}^{4} \frac{1}{2^2} \ln_2 \frac{1}{2^2}$

$$= -K_S \sum_{i=1}^{K} P_i \ln P_i = -\sum_i P_i \ln_2 P_i$$

⟹ (Ex) Lumpy DNA sequence

add extra information

→ ignorance ↓

→ Entropy ↓ !!

└ Each pattern appears with a different probability

| | G | C | A | T |
|---|---|---|---|---|
| | 50% | 25% | 12.5% | 12.5% |
| | = 1/2 | 1/4 | 1/8 | 1/8 |
| → | 0 | 10 | 110 | 111 |
| | (1 bit) | (2 bits) | (3 bits) | |

P 균정 → $S_s$ 균정

$\frac{110}{A}\ \frac{10}{C}\ \frac{111}{T}\ \frac{0}{G}$ ...

(Average bit we used)

$$= \frac{1}{2}\times 1 + \frac{1}{4}\times 2 + \frac{1}{8}\times 3 + \frac{1}{8}\times 3$$

$$= -\sum P_i \ln_2 P_i = 1.75 \text{ bits}$$

(*) More realistic example.

In English text, each letter has different freq.

| e | t | a | ... | q | z | |
|---|---|---|---|---|---|---|
| 12.7 | 9.1 | 8.2 | | 0.1 | 0.1 | % |

$S = -\sum P_i \ln_2 P_i = 4.17.$

$2^4 = 16 < \underline{26} < 2^5 = 32$

↳ $x = \ln_2 26 = 4.7.$

< Proven by Shannon, claim >

$S_{\text{Shannon}} = -\sum P_i \ln_2 P_i =$ Minimal number of bits on average.

⇒ This is known as the "Source Coding theorem"

Using words, $S \simeq 2.62$

ASCII (Extended) > $\underline{4.7}$ > $\underline{4.17}$ > $\underline{2.62}$

7 bits 8 bits = 1 byte

for 26 letter with $P_i$ = const

using freq of letter

using words

Compression rate

Connection between information entropy and thermodynamic entropy

$\underbrace{-k_s}_{??} \sum_i P_i \ln_2 P_i \xrightarrow[\times k_B \ln 2]{} -k_B \sum P_i \ln P_i$

information entropy

Gibbs entropy

· Under free expansion, $V \to 2V$

$\Delta S = \underbrace{k_B \ln 2}_{\text{thermodynamic}} \times N$ ↳ Information

(*) Landauer's erasure principle

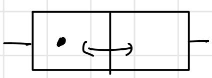
(IBM person)

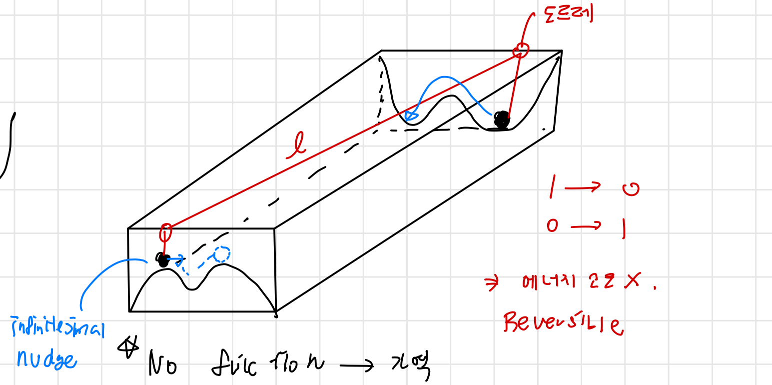
Made a breakthrough work in 1961 in connecting information to thermodynamic c

"Any logically irreversible manipulation of information such as the erasure of a bit or merging of two computation paths must be accompanied by an entropy increase in non-information bearing degree of freedom of information processing apparatus or its environment.

NOT operation $0 \leftrightarrow 1$

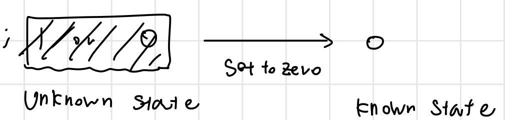
Ex) double well


※ No friction → 가정

Set To Zero operation




⇒ This operation cannot be done in any reversible process

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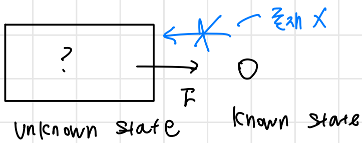
Connection between information entropy and thermodynamics

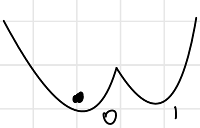
1) SetToZero




→ erasure by resetting

Claim: This can not be done in any reversible process

⇔ Invertible mapping.

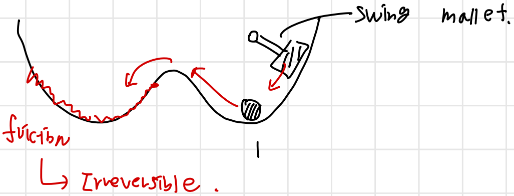



represented by $(\vec{q_i}^0, \vec{p_i}^0)$ represented by $(\vec{q_i}^1, \vec{p_i}^1)$

⇒ No invertible function F that

$$F(\vec{q_i}^0, \vec{p_i}^0) = (\vec{q_i}^0, \vec{p_i}^0)$$
$$F(\vec{q_i}^1, \vec{p_i}^1) = (\vec{q_i}^0, \vec{p_i}^0)$$

· Resolution is "dissipation."




Landauer investigated the physical limitation on building a device to implement a computation

⇒ His argument : logical system ⇒ Logical states.
– manipulated by logical operations
[ logical reversible
logical irreversible

Logical reversible ⇒ Does not involves compression of logical states

compression of implemented (realized)

Logical irreversible ⇒ involves compression of logical states.
→ Compression of physical states.

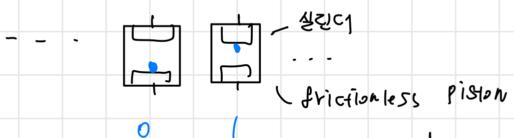
Physical system ⇒ physical states

## Landauer's claim

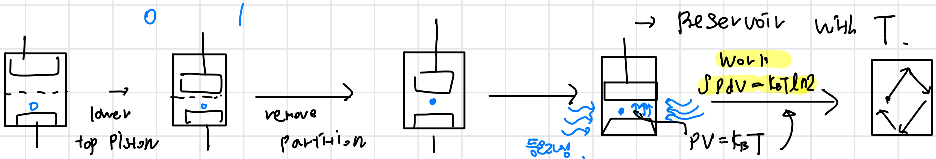
Compression of physical states causes dissipation
→ entropy increase

⟨ Minimum dissipation work by Charles "Bennet" in 1980's ⟩

· "Digital memory tape" with one atom to store each bit

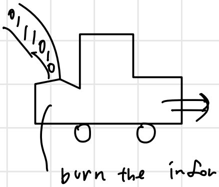



0 atom in the bottom
1 atom on top




No information
Unknown state
0 or 1

known state 의 (fuel)



burn the information

Nice observation is that work was done by burning information fuel.

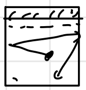
→ Szslard's Engine.

$\Delta S_{Gibbs} = k_B \ln 2$

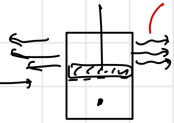
$\Delta S_{Shannon} = \ln_2 2 = 1$

역과정

add partition to the highest near the top



move partition to the center



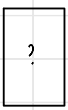
"dissipation" cannot avoid.

Take top piston to initial position

(work applied) → Added work $k_B \ln 2$ dissipated as heat

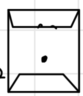
(sets minimum)

Introduced an intelligent being : Maxwell's demon in 1871



Unknown states

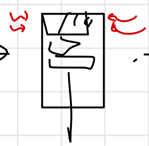
demon



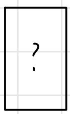
0 or 1

known states

wake up the bottom piston



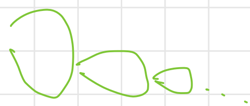
Remove partition



Unknown state

demon's brain :

→ 영구기관 같이 작동.



(Claim) knows where the atom is, using ~~negligible~~ amount of work

불가능, not negligible! $= k_B T \ln 2$

① This set to zero was done on Cylinder

② If not, then we need another sub structure to memorize.

⇒ Infinite memory structure layer, but finite memory space!

→ Size of a brain is "finite".

# Ensembles

We're interested only in the behavior of a system based on the possible microstates that share some macroscopic quantities $(E, V, N)$

· Ensemble (not unique choice)

- we have a choice in fixing macroscopic properties

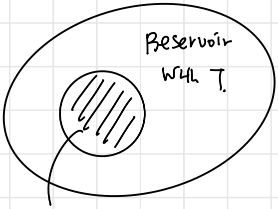
1) microcanonical ensemble $\equiv$ $E, V, N$ Fixed.

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

$\hookrightarrow$ number of microstates, with fixed $E, V, N$ $\quad \sum 1 = \Omega$

여기서 유도된 macroscopic 성질.

Secondary
$$\begin{cases} \dfrac{\mu}{T} = -\left.\dfrac{\partial S}{\partial N}\right|_{E,V} \\ \dfrac{1}{T} = \left.\dfrac{\partial S}{\partial E}\right|_{V,N} \\ \dfrac{P}{T} = \left.\dfrac{\partial S}{\partial V}\right|_{E,N} \end{cases}$$




System of interest $\rightarrow$ T 만 fixed. E 교환 가능 with reservoir $\rightarrow$ micro~~canonical~~ ...?

2) Canonical Ensemble (Varying E)

- Deals with number of microstates start with fixed T, V, N

$$Z(\beta) = \sum_k e^{-\beta E_k} \text{ (partition function)} \longrightarrow \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

3) Gibbs Ensemble (Varying V, E)

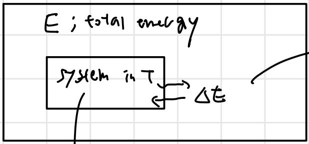
- Number of microstates with fixed N, T, P

4) Grand Canonical Ensemble (varying E, N)

- Number of microstates with fixed V, T, P
- start with $\quad Z(\beta, \mu) = \sum_k e^{-\beta E_k} \cdot e^{-\beta \mu N_k}$

(*) Canonical Ensemble : Fixed T, but varying E

└ conceptual trick for const T = heat reservoir
"with much more energy than the system"




heat reservoir of T

$V, N$ fixed.

$(k, E_k)$ states

Q. The prob that our system is in a state k with energy $E_k$

– phase space factorizable

– $p_k \propto \underline{\Omega_2(E - E_k)}$

↳ # of microstates of heat bath with $E - E_k$ $(E \gg E_k)$

$$\ln \Omega_2(E - E_k) \simeq \ln \Omega_2(E) - E_k \cdot \underbrace{\frac{\partial \ln \Omega(E)}{\partial E}}_{= 1/k_B T}$$

$(E \gg E_k)$

truncate here

$$\therefore \ \Omega_2(E - E_k) = \Omega_2(E) \cdot e^{-E_k/k_B T}, \quad \sum p_k = 1 \Rightarrow p_k = \underbrace{\frac{e^{-E_k/k_B T}}{\sum_k e^{-E_k/k_B T}}}$$

= partition function

$$Z = \sum_k e^{-E_k/k_B T} = \int \frac{dP\,dQ}{h^{3N}} e^{-\mathcal{H}(P,Q)/k_B T}$$

$$= \sum_{\substack{\text{energies} \\ i}} g_i \cdot e^{-E_i/k_B T} \xrightarrow[\text{limit}]{\text{Continuum}} \int dE \cdot \underbrace{g(E)}_{} e^{-E/k_B T}$$

↖ degeneracy

= number of states in $(E, E+dE)$

① Internal energy

$$\langle E \rangle = \sum_k E_k p_k = \frac{\sum_k E_k e^{-\beta E_k}}{Z} = -\frac{\partial \ln Z}{\partial \beta}$$

② Specific heat (Energy to increase one unit of temperature)

$$C_V = N c_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

$$= -\frac{1}{k_B T^2} \cdot \frac{\partial}{\partial \beta}\left(\frac{\sum E_k e^{-\beta E_k}}{Z}\right) = \frac{1}{k_B T^2}\left(\langle E^2 \rangle - \langle E \rangle^2\right) = \frac{\sigma_E^2}{k_B T^2}$$

→ Much easier!!!

$$\frac{\sigma_E}{N} = \frac{\sqrt{(k_B T)(C_V T)}}{\sqrt{N}} \sim \frac{1}{\sqrt{N}} \quad \rightarrow \quad E = \langle E \rangle + \sigma_E$$

$\sim N \qquad \sim \sqrt{N}$

⇑ ↑.

③ Entropy

$$S = -k_B \sum_k p_k \ln p_k = \frac{\langle E\rangle}{T} + k_B \ln Z \qquad \left(p_k = \frac{e^{-\beta E_k}}{Z}\right)$$

$$N! = N\ln N - N$$

$$\int_{-\infty}^{\infty} dp \cdot e^{-\beta \frac{p^2}{2m}} = \sqrt{\frac{2\pi m}{\beta}}$$

④ Application to ideal gas

$$E = \sum_{\alpha=1}^{3N} \frac{p_\alpha^2}{2m}$$

$$Z = \frac{1}{N!}\int \prod_{\alpha=1}^{3N} \frac{dp_\alpha dq_\alpha}{h}\, e^{-\beta\frac{p_\alpha^2}{2m}} = e^N\left(\frac{V}{Nh^3}\right)^N\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} \propto \beta^{-3N/2}$$

$$\Rightarrow \langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{3}{2}N\cdot\frac{1}{\beta} = \frac{3}{2}Nk_BT$$

$$\rightarrow \frac{\langle E\rangle}{T} + k_B\ln Z = Nk_B\left(\ln\frac{V}{Nh^3} + \frac{3}{2}\ln\frac{4\pi mE}{3N} + \frac{5}{2}\right) \longrightarrow S$$

$$= Nk_B\left(\frac{5}{2} - \ln(\rho\lambda^3)\right) \qquad \rho = \frac{N}{V} \equiv \frac{1}{d^3} \quad (d = \text{interparticle distance})$$

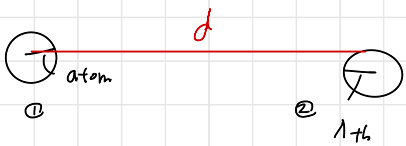
$$\lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}} = \frac{1}{\sqrt{2\pi}}\cdot\lambda_{\text{de Broglie}} \qquad \Rightarrow \rho\lambda_{th}^3 = \frac{N}{V}\cdot\lambda_{th}^3 = \left(\frac{\lambda_{th}}{d}\right)^3$$

└ Thermal de Broglie wavelength

$$\left(\because \lambda_{\text{de Broglie}} = \frac{h}{p} = \frac{h}{\sqrt{mk_BT}}\right)$$

$$\left(\because \frac{p^2}{2m} = \frac{1}{2}k_BT\right)$$

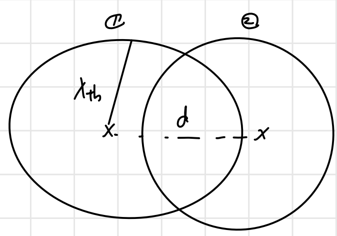
i)




①이 ②를 입자로 관측

$\frac{\lambda_{th}}{d} \ll 1 \Rightarrow$ Maxwell - Boltzmann distribution 따른다.

ii)




$\frac{\lambda_{th}}{d} \gtrsim 1$

①이 ②를 파동으로 관측

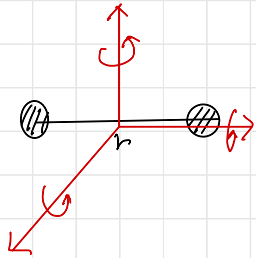
ex) $T$ = room temp. $N_2$ in the air

$$\lambda_{th} = \frac{h}{\sqrt{2\pi m_{N_2} k_B T_{room}}} \fallingdotseq 0.02\,\text{nm}$$

$$d = 3.3\,\text{nm}$$

[ Fermi - Dirac : Fermion
[ Bose - Einstein : Boson

Application to vibrational modes of diatomic molecules, $H_2$




3 transitional modes → 3 DOF

$$\frac{c_v}{k_B} = \frac{C_v}{N k_B} = 3 \times \frac{1}{2} = 1.5 \quad \text{vs} \quad 2.45 \text{ at } T \simeq 15° \text{ and } P = 1\,\text{atm}$$

① Rotation

$$E = \underbrace{\frac{1}{2} I \omega_1^2 + \frac{1}{2} I \omega_2^2}_{2\ \text{DOF}} + \cdots \quad \rightarrow \text{How??}$$

$$\Rightarrow \Delta\left(\frac{C_v}{k_B}\right) = 2 \times \frac{1}{2} = 1$$

② Vibration $\quad E = \frac{1}{2}\mu \dot{x}^2 + \frac{1}{2} k x^2 \rightarrow 2\ \text{DOF}$

$$\Delta\left(\frac{C_v}{k_B}\right) = 2 \times \frac{1}{2} = 1$$

$$\therefore \frac{C_v}{k_B} = (3 + 2 + 2) \times \frac{1}{2} = 3.5 > 2.45. \longrightarrow \text{still problem}$$

· In reality, each mode has a threshold to get excited.

$$e_j = j(j+1)\frac{\hbar}{2\mu c r_0^2} = \frac{j(j+1)}{2} \underbrace{\varepsilon_{rot}}_{7.4\,\text{meV}} \quad ??$$

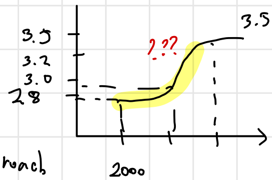
$$\varepsilon_n = \hbar\sqrt{\frac{k}{\mu}}\left(n + \frac{1}{2}\right) \underbrace{\varepsilon_{vib}}_{0.54\,\text{eV}} \qquad \left(n+\frac{1}{2}\right)\hbar\omega$$

$$\frac{\varepsilon_{vib}}{k_B} = 6300\,K \qquad \frac{\varepsilon_{rot}}{k_B} = 86\,K \qquad (\text{room temp} = 298\,K)$$

→ rotation + transitional $= \frac{1}{2} \times (2 + 3) = \frac{5}{2}. \simeq 2.45$ !!

· 실제로 6300K 보다 훨씬 낮은 온도에서 Vibration 활성화.

$$\frac{C_v}{k_B} = \frac{5}{2} + c^{vib}(T)$$




$\frac{\partial^2}{\partial \beta}$ $\quad \frac{1}{2}$

· Canonical ensemble approach

$$Z = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})} = e^{-\frac{1}{2}\beta\hbar\omega} \underbrace{\sum_n e^{-n\beta\hbar\omega}}_{\frac{1}{1-e^{-\beta\hbar\omega}}} = \frac{1}{2\sinh\left(\frac{\beta}{2}\hbar\omega\right)}$$

$$\text{Then, } \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \hbar\omega\left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right)$$

$$C^{vib}(T) = \frac{\partial \langle E \rangle}{\partial T} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\hbar\omega/k_B T}}{(1-e^{-\hbar\omega/k_B T})^2} \quad \text{where } T_{vib} \equiv \frac{\hbar\omega}{k_B} \simeq 6300\text{K}$$

$$= k_B \left(\frac{T_{vib}}{T}\right)^2 \frac{e^{-T_{vib}/T}}{(1-e^{-T_{vib}/T})^2} \longrightarrow \text{well explanation}$$

## (*) Gibbs Ensemble

- E and V are varied while fixing N.

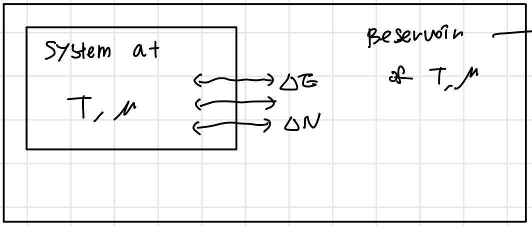
$$Z = \sum_n e^{-\beta E_k \underbrace{- \beta P V_k}_{\text{not practical}}}$$

## (*) Grand Canonical Ensemble

- E and N are varied while fixing V

$$Z = \sum_k e^{-\beta E_k + \beta \mu N_k}$$

eg. Chemical reaction $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$.




with "much more energy" and particle number than the system

$$P_k \propto \Omega_2 (\underbrace{E}_{\text{total energy}} - E_k, N - N_k)$$

$$\Rightarrow \ln \Omega_2 (E - E_k, N - N_k) \simeq \ln \Omega_2 (E, N) - E_k \underbrace{\frac{\partial \ln \Omega_2}{\partial E}}_{= \frac{1}{k_B T}} - N_k \underbrace{\frac{\partial \ln \Omega}{\partial N}}_{= -\frac{\mu}{k_B T}}$$

$$P_k = \frac{e^{-\beta E_k + \beta \mu N_k}}{\underbrace{\sum_k e^{-\beta E_k + \beta \mu N_k}}_{=: Z(T,\mu)}}$$

- Internal energy $\langle E \rangle = \sum_k P_k E_k = -\frac{\partial \ln Z}{\partial \beta} - \mu \langle N \rangle$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}$$

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{k_B T} \left( \langle N^2 \rangle - \langle N \rangle^2 \right)$$

Canonical Ensemble

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

· Entropy $S = -k_B \sum p_k \ln p_k = \frac{\langle E \rangle}{T} - \mu \frac{\langle N \rangle}{T} + k_B \ln Z$

For monatomic ideal gas

$$\mu = -T \frac{\partial S}{\partial N}\Big)_{T,V} = -T \frac{\partial}{\partial N}\left[ N k_B \left( \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{4\pi m E}{3 N h^2} \right) + \frac{5}{2} \right) \right]$$

└ how?

$$= -k_B T \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \left( \frac{4\pi m E}{3 N h^2} \right) \right]$$

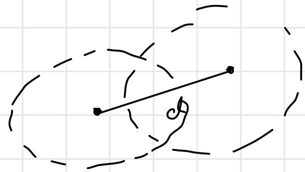
$E = \frac{3}{2} N k_B T \qquad \rho = \frac{N}{V} \qquad \lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$

$$= k_B T \ln (\rho \lambda_{th}^3)$$

$$\mu = k_B T \ln (\rho \lambda_{th}^3) = k_B T \ln \left( \frac{\lambda_{th}}{d} \right)^3$$

$\frac{\lambda_{th}}{d} \ll 1$  

$\to \mu < 0$




$\frac{\lambda_{th}}{d} \gg 1$

$\rho = \frac{1}{\lambda^3} e^{\mu / k_B T}$. $\to$ doubling $\rho$ amounts to

$\mu \to \mu + \ln 2$ (Naively $\rho \propto e^{\mu - \varepsilon}$)

↳ factor $\approx 1$

· In reality, offset exists. $E = E_{kin} + \underline{E_{offset}}$

$= N\varepsilon \quad \to \quad \mu = k_B T \ln (\rho \lambda_{th}^3) + \varepsilon$

$$\rho = \frac{1}{\lambda^3} e^{\frac{\mu - \varepsilon}{k_B T}}$$

Haber process : $3H_2 + N_2 \rightleftarrows 2NH_3$

- Introduce "Concentration" of molecule J.
  (= molar number density) denoted by $[j] = \rho_j$ in mole unit.

- In equilibrium, $[H_2], [N_2], [NH_3]$ are related

  = Law of mass action

$$\mu = -T \left.\frac{\partial S}{\partial N}\right)_{E,V}$$

---

We fix total energy and volume and vary concentrations

$$dS = \frac{\partial S}{\partial [H_2]} d[H_2] + \frac{\partial S}{\partial [N_2]} d[N_2] + \frac{\partial S}{\partial [NH_3]} d[NH_3] = 0$$

→ For every a mole of $N_2$, exactly 3 moles of $H_2$ are consumed

⇒ and 2 moles of $NH_3$ are produced.

$$\Rightarrow \left.\begin{aligned} d[H_2] &= 3\,d[N_2] \\ d[NH_3] &= -2\,d[N_2] \end{aligned}\right] \text{Constraints}$$

$$\longrightarrow \boxed{3\mu_{H_2} + \mu_{N_2} = 2\mu_{NH_3}}$$

- For monatomic ideal gas; $\rho_j = [j] = \frac{1}{\lambda^3} e^{-\frac{\varepsilon_j - \mu_j}{k_B T}}$

$$\Rightarrow \mu_j = k_B T \ln\left[ [j] \lambda^3 \right] + \varepsilon_j$$

$$\Rightarrow \frac{[H_2]^3 [N_2]}{[NH_3]^2} = \frac{\lambda_{NH_3}^6}{\lambda_{H_2}^9 \lambda_{N_2}^3} e^{-\frac{\Delta\varepsilon}{k_B T}}$$

$3\varepsilon_{H_2} + \varepsilon_{N_2} - 2\varepsilon_{NH_3} = 92.4$ kJ/mole

$\propto \frac{1}{T_3}$

- How to characterize the equilibrium properties of a system for a given $T$ and/or $P$

- Construct new properties, called Free energy

  function of $T, P$ and/or $\mu$

# Lec 8. Free energy

$dE = TdS - PdV + \mu dN$  $\quad (\overbrace{E, S, V, N}^{\text{extensive}}) \rightarrow$ mutually dependent.

→ General relation in many different ensemble.

$$\left\{\begin{array}{l} F = E - TS \rightarrow \text{T 일정 유용.} \\ H = E + PV \\ G = E + PV - TS \\ \Phi = E - TS - \mu N \end{array}\right.$$

Legendre transformation

함수 변경 x (대칭성 약)

(E,V,N)

$\boxed{S \text{ is extensivity}}$ (i.e. $S_1 + S_2 = S$)

$\Rightarrow S(cE, cV, cN) = c \cdot S.$

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

$\rightarrow SdT - VdP + Nd\mu = 0$

$F = F(V,N,T) \rightarrow dF = -PdV - SdT + \mu dN$

→ T, V, N 쉽게 측정 가능.

일정 → if V change ⇒ 열을 bath 에 준다

$V, T$ i=f.

Work max = ?

$$\Rightarrow \Delta F = \Delta E - T\Delta S \leq -W + Q - T\frac{Q}{T} = -W.$$

"free energy" = "일을 할 수 있는 에너지"

$\xrightarrow[W=0]{\hspace{2cm}} \Delta F \leq 0. \rightarrow$ 평형상태, (T, V) 일때는 F 가 최소. → 때 되음.

⇔ $S_{tot}$ 가 최대

1. F는 T가 일정할 때, E가 mech system 에서 가지는 역할.

2. F → T, V = C 인 때 일할 수 있는 에너지

3. $T, V = C$ ; $W = 0 \Rightarrow \Delta F \leq 0.$

4. Isolated sys ⇒ F → $F_{min}$

5. F → system 의 안정.

$$S_{canon} = \frac{\langle E \rangle}{T} + k_B \ln Z. \xrightarrow[\langle E \rangle = E]{} \underbrace{F = E - TS = -k_B T \ln Z}_{\text{동일한 정보.}}$$

$$\Rightarrow Z = e^{-\frac{F}{k_B T}} = \sum_i e^{-\frac{\varepsilon_i}{k_B T}}$$

↳ Canonical에서 분배함수!

$E(S,V,N)$

$$-L(q,\dot{q}) + p\dot{q} = \mathcal{H}(p,q)$$

$\longrightarrow$ Helmholtz free energy $F = E(S,V,N) - TS$

$= F(T,V,N)$

Enthalpy $H = E(S,V,N) + PV = H(S,P,N)$

V 제거

Gibbs free energy $G = E(S,V,N) - TS + PV = G(T,P,N)$

Grand free energy $\Phi = E(S,V,N) - TS - \mu N = \Phi(T,$

$\hookrightarrow$ N 변환

· $F = E - TS$. $\quad dF = \underline{dE} - dT \cdot S - T\cancel{dS} = -PdV + \mu dN - SdT$

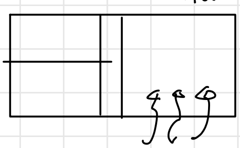
$= \cancel{TdS} - PdV + \mu dN$

$\therefore P = -\left.\dfrac{\partial F}{\partial V}\right)_{N,T}, \quad \mu = \left.\dfrac{\partial F}{\partial N}\right)_{V,T}$

Ex) Free energy turns out to be very powerful espicially at constant temperature

$\Rightarrow dF = dE - TdS$ $\qquad$ Isothermal system

Heat bath



Q.

$\Delta S_{bath} = -\dfrac{Q}{T}$

$\Delta S_{total} = \Delta S_{bath} + \Delta S_{system} \geq 0.$

$\Rightarrow \Delta S_{system} \geq \dfrac{Q}{T}$

$=$ for reversible process

· Energy conservation $\Delta E_{system} = Q - W$

heat from heat bath

Work done by system

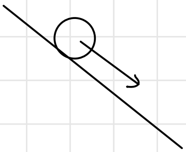
$$\boxed{\Delta F_{system} = \Delta E_{system} - T\Delta S_{system} \leq Q - W - T\left(\frac{Q}{T}\right) = -W}$$

$\Rightarrow F_f \leq F_i - W$

$\Rightarrow$ Free energy is depleted to do work, or it is energy available "free" to do work at finite temperature.

· If $W=0$, $F_f \le F_i$, $\Delta F_{system} \le 0$.

· in a system kept at constant temp, Interacting with surrounding only through an exchange of heat



(Rolling)

i) $N \sim 10^{24}$, Equipartition

ii) Free energy ( 킈(온도

$$S = \frac{\langle E \rangle}{T} + k_B \ln Z \quad \text{(canonical ensemble)}$$

$$\Rightarrow \underbrace{\langle E \rangle - TS}_{=F} = -k_B T \ln Z$$

$$\boxed{e^{-F/k_BT} = Z = \sum_k e^{-E_k/k_BT}}$$

$$\Delta F_{system} = \Delta E_{system} - T\Delta S_{system} = -T\left[\Delta S_{system} + \frac{\overbrace{-\Delta E_{system}}^{=Q}}{T}\right]$$

$(\Delta E_{system} = Q$ when $W=0)$

$$= -T\left(\Delta S_{system} + \Delta S_{surrounding}\right)$$

$$= -T\Delta S_{total}$$

(*) Enthalpy (useful when $P = $ const) 화학반응

· $E + PV = H(S, P, N)$

$$dH = \underbrace{dE}_{=TdS - P\cancel{dV} + \mu dN} + dPV + \cancel{PdV} = TdS + VdP + \mu dN$$

상압 (dP=0) 유용.

· At constant pressure,

$$\Delta H = \Delta E + P\Delta V \Rightarrow \Delta E = \Delta H - P\Delta V \quad \cdots ①$$

$$\Delta E = Q - P\Delta V \quad \cdots ②$$

$Q = \Delta H$

(*) Gibbs free energy

$$G = E + PV - TS = G(T, P, N) \rightarrow dG = -SdT + VdP + \mu dN$$

↳ T, P 상수 조건. F 대신한다.

# Lec 10. Q.S.M.

Classical

① $E, \vec{P}, \vec{q}$ 양자화 $\Delta p \cdot \Delta q \geq \frac{\hbar}{2}$, state는 이산적, $\sum_n \longrightarrow \int dn = \int \frac{dp\,dq}{\hbar}$.

② $k_B T \sim \varepsilon_0$ 인 때 포함 T.

$\downarrow$

Q.S.M. : Indistinguishable particles
- Fermion (half-integer) : Anti-sym
- Boson (integer) : sym.

$\Downarrow$

관찰자의 '특성'에 의해 결정. $V^N \rightarrow \frac{V^N}{N!}$ (M-B 분포 : 구별 불가능, 근사적 :)

$\xrightarrow[\text{더 강한 조건}]{}$ "Identical particle"

$\Rightarrow$ indistinguishable + $\begin{pmatrix} \text{sym} \\ \text{antisym} \end{pmatrix}$ condition
- F-D
- B-E

$\Downarrow$

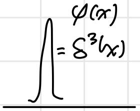
single state가

여러 입자에 의해 점유될

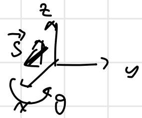
확률이 다르다

| MB | FD | BE |
|---|---|---|
| $\simeq 0$ | $= 0$ | $\Uparrow$ |

$$\psi(x_1, x_2, s_1, s_2) = \pm\,\psi(x_1, x_2, s_1, s_2)$$



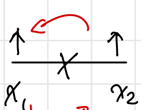
$\psi(x) = \delta^3(x)$



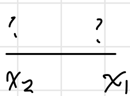
$\Rightarrow |\psi\rangle = e^{is\theta}|\psi\rangle$

- $s$ 정수 : $2\pi \cdot s = 2\pi$
- $s$ half 정수 : $2\pi \cdot s = \pi$.

분배함수 $\quad \frac{1}{N!}\sum_k e^{-\beta E_k} \quad \sum_k e^{-\beta E_k} \quad \sum_k e^{-\beta E_k}$



$\Rightarrow$



- $e^{2is} = 1$ (boson)
- $e^{2is} = -1$ (Fermion)

(ex) $E_1 \quad E_2 \quad E_3$ / A, B

상태수 $\quad \frac{1}{2}m^2 \quad \frac{1}{2}m(m+1) \quad \frac{1}{2}m^2 - \frac{1}{2}m$

$\xrightarrow[m\ \text{large}]{}$ $\begin{pmatrix} \text{Boson} \\ \text{Fermion} \end{pmatrix}$ 차이 $\downarrow$

Non-interacting gases $\left[\begin{array}{l}\sum n_i = N \\ \sum n_i \varepsilon_i = E\end{array}\right)$ canon microcanon '어려움 → Grand!

$$Z = \sum_{N,E} e^{-\beta(E - N\mu)} \xrightarrow[n_i,\ i]{} \underbrace{\prod_i \sum_{n_i=0}^{\infty} e^{-n_i\beta(\varepsilon_i-\mu)}}_{\text{단일입자 상태.}} = \prod_i Z_i$$

$\mu$ fix해서 가능. ( ex) $i=1$ : $Z_1$

$Z_3$, $Z_2$, $Z_1$

1) Boson

$$Z_i = \sum_{n_i=0}^{\infty} e^{-n_i \underbrace{\beta(\varepsilon_i-\mu)}_{\text{공비}}}$$

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

$$\langle n_i \rangle = \frac{\sum n_i e^{-n_i\beta(\varepsilon_i-\mu)}}{Z_i} = \frac{\partial \ln Z_i}{\partial(\beta\mu)}$$

$$\langle n_i \rangle = \frac{1}{\beta}\cdot\frac{\partial \ln Z}{\partial \mu} = \frac{1}{\beta Z}\cdot\frac{\partial Z}{\partial \mu} = \frac{1}{Z}\cdot = \frac{1}{e^{+\beta(\varepsilon_i-\mu)}-1}$$

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

BE Distribution

$\Rightarrow \varepsilon_i > \mu \ (\forall i)$ ; $\varepsilon_0 = 0 \rightarrow \mu < 0$.

2) Fermion

$$Z_i = 1 + e^{-\beta(\varepsilon_i-\mu)} \quad (\because \text{Pauli exclusive})$$

$$Z = \prod\left(1+e^{-\beta(\varepsilon_i-\mu)}\right) \longrightarrow \langle n_i \rangle = \frac{1}{1+e^{+\beta(\varepsilon_i-\mu)}}$$

$$\varepsilon_F = \mu(T=0)$$

# Quantum Statistical Mechanics.

Randomness + Q.M.

· classical statistical mechanics

· Ensemble : we do not know which a definite state of a system is on, but we could talk about prob distribution for given some macroscopic quantities

$\longrightarrow$ Just like C.M.

Analogy

we might not have a complete knowledge of what state the system is in. but we only know the prob distribution of system in "various states"

collection of these quantum states makes ensemble in Q.M. ) $\Rightarrow$ Mixed States.

= incoherent mixture.

· Each state labeled by $|\varphi_n\rangle$

occurs with prob. $P_n$ not necessarily [ eigenstate / orthogonal ]

· $A$ : operator.

For a particle state $n$, $A_n = \langle \varphi_n | A | \varphi_n \rangle = \int dQ\, A\, \varphi_n^{*}(Q)\, \varphi_n(Q)$

$= \langle A \rangle_n$ $\qquad \varphi_n(Q) = \langle Q | \varphi_n \rangle$

$1 = \int dQ\, |Q\rangle\langle Q|$ position.

→ Mixed state ensemble average

$$\langle A \rangle = \sum P_n \langle A \rangle_n$$

· We want basis-independent description $1 = \sum_\alpha |\Phi_\alpha\rangle\langle \Phi_\alpha|$ for complete orthogonal basis

$$\langle A\rangle = \sum_n P_n \sum_\alpha \langle \varphi_n|\Phi_\alpha\rangle\langle\Phi_\alpha|A|\varphi_n\rangle$$

$$= \sum_n P_n \sum_\alpha \langle\Phi_\alpha|A|\varphi_n\rangle\langle\varphi_n|\Phi_\alpha\rangle$$

$$= \sum_\alpha \langle\Phi_\alpha|A \underbrace{\sum_n P_n|\varphi_n\rangle\langle\varphi_n|}_{=\,\rho\,=\,\text{density matrix}}\Phi_\alpha\rangle \qquad = \mathrm{Tr}(A\rho)$$

$$\rho \equiv \sum_n P_n|\varphi_n\rangle\langle\varphi_n| = \sum_{\alpha,\beta} \rho_{\alpha\beta}\, |\Phi_\alpha\rangle\langle\Phi_\alpha|$$

$$\rho_{\alpha\beta} \to \langle\Phi_\alpha|\rho|\Phi_\beta\rangle$$

$$\mathrm{Tr}(\rho) = \mathrm{Tr}\left(\sum_n \rho_n|\varphi_n\rangle\langle\varphi_n|\right) = \sum_n P_n \mathrm{Tr}(|\varphi_n\rangle\langle\varphi_n|) = \sum_n P_n = 1$$

(*) Pure state

$$\rho_{pure} = |\Phi\rangle\langle\Phi| \qquad \rho_{pure}^2 = |\Phi\rangle\langle\Phi|\Phi\rangle\langle\Phi| = \rho_{pure}.$$

$$\rho = \begin{pmatrix} \frac{2}{3} & 0 \\ 0 & \frac{1}{3}\end{pmatrix} = \sum_n P_n|\varphi_n\rangle\langle\varphi_n| = \sum_{n=1}^{2} P_n|\varphi_n\rangle\langle\varphi_n| = \frac{2}{3}|+\rangle\langle+| + \frac{1}{3}|-\rangle\langle-|$$

$$= \frac{1}{2}|\varphi_1\rangle\langle\varphi_1| + \frac{1}{2}|\varphi_2\rangle\langle\varphi_2|$$

$$\varphi_1 \equiv \sqrt{\tfrac{2}{3}}|+\rangle + \sqrt{\tfrac{1}{3}}|-\rangle \qquad \varphi_2 \equiv \sqrt{\tfrac{2}{3}}|+\rangle - \sqrt{\tfrac{1}{3}}|-\rangle$$

· Suppose $|\varphi_n\rangle$ is energy eigen state.

$$\rho_{can} = \sum P_n|\varphi_n\rangle\langle\varphi_n| = \sum_n \frac{e^{-\beta E_n}}{Z}\cdot|E_n\rangle\langle E_n| = \sum_n e^{-\beta H}\cdot|E_n\rangle\langle E_n|$$

$E_n \to H$

$$= e^{-\beta H}.$$

energy eigenstate

$$Z = \sum_n e^{-\beta E_n} = \sum_n \langle E_n|e^{-\beta H}|E_n\rangle \equiv \mathrm{Tr}(e^{-\beta H})$$

?!

$$\rho_{canon} = \frac{e^{-\beta H}}{\mathrm{Tr}(e^{-\beta H})}$$

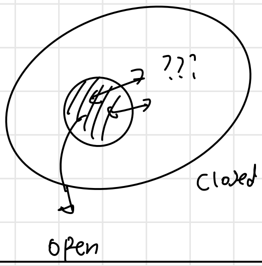
Quantum mechanical entropy : Von Neumann entropy.

$$S = -k_B \, \mathrm{Tr}(\rho \ln \rho)$$

In the basis where $\rho$ is diagonal: $\rho = \sum_n P_n |\varphi_n\rangle\langle\varphi_n|$

$$S = -k_B \sum_n P_n \ln P_n \quad \rightarrow \quad S = 0 \text{ for pure state.}$$

· The observations we make are always limited to small part of a much larger system ⇒ open system




$\rho = \underbrace{|\psi\rangle_{univ}}_{}\langle\psi|_{univ}$ → entire universe = closed

$P = 1$

$S = 0$

Ex) Two qubit world

· qubit A — Measurement

We can access only to this part

· qubit B

· Can not access to this part (unmeasurable part)

→ A quantum state of AB system

$$|\psi\rangle_{AB} = a|0\rangle_A|0\rangle_B + b|1\rangle_A|1\rangle_B$$

- Projecting onto $|0\rangle_A$, $|1\rangle_A$ by measuring qubit A

  · $|0\rangle_A \otimes |0\rangle_B$ with $|a|^2$

  · $|1\rangle_A \otimes |1\rangle_B$ with $|b|^2$

pure state : $\rho_{AB} = |\psi\rangle_{AB}\langle\psi|_{AB}$ with $P = 1$ ⇒ $S = 0$.

· Open pure state: $\rho_{pure} = |\Phi\rangle\langle\Phi|$.

→ Introduce an observable acting on qubit A only : $A \otimes I_B$

$$\langle A \rangle = \langle \psi | A \otimes I_B | \psi \rangle = \left( a^* \langle 00| + b^* \langle 11| \right) \left( A \otimes I_B \right) \left( a|00\rangle + b|11\rangle \right)$$

$$= |a|^2 \langle 0 | A | 0 \rangle + |b|^2 \langle 1 | A | 1 \rangle$$

$$= \sum_n p_n \langle A \rangle_n = tr(A \rho_A) \qquad (\rho_A = Tr_B(\rho_{AB}))$$

: pure state $\rightarrow$ mixed state. $\rightarrow$ Course-graining!

# Bose and Fermi statistics

in QM, all the information is carried in the wave function.

- Identical particles have quantum wave functions same up to an overall phase change when coordinates are swaped.

Ex) 2 identical electrons

$\psi = \psi(\underbrace{x_1, s_1}_{\text{1st electron}}, \underbrace{x_2, s_2}_{\text{2nd electron}})$

$|\psi(x_1, s_1, x_2, s_2)|^2 = |\psi(x_2, s_2, x_1, s_1)|^2 \rightarrow$ I.P의 필요조건.

- At the level of wave function:

$\psi(x_1, s_1, x_2, s_2) = $ "$\eta$" $\psi(x_2, s_2, x_1, s_1)$ $\quad \eta^2 = 1$

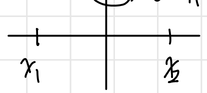
$\hookrightarrow e^{i\theta}$

$\eta = 1$ (Boson)

$\eta = -1$ (Fermion)

$|\psi\rangle$

$\theta = \pi$



For each particle: $|\psi\rangle \rightarrow e^{i\theta J_z}|\psi\rangle = e^{i\theta J}|\psi\rangle$

2개 ∧ 2

$\Rightarrow \eta = e^{2i\pi s}$, $s = \frac{1}{2}, 0$

(※) 3 types of statistics

① Maxwell - Boltzmann statistics (Relevant for classical statistics)

- In microcanonical ensemble: $\Omega = \frac{1}{N!}\sum_{\text{micro states}} 1$ by canonical ensemble.

- In Canonical ensemble: $Z = \frac{1}{N!}\sum_{k} e^{-\beta E_k}$

$\frac{1}{N!} \rightarrow$ indistinguishable factor

② Bose - Einstein statistics

· multiple particles can occupy the same state. $Z = \sum_k e^{-\beta E_k}$

③ Fermi - Dirac

No $N!$ added.

· No two particles can occupy the same state.

· $Z = \sum_k e^{-\beta E_k}$

· Imagine putting 2 particles into 3 possible single particle states with energies of $\varepsilon_1, \varepsilon_2, \varepsilon_3$.

① = A ② = B

| $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_3$ |
|---|---|---|
| A B | | |
| A | B | |
| A | | B |
| | A B | |
| | A | B |
| | B | A |
| B | | A |
| | | A B |
| B | A | |

9

$$Z = \frac{1}{2!}\left(e^{-2\varepsilon_1} + e^{-2\varepsilon_2} + e^{-2\varepsilon_3} + 2e^{-\varepsilon_1-\varepsilon_2} + 2e^{-\varepsilon_1-\varepsilon_3} + 2e^{-\varepsilon_2-\varepsilon_3}\right)$$

$\frac{\varepsilon_i}{k_B T} \ll 1$ (i.e. $\varepsilon_i \ll 1$ in $k_B T = 1$ unit)

$$= \frac{1}{2!}(3^2) \rightarrow \frac{1}{2!} m^2 \text{ for } m \text{ levels.}$$

② Bose - Einstein statistics

$A = B$.

| $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_3$ |
|---|---|---|
| AA | | |
| A | A | |
| A | | A |
| | AA | |
| | A | A |
| | | AA |

6

$$Z = e^{-2\varepsilon_1} + e^{-2\varepsilon_2} + e^{-2\varepsilon_3} + e^{-\varepsilon_1-\varepsilon_2} + e^{-\varepsilon_1-\varepsilon_3} + e^{-\varepsilon_2-\varepsilon_3}$$

$$\xrightarrow[\varepsilon_i \ll 1]{} 6 = \frac{1}{2}3^2 + \frac{1}{2}3 = \frac{1}{2}m(m+1)$$

③ Fermi-Dirac statistics

| $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_3$ |
|---|---|---|
| A | A | |
| A | | A |
| | A | A |

$$Z = e^{-\varepsilon_1-\varepsilon_2} + e^{-\varepsilon_1-\varepsilon_3} + e^{-\varepsilon_2-\varepsilon_3}$$

$$\xrightarrow[\varepsilon_i \ll 1]{} \quad Z = \frac{1}{2}Z^2 - \frac{1}{2}Z = \frac{1}{2}m(m-1)$$

when $m \gg 1$ : $Z$ 값은 모두 $\frac{1}{2}m^2$으로 수렴.

- Non-interacting bosons and Fermions

$$\mathcal{H}_{total} = \sum_{i=1}^{N} \mathcal{H}(\vec{p}_i, \vec{r}_i) \qquad \mathcal{H}\psi_k = \varepsilon_k \psi_k \rightarrow \text{Single particle eigenstate}$$

For given $N, E$.

$\sum n_i = N$

$\sum n_i \varepsilon_i = E$

| $e$ | |
|---|---|
| $\varepsilon_i$ | $n_i$ |
| $\vdots$ | $\vdots$ |
| $\varepsilon_2$ | $n_2$ |
| $\varepsilon_1$ | $n_1$ |

correlated

if $N$ varys,

- Bose-Einstein

$$Z = \sum e^{-\beta E_k} = e^{-2\varepsilon_1} + e^{-2\varepsilon_2} + e^{-2\varepsilon_3} + e^{-(\varepsilon_1+\varepsilon_2)} + e^{-(\varepsilon_1+\varepsilon_3)} + e^{-(\varepsilon_2+\varepsilon_3)}$$

$$= \sum_{i=1}^{3}\sum_{j=1}^{3} e^{-(\varepsilon_i+\varepsilon_j)} = \sum_{i\le j} e^{-(\varepsilon_i+\varepsilon_j)}$$

Fermion

$$\xrightarrow[\text{to N particles}]{\text{Generalize}} \quad Z = \sum_{i_1 \le i_2 \le \cdots \le i_N} e^{-(\varepsilon_{i_1}+\varepsilon_{i_2}+\cdots+\varepsilon_{i_N})}$$

fermion

- The grand partition function $\displaystyle \mathcal{Z} = \sum_{\substack{\text{microstates} \\ k}} e^{-\beta E_n + \beta\mu N_k}$

$$Z = \sum_k e^{-\beta \sum_{i=1}^{\infty} n_i \varepsilon_i + \beta \sum_{i=1}^{\infty} n_i \mu} \qquad E_k = \sum \varepsilon_i n_i, \; N_k = \sum n_i$$

$$= \sum_k \prod_i e^{-\beta n_i \varepsilon_i + \beta \mu n_i} = \prod_i \sum_k e^{-\beta n_i \varepsilon_i + \beta \mu n_i}$$

switch하여도 된다.

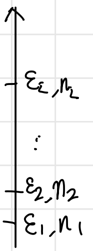
Eg. Fermionic case : $n_i = 0, 1$

let $m = 3$, $Z = \left(1 + e^{-\beta(\varepsilon_1 - \mu)}\right)\left(1 + e^{-\beta(\varepsilon_2 - \mu)}\right)\left(1 + e^{-\beta(\varepsilon_3 - \mu)}\right)$

$$= \underbrace{1}_{n=0} + \underbrace{e^{-\beta(\varepsilon_1 - \mu)} + e^{-\beta(\varepsilon_2 - \mu)} + e^{-\beta(\varepsilon_3 - \mu)}}_{n=1} + \cdots$$

Canonical ensemble with particle number $n$

$$+ \underbrace{e^{-\beta(\varepsilon_1 + \varepsilon_2 - 2\mu)} + \cdots}_{n=2}$$




$N = \sum n_i \ , \ E = \sum \varepsilon_i n_i \longrightarrow$ Correlated ($\because$ constraint)

- For N particles :

$$Z_{canon} = \sum_{i_1 \leq i_2 \leq \cdots \leq i_n} e^{-\beta(\varepsilon_{i_1} + \varepsilon_{i_2} + \cdots + \varepsilon_{i_N})}$$

The grand partition function

$$Z = \sum_{\substack{\text{microstate} \\ k}} e^{-\beta \underbrace{E_k}_{=\sum \varepsilon_i n_i} + \beta\mu \underbrace{N_k}_{=\sum n_i}} = \sum_k \prod_i e^{-\beta \varepsilon_i n_i + \beta\mu n_i}$$

$$= \prod_i \underbrace{\sum_{n_i=0}^{\infty} e^{-\beta \varepsilon_i n_i + \beta\mu n_i}}_{} = Z_i \qquad = \prod_i Z_i$$

(Sum over all possible occupacies)

Ex) Fermioni case of three single particle states with two particles

$$= \left(\underset{\substack{\uparrow \\ n=0}}{1} + \underset{\substack{\uparrow \\ n=1}}{e^{-\beta(\varepsilon_i - \mu)}}\right)\left(1 + e^{-\beta(\varepsilon_i - \mu)}\right)\left(1 + e^{-\beta(\varepsilon_i - \mu)}\right)$$

$$= Z_{can}^{N=0} + Z_{can}^{N=1} + Z_{can}^{N=2} + Z_{can}^{N=3}$$

(*) Boson

All fillings $n_i$ are allowed.

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

$\Rightarrow$ Full partition function $Z = \prod_i Z_i = \prod_i \dfrac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}}$

- Grand free energy

$$\Phi = E - TS - \mu N = \Phi(T, V, \mu) \qquad d\Phi = SdT - PdV - Nd\mu$$

$$\boxed{N = \frac{-\partial \Phi}{\partial \mu}} \longrightarrow Z = \sum_k e^{-\beta E_k + \beta\mu N_k}, \quad \boxed{\Phi = -k_B T \ln Z}$$

$$\therefore \Phi_i = -\frac{1}{\beta} \cdot \ln Z_i = \frac{1}{\beta} \ln\left(1 - e^{-\beta(\varepsilon_i - \mu)}\right)$$

$\Rightarrow$ The occupation number for each state

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

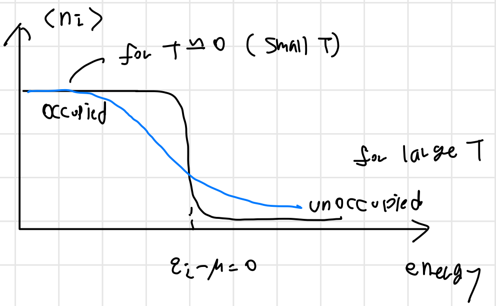
... Bose-Einstein distribution

$\langle n_i \rangle \geq 0 \Rightarrow \varepsilon_i \geq \mu$ for $\forall \varepsilon_i$.

- Fermion

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

$\Rightarrow$ The occupation number $\langle n_i \rangle = -\dfrac{\partial \Phi_i}{\partial \mu} = \dfrac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$




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

$\mu(T \simeq 0) = \varepsilon_F$ (Fermi energy)

$\geq 0$

$\Rightarrow$ μ는 뭐에서 나지?

(*) Maxwell - Boltzmann distribution.

$\boxed{Z = \prod_i Z_i}$ 목표. Global to local

$\to N!$

$$\underbrace{\left(\sum_i e^{-\beta \varepsilon_i}\right)}_{= Z_1}{}^{N}$$

$$= \sum_{i_1} \cdots \sum_{i_N} e^{-\beta(\varepsilon_{i_1} + \cdots + \varepsilon_{i_N})}$$

The grand canonical partition function

$$Z = \sum_N Z_N e^{\beta \mu N}$$

where $Z_N = \dfrac{1}{N!} \underbrace{\sum_K e^{-\beta E_K}}_{\text{microstates}} = \dfrac{1}{N!} Z_1^N$

$$\Rightarrow \boxed{Z} = \sum_N \frac{1}{N!} Z_1^N e^{\beta \mu N} = e^{Z_1 e^{\beta\mu}} = e^{\sum_i e^{-\beta(\varepsilon_i - \mu)}} = \prod_i \exp\underbrace{\left[e^{-\beta(\varepsilon_i - \mu)}\right]}_{= Z_i}$$

$$\boxed{= \prod_i Z_i}$$

$$\therefore\ Z_i = \exp\left(e^{-\beta(\varepsilon_i-\mu)}\right) = \sum_{n_i=0}^{\infty} \frac{1}{n_i!} e^{-\beta n_i(\varepsilon_i-\mu)}$$

looks like grand canonical partition function for a single state using M-B distribution.

The grand free energy for $i$th :

$$\Phi_i = -\frac{1}{\beta}\ln Z_i \qquad \langle n_i\rangle = -\frac{\partial}{\partial\mu}\Phi_i = e^{-\beta(\varepsilon_i-\mu)} \ll 1$$

$$\langle n_i\rangle_{MB} = e^{-\beta(\varepsilon_i-\mu)}$$

When states are multiply occupied, using classical statistics is no longer justified and we must use Bose or Fermi statistics.

$\varepsilon_i \geq \mu$

$\varepsilon_0 = 0 \Rightarrow \mu \leq 0$ (negative) to be consistent.

$$\langle n\rangle_{BE/FD} = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \mp 1}$$

(*) Classical limit,

When the prob that two particles are in the same state is irrelevant, or $\langle n_i\rangle \ll 1$

$$\langle n\rangle_{MB} = e^{-\beta(\varepsilon_i-\mu)} \ll 1$$

$$= e^{-\frac{\varepsilon_i-\mu}{k_BT}} \ll 1$$

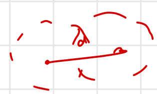
이 조건하에 FD/BE → MB.

① Take $\beta\to\infty$ ($= T\to 0$) while $\mu$ is being fixed
low T limit with fixed $\mu$ ⇒ ???

② Trade $\mu$ for $N$ like a canonical ensemble and assume $\mu$ is dependent with fixed $N$.

$$\Rightarrow \mu = k_BT\cdot\ln(\rho\lambda^3), \quad \rho = \frac{N}{V}, \quad \lambda = \frac{h}{\sqrt{2\pi m k_BT}}$$

$$e^{\beta\mu} = \rho\lambda^3 = \frac{N}{V}\left(\frac{h^2}{2\pi m k_BT}\right)^{3/2} = \left(\frac{\lambda}{d}\right)^3 \lesssim 1$$



$$\therefore \langle n_i \rangle \sim e^{-\beta(\varepsilon_i - \mu)} = \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} e^{-\varepsilon_i / k_B T}$$

(Density ↓)

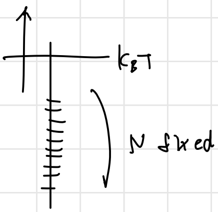
Since $\underline{N \text{ is fixed}}$ : $\langle n_i \rangle \to 0$ as $V \to \infty$ (Large volume limit)

$T \to \infty$ (High temperature limit)

(드브로이 파장 ↓, 고전적 입자)

$$\left( \downarrow \frac{\partial \mu}{\partial T} = -\frac{S}{N} < 0 \right)$$

$\mu$ 값은; $\underline{\mu < 0}$




$$\lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \gtrsim \underbrace{\left(\frac{V}{N}\right)^{\frac{1}{3}}}_{\text{spacing}}$$