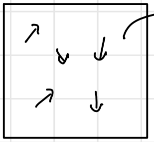
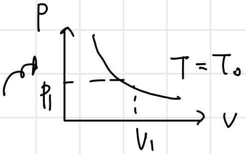
Introduction

Thermodynamics : Transformations between heat and work relationships between macroscopic properties of a macroscopic system.



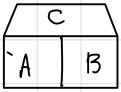
$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases} \xrightarrow{N \ggg 1} f(P,T,V) = 0$$



↳ Thermodynamic System : Large numbers of Particle

⇒ It obeys Thermodynamic Laws

0th Law : Thermal equilibrium ↪ Definition of temperature



$T_A = T_C$, $T_B = T_C$ ⇒ $T_A = T_B$

1st Law : Conservation of Energy ↪ Form of a Transition

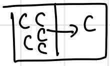
$\Delta U = Q \mp W$ with $W = \pm P dV$ (work done by a system)

Q = Heat observed by a system

2nd Law : Entropy,
$$\begin{cases} \Delta S \geq 0 & \text{for an isolated system} \\ \Delta S = \dfrac{\Delta Q}{T} & \text{열적 평형 } T. \end{cases}$$

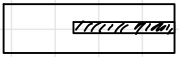
(*) Historical Development.

- 1824, Carnot heat engine : Engine Limitation of Performance
- Misconcept of theory : Heat Particle, Caloric (열소)의 fluid로 이해.



⟶ Tompson's Cannon Drilling

반박



- 1842, Mayer : Heat & work thm
- 1850, Clausius, kelvin : Classical thermodynamics
- Atomic approach : Desire to explain in microscopic scale
  - 1859, Maxwell
  - 1872, Boltzman ⋯ 등 ~19|X 까지

  ] ⟶ Kinetic theory

- Gibbs
- Boltzmann

] → Probabilitic approach → statistical mech.

I. Preliminary Probability Theory

1. Definition and Simple Properties

S의 하위집합

Let $x \to S = \{x_1, x_2, \cdots x_n\}$ and $E \subset S$ (E = events)

Then, Probability of the event $P(E)$ can be defined as

- Objective (Experimental) way : $P(A) = \lim_{N \to \infty} \frac{N_A}{N}$
- Subjective (Theorical) way : Lack of information (Uncertainty)
  → Theorical Estimate.

집합 이론에 의거, 다음 성질들이 성립한다.

$$P(A \cup B) = P(A) + P(B) - P(A \cap B) \xrightarrow{\text{mutually exclusive}} P(A) + P(B)$$

$$P(B|A) = \frac{P(A,B)}{P(A)} \xrightarrow[P(B|A)=P(B)]{} P(A \cap B) = P(A)P(B)$$

(independence)

A가 일어났을 때 B가 일어날 확률

$$\Rightarrow P(A|B) = \frac{P(A)}{P(B)} P(B|A)$$

$$\Rightarrow P(B) = \sum_{i=1}^{n} P(A_i) P(B|A_i)$$

(when A_i are mutually exclusive)

- Permutation (order-dependence) = $_nP_k = \frac{n!}{(n-k)!}$

Binomial Coefficient

- Combination (Order-Independence) = $_nC_k = \binom{n}{k} = \frac{n!}{(n-k)!\,k!}$

(*) Sort of Probability

① Discrete Probability Distribution

$x \to x_i$ with P_i

$$\begin{cases} \sum_i P_i = 1 \\ \langle x \rangle = \sum x_i P_i \\ \langle f(x) \rangle = \sum f(x_i) P_i \end{cases}$$

(Mean, Expectation, Average)

② Continuous Prob Distbn

$\underbrace{P(x)}_{\text{density}}dx = \text{Prob s.t. } E \in [x, x+dx]$

$$\begin{cases} \int P(x)\,dx = 1 \\ \langle x \rangle = \int dx \cdot x P(x) \\ \langle f(x) = \int dx \cdot f(x) P(x) \end{cases}$$

(*) Variance (Dispersion, mean-squared deviation)

$x - \langle x \rangle \equiv$ Deviation from the mean value.

$\Rightarrow \langle x - \langle x \rangle \rangle = \langle x \rangle - \langle x \rangle = 0$ ($\because$ Positive & negative deviation cancel)

$\therefore \sigma_x^2 \equiv \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$

$\rightarrow \sigma_x \equiv \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$ (Standard Deviation, RMS)

$\hookrightarrow \sigma^2 = \begin{cases} \sum_j (x_j - \langle x \rangle)^2 P_j \\ \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 P(x)\,dx. \end{cases}$

(*) Definition of nth moment

$$\mu_n \equiv \langle x^n \rangle = \int dx \cdot x^n P(x)$$

(*) Linear Transform

if $y = ax + b$ ($a, b = \text{const}$)

① $\langle y \rangle = a \cdot \langle x \rangle + b.$

② $\begin{cases} \langle y^2 \rangle = \langle a^2x^2 + 2abx + b^2 \rangle = a^2\langle x^2 \rangle + 2ab\langle x \rangle + b^2. \\ \langle y \rangle^2 = a^2 \cdot \langle x \rangle^2 + 2ab\langle x \rangle + b^2 \end{cases}$

$\Rightarrow \sigma_y^2 = \langle y^2 \rangle - \langle y \rangle^2 = a^2 \cdot (\langle x^2 \rangle - \langle x \rangle^2) = a^2 \cdot \sigma_x^2$ $\quad \sigma_y = a\sigma_x$

for continuous variable, $\langle y \rangle = \int_{-\infty}^{\infty} y \underbrace{g(y)dy}_{\text{same}} = \int_{-\infty}^{\infty} (ax+b) \underbrace{f(x)dx}_{\text{same}}$

$= a \cdot \langle x \rangle + b.$ $\quad \sigma_y^2 = \int_{-\infty}^{\infty} [y - (a\langle x \rangle + b)]^2 g(y)\,dy = a^2 \cdot \sigma_x^2.$

cf) Chebychev inequality $\quad P(|x - \langle x \rangle| \geq k\sigma) \leq \frac{1}{k^2}$

2. Binomial Distribution

Prob distbn of getting k heads of N indepependent Bernoulli trials

$$P_N(k) = \binom{N}{k} p^k q^{N-k} = \binom{N}{k} p^k (1-p)^{N-k}$$ (Repeated Individual)

$(p+q=1)$

$\Rightarrow$ By binomial expansion, $(x+y)^N = \sum_{k=0}^{N} \binom{N}{k} x^k y^{N-k}$ 이때 $x=p,\ y=q$

$$= \sum P_N(k) = 1$$ (makes sense)

① Mean $$\langle k \rangle = \sum_{k=0}^{N} k \cdot P_N(k) = \sum_{k=0}^{N} \binom{N}{k} \underbrace{k \cdot p^k}_{=\left(p\cdot\frac{\partial}{\partial p}\right)p^k} \cdot q^{N-k}$$

$$= p\cdot\frac{\partial}{\partial p} \sum_{k=0}^{N} \binom{N}{k} p^k q^{N-k}$$

$$= p\cdot\frac{\partial}{\partial p}(p+q)^N = p\cdot N\cdot(p+q)^{N-1} = Np \qquad \therefore \langle k \rangle = Np$$

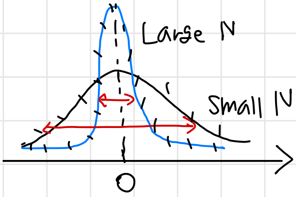
② Variance : $\sigma_k^2 = \langle k^2 \rangle - \langle k \rangle^2$

$$\langle k^2 \rangle = \sum_{k=0}^{N} k^2 \cdot P_N(k) = \sum_{k=0}^{N} \binom{N}{k} \underbrace{k^2 p^k}_{=\left(p^2\cdot\frac{\partial^2}{\partial p^2} + p\frac{\partial}{\partial p}\right)p^k} q^{N-k} = \left(p^2\frac{\partial^2}{\partial p^2} + p\frac{\partial}{\partial p}\right)(p+q)^N$$

$$= N(N-1)p^2 + Np = N^2p^2 - Np^2 + Np = N^2p^2 + Np(1-p)$$

$$\Rightarrow \sigma_k^2 = N^2p^2 + Np(1-p) - N^2p^2 = Npq \qquad \sigma_k = \sqrt{Npq}$$

③ Relative width $$\equiv \frac{\sigma_k}{\langle k \rangle} = \frac{\sqrt{Npq}}{Np} \sim \frac{1}{\sqrt{N}} \xrightarrow{N \ggg 1} 0$$

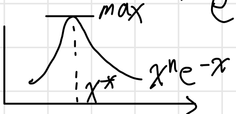


$\downarrow$ Sharp Peak

(*) Sterling's Approximation for very large $N (\sim 10^{23})$

$$n! = \int_0^\infty \underbrace{x^n e^{-x}}_{\parallel} dx$$ (Gamma function) $\rightarrow$ (부분적분 하면 증명가능)

$$e^{f(x)} = e^{n\ln x - x}$$



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

To determine x^*, $f'(x)\Big|_{x^*} = \left(\frac{n}{x} - 1\right)\Big|_{x^*} = 0$. $\therefore x^* = n$.

and, $f''(x) = -\frac{n}{x^2}$ 이므로 $f''(x^*) = -\frac{1}{n} < 0$.

Taylor expand, $f(x) \simeq f(x^*) + f'(x^*)(x - x^*) + \frac{f''(x^*)}{2!}(x - x^*)^2$

$= (n \cdot \ln n - n) + 0 \cdot (x - 0) - \frac{1}{2n} \cdot (x - n)^2 \quad (\because x^* = n)$ (up to 2nd order)

$$\Rightarrow n! \simeq \int_0^{\infty} e^{n\ln n - n - \frac{(x-n)^2}{2n}} dx = e^{n\ln n - n} \underbrace{\int_{0\,-\infty}^{\infty} e^{-\frac{(x-n)^2}{2n}} dx}$$

$= \sqrt{2\pi n}$, Gaussian Integration

$\therefore n! \simeq \sqrt{2\pi n} \left(\frac{n}{e}\right)^n$ for Large n.

$\Leftrightarrow \ln n! = n \cdot \ln n - n + \frac{1}{2} \ln(2\pi n) \simeq \boxed{n \cdot \ln n - n}$

(*) From Binomial to Gaussian

$P_N(k)$ for Large enough N, $\ln P_N(k) = \ln N! \overset{-\ln k!}{\surd} - \ln(N-k)! + k\ln p + (N-k) \cdot \ln q$.

By using Sterling approximation,

$$\ln P_N(k) \simeq (N \cdot \ln N - \cancel{N}) - \left[(N-k)\ln(N-k) - (\cancel{N} - \cancel{k})\right] + k\ln p + (N-k)\ln q - k\ln k + \cancel{k}$$

→ 최댓값을 가지는 k^* 값을 구해보자

$$\frac{\partial}{\partial k} \ln P(k)\Big|_{k^*} = -\ln k - \cancel{1} + \ln(N-k) + \cancel{1} + \ln p - \ln q \Big|_{k^*} = 0$$

$\therefore (N - k^*)p = k^* q$. $k^*(p+q) = Np = \langle k \rangle$ $\quad \langle k \rangle = k^*$.

then, $\frac{d^2}{dk^2} \ln P(k)\Big|_{k^*} = -\frac{1}{k} - \frac{1}{N-k}\Big|_{k^* = \langle k \rangle} = -\frac{N - k + k}{k(N-k)}$

$= \frac{-N}{Np(N - Np)} = \frac{-1}{Np(1-p)} = \frac{-1}{Npq} = -\frac{1}{\sigma_k^2}$

$\xrightarrow[\text{Taylor expansion}]{} \ln P(k) \simeq \ln P(k^*) + 0 \cdot (k - k^*) + \frac{1}{2!}\left(-\frac{1}{\sigma_k^2}\right)(k - k^*)^2$

$\therefore P_N(k) \simeq C_1 \cdot e^{-\frac{1}{2\sigma_k^2}\cdot(k-k^*)^2}$ 확률 분포 조건에 의해 C를 구하면

$$\sum P_N(k) \longrightarrow \int_0^{\infty} dk\cdot P(k) = \int_{-\infty}^{\infty} dk\, P(k) = \int_{-\infty}^{\infty} dk\cdot C\cdot \underbrace{e^{-\frac{(k-\langle k\rangle)^2}{2\sigma_k^2}}}_{\text{Gaussian Int.} = \sqrt{2\pi\sigma_k^2}} = 1$$

$$\therefore C = \frac{1}{\sqrt{2\pi\sigma_k^2}}$$

$$P_N(k) = \frac{1}{\sqrt{2\pi\sigma_k^2}}\, e^{-\frac{(k-\langle k\rangle)^2}{2\sigma_k^2}}$$

: for Large N, 이항분포를 가우스 분포로 근사 가능하다.

⟨Summary⟩

$P(x)dx$: Probability of events

$\langle x\rangle$: Expectation value

$\sigma^2 \equiv \langle (x-\langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2$

Binomial Distribution $\xrightarrow{N>>>1}$ Gaussian Distrib

$\Rightarrow P_N(k) = \binom{N}{k} p^k q^{N-k}$

$$P(k) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{(k-\mu)^2}{2\sigma^2}}$$

ex) Coin Toss HTTH

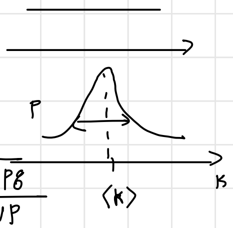
$P_4(2) = \binom{4}{2}\left(\frac{1}{2}\right)^4$

as $\bar{k} = \mu = Np$

$\sigma^2 = Npq$

$\Rightarrow$ for sequence $p^k \cdot q^{N-k} = p^N$ for "unbiased" events (Randomness)

$\Rightarrow$ for Given Composition (ex: $k=2$) neglecting "sequence" events can be predictable



$$\frac{\sigma}{\langle k\rangle} = \frac{\sqrt{Npq}}{Np} \sim \frac{1}{\sqrt{N}} \xrightarrow{N\to\infty} 0$$

So ⟨k⟩에서 sharp 해지니 다른 ⟨k⟩로부터 먼 event 무시 가능.

3. Moments & Cumulants

By definition, n th moment of variable x from the origin is $\mu_n = \langle x^n \rangle = \int dx \cdot x^n p(x)$

But, Integration is complex... Let's introduce convenient skill

(*) Characteristic function & moment generating function cf1) $\tilde{p}(k) =$

Def) $\tilde{p}(k) = \langle e^{-ikx} \rangle = \int dx \cdot e^{-ikx} \cdot p(x)$ cf2) $e^{(-ikx)} = 1 + \sum \frac{(-ikx)^n}{n!}$

$$= \int dx \cdot \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} x^n p(x)$$

$$= \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \cdot \underbrace{\int dx \cdot x^n p(x)}_{\mu_n}$$

$$\Rightarrow \left. \frac{\partial^n \tilde{p}(k)}{\partial k^n} \right|_{k=0} = (-i)^n \cdot \mu_n$$

$$\boxed{\therefore \mu_n = i^n \cdot \left. \frac{\partial^n \tilde{p}(k)}{\partial k^n} \right|_{k=0}} \quad \left(\because \frac{1}{(-i)^n} = \frac{i^{4n}}{i^{3n}}\right)$$

$$\hookrightarrow = \left(-\frac{\partial}{\partial(ik)}\right)^n \tilde{p}(k) \Big|_{k=0}$$

(*) Cumulant generating function

Def) $\ln \tilde{p}(k) = \ln \langle e^{-ikx} \rangle = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n} \cdot \langle x^n \rangle_c$. 을만족하는 $\langle x^n \rangle_c$

then, 특성함수 정리에 의해 $\langle x^n \rangle_c = (i^n) \cdot \frac{\partial^n}{\partial k^n} \left[\ln \tilde{p}(k) \right] \Big|_{k=0}$ 가 된다.

① $\langle x^1 \rangle_c = i \frac{\partial}{\partial k} \cdot \ln \tilde{p}(k) \Big|_{k=0} = i \cdot \frac{1}{\tilde{p}(k)} \cdot \frac{\partial \tilde{p}}{\partial k} \Big|_{k=0}$

Mean

$$= \frac{1}{\tilde{p}(0)} \cdot \mu_1 = \mu_1 = \langle x \rangle \qquad \therefore \langle x^1 \rangle_c = \langle x \rangle$$

$$\left(\because \tilde{p}(0) = \langle e^0 \rangle = \langle 1 \rangle = 1\right)$$

Variance

② $\langle x^2 \rangle_c = i^{-2} \cdot \frac{\partial^2}{\partial k^2} \cdot \ln \tilde{p}(k) \Big|_{k=0} = i^{-2} \left[\frac{1}{\tilde{p}(k)} \frac{\partial^2 \tilde{p}(k)}{\partial k^2} - \frac{1}{(\tilde{p}(k))^2} \left(\frac{\partial \tilde{p}}{\partial k} \right)^2 \right]_0$

$$= \mu_2 - \mu_1^2 = \langle x^2 \rangle - \langle x \rangle^2 = \sigma^2. \qquad \therefore \langle x^2 \rangle_c = \sigma^2$$

③ $\langle x^3 \rangle_c = i^3 \cdot \frac{\partial^3}{\partial k^3} \cdot \ln \tilde{p}(k) \Big|_{k=0}$

$$= i^{-3} \cdot \left[\frac{1}{\tilde{p}(k)} \cdot \frac{\partial^3 \tilde{p}(k)}{\partial k^3} - \underbrace{\frac{1}{(\tilde{p}(k))^2} \left(\frac{\partial \tilde{p}}{\partial k}\right)\left(\frac{\partial^2 \tilde{p}}{\partial k^2}\right)}_{-1\text{배}} + \frac{2}{(\tilde{p}(k))^3} \cdot \left(\frac{\partial \tilde{p}}{\partial k}\right)^3 - \underbrace{\frac{1}{(\tilde{p}(k))^2} \cdot 2 \left(\frac{\partial \tilde{p}}{\partial k}\right) \cdot \left(\frac{\partial^2 \tilde{p}}{\partial k^2}\right)}_{-2\text{배}} \right]_{k=0}$$

(i^{-3}을 각 미분항에 분배하여 정리)

$$= \mu_3 - 3 \cdot \mu_1 \mu_2 + 2 \mu_1^3 = \langle x^3 \rangle - 3 \langle x \rangle \langle x^2 \rangle + 2 \langle x \rangle^3$$

Skewness

⟨Usefull skill, Diagrammatic representation⟩

nth Cumulant $\langle x^n \rangle_c$: Cluster connected among n Points

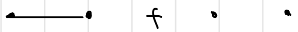
nth moment $\langle x^n \rangle$: All possible ways of distributing n points into smaller clusters

(ex)

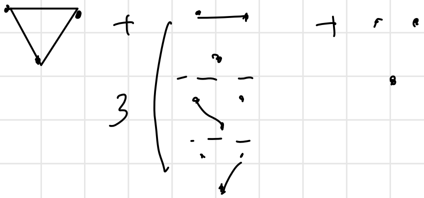
(n=1)  $\langle x^1 \rangle = \langle x^1 \rangle_c$

대입정리

$\Rightarrow \langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2$

(n=2) 

$\Rightarrow \langle x^2 \rangle = \langle x^2 \rangle_c + \langle x^1 \rangle_c \langle x^1 \rangle_c$

(n=3) 

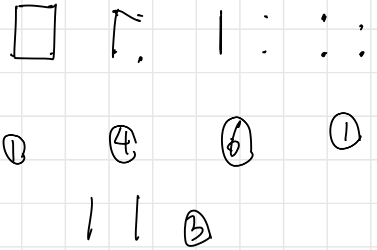
$$\Rightarrow \langle x^3 \rangle = \langle x^3 \rangle_c + 3 \cdot \langle x^2 \rangle_c \langle x^1 \rangle_c + \langle x^1 \rangle_c^3$$

$$= \langle x^3 \rangle_c + 3 \cdot \left[\langle x^2 \rangle - \langle x \rangle^2 \right] \langle x \rangle + \langle x \rangle^3$$

$$\therefore \langle x^3 \rangle_c = \langle x^3 \rangle - 3 \langle x^2 \rangle \langle x \rangle + 2 \langle x \rangle^3 .$$

after n = 4, 5, 6 ⋯ go on.

$$\langle x^4 \rangle = \langle x^4 \rangle_c + 4 \cdot \langle x^3 \rangle_c \langle x^1 \rangle_c + 6 \cdot \langle x^2 \rangle_c \langle x^1 \rangle_c^2 + \langle x^1 \rangle_c^4 + 6 \cdot \langle x^2 \rangle_c^2$$



$$\Rightarrow \langle x^4 \rangle_c = \langle x^4 \rangle - 4 \cdot \left[\langle x^3 \rangle - 3 \langle x^2 \rangle \langle x \rangle + 2 \langle x \rangle^3 \right] \langle x \rangle - 6 \cdot \left(\langle x^2 \rangle - \langle x \rangle^2 \right) \langle x \rangle^2 + \langle x \rangle^4 - 3 \left(\langle x^2 \rangle - \langle x \rangle^2 \right)^2$$

$$= \langle x^4 \rangle - 4 \langle x^3 \rangle \langle x \rangle + 12 \langle x^2 \rangle \langle x \rangle^2 - 8 \langle x \rangle^4 \cancel{- 6 \cdot \langle x^2 \rangle \langle x \rangle^2} + 6 \langle x \rangle^4 + \langle x \rangle^4 - 3 \langle x^2 \rangle^2 + \cancel{6 \langle x^2 \rangle \langle x \rangle^2} - 3 \cdot \langle x \rangle^4$$

4. Several Random Variables

(*) Joint Probability Distribution : $p(x_1,x_2,\cdots,x_N)\,dx_1\cdots dx_N = \text{Prob}\left[E\in[\vec{x},\vec{x}+d\vec{x}]\right]$ 이다.

결합

Joint Characteristic function $\equiv \tilde{p}(k_1,k_2,\cdots,k_N) = \left\langle e^{-i(k_1x_1+k_2x_2+\cdots+k_Nx_N)}\right\rangle$

$$= \int \prod_{\alpha=1}^{N} dx_\alpha\, e^{-i\cdot k_\alpha x_\alpha}\cdot p(x_1,x_2,\cdots,x_N)$$

① Joint moment $\langle x_1^{m_1}x_2^{m_2}\cdots x_N^{m_N}\rangle = \int \prod_{\alpha=1}^{N} dx_\alpha\cdot x_\alpha^{m_\alpha}\, p(x_1,x_2,\cdots,x_N)$

$$= \left(-\frac{\partial}{\partial(ik_1)}\right)^{m_1}\left(-\frac{\partial}{\partial(ik_2)}\right)^{m_2}\cdots\left(-\frac{\partial}{\partial ik_N}\right)^{m_N}\tilde{p}(k_1\cdots k_N)\Big|_{\vec{k}=0}$$

② Joint Cumulant by symmetry,

$$\langle x_1^{m_1}x_2^{m_2}\cdots x_N^{m_N}\rangle_c = \left(-\frac{\partial}{\partial ik_1}\right)^{m_1}\cdots\left(-\frac{\partial}{\partial ik_N}\right)^{m_N}\ln\tilde{p}(k_1\cdots k_N)\Big|_{\vec{k}=0}$$

(*) Statistical Independency

Def) $p_N(x_1,x_2,\cdots,x_N) = p_1(x_1)\,p_2(x_2)\cdots p_N(x_N)$

$\langle f(x_1)g(x_2)\rangle = \int dx_1dx_2\, f(x_1)g(x_2)\,p(x_1,x_2)$ 에서, If x_1,x_2 is Statistically independent,

$$= \int dx_1dx_2\, f(x_1)\,p(x_1)\,g(x_2)\,p(x_2) = \langle f(x_1)\rangle\langle g(x_2)\rangle$$

So, under the same condition, the characteristic function becomes

$$\Rightarrow \tilde{p}(k_1,\cdots,k_N) = \int\prod_{\alpha=1}^{N} dx_\alpha\, e^{-ik_\alpha x_\alpha}\,\underbrace{p(x_1,\cdots,x_N)}_{=\prod_{\alpha=1}^{N}p_\alpha(x_\alpha)}$$

$$= \prod_{\alpha=1}^{N}\int dx_\alpha\, e^{-ik_\alpha x_\alpha}\,p_\alpha(x_\alpha)$$

$$= \prod_{\alpha=1}^{N}\tilde{p}_\alpha(k_\alpha)$$

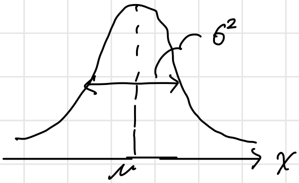
Similarly, $\langle x_1^{m_1}x_2^{m_2}\cdots x_N^{m_N}\rangle = \langle x_1^{m_1}\rangle\langle x_2^{m_2}\rangle\cdots\langle x_N^{m_N}\rangle$

But, cumulant became little bit different.

$$\langle x_1^{m_1} x_2^{m_2} \cdots x_N^{m_N} \rangle_c = \left(-\frac{\partial}{\partial ik_1}\right)^{m_1} \cdots \left(-\frac{\partial}{\partial ik_N}\right)^{m_N} \sum_{\alpha=1}^{N} \ln \tilde{p}_\alpha(k_\alpha)$$

$$= 0 \text{ for any } m_i \cdot m_j \neq 0. \quad (\because \ln p_1 p_2 \cdots p_N = \ln p_1 + \ln p_2 + \cdots)$$

(*) Moments / Cumulants of Gaussian distribution



(P.D.F) $$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

(Characteristic Function) $$\tilde{p}(k) = \langle e^{-ikx} \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx\, e^{-ikx - \frac{(x-\mu)^2}{2\sigma^2}} \quad (x-\mu = y)$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dy\, e^{-\frac{y^2}{2\sigma^2} - iky - ik\mu} \quad \left(\int = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dy \cdot e^{-\frac{1}{2\sigma^2} \cdot (y + \sigma^2 ik)^2} = 1 \text{ 이므로} \right)$$

$$= e^{-ik\mu - \frac{\sigma^2 k^2}{2}}$$

$\therefore \ln \tilde{p}(k) = -ik\mu - \frac{\sigma^2 k^2}{2}$ 이다. 따라서, 이는 cumulant generating function으로부터

$$\langle x^1 \rangle_c = -\frac{\partial}{\partial(ik)} \ln \tilde{p}(k) \Big|_{k=0} = \mu = \langle x^1 \rangle$$

$$\langle x^2 \rangle_c = \frac{\partial^2}{\partial k^2} \left(\frac{\sigma^2 k^2}{2} \right) = \sigma^2.$$ 이고, $\ln \tilde{p}(k)$의 k에 대한 최고차가 2이므로

$$= \langle x^2 \rangle - \langle x \rangle^2. \quad (\because \text{cumulant - moment relation})$$

$$\langle x^n \rangle_c = 0 \text{ for } n > 2.$$

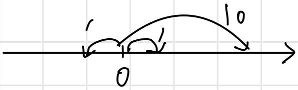
∴ mean = μ, variance = σ^2 인 distribution이 된다.

→ Gaussian distribution의 중요한 성질. 1-1 mapping으로 이 성질을 가진 분포를 대응할 것.

cf) for arbitary Gaussian, $$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}$$

5. Probability Distribution for Large N : Central limit theorem

(*) $X = \sum_{i}^{N} x_i$ variable   ex)



after N step, final displacement?

$$P(X) = \int\cdots\int P(x_1,\dots,x_N)\,dx_1\cdots dx_N$$

$X = \sum x_i \rightarrow$ constraint

cf) $\int_{-\infty}^{\infty}\delta(\alpha)\,d\alpha = 1$

$$\int P(X)\cdot\delta(X-\sum x_i)\,dX = \int\cdots\int_{X=-\infty}^{X=+\infty} dx_1\cdots dx_N\cdot\underbrace{P(x_1,x_2,\dots,x_N)}_{\text{Independence } = P_1(x_1)P_2(x_2)\cdots P_N(x_N)}\cdot\underbrace{\delta(X-\sum x_i)}_{=\frac{1}{2\pi}\int_{-\infty}^{\infty}dk\,e^{ik(X-\sum x_i)}}\,dX$$

$P(X)$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty}dk\,e^{ikX}\cdot\int\cdots\int\left(dx_1\,e^{-ikx_1}P(x_1)\cdot\right)\left(dx_2\cdot e^{-ikx_2}\cdot P(x_2)\right)\cdots$$

→ 적절히 곱셈항 분배해 (up to N term)

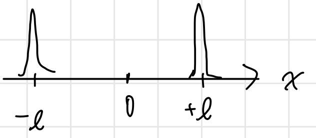
$$= \frac{1}{2\pi}\int_{-\infty}^{\infty}dk\cdot e^{+ikX}\cdot\left(\tilde{P}_1(k)\,\tilde{P}_2(k)\cdots\tilde{P}_N(k)\right) \text{ ″ } \left(\tilde{P}(k)\right)^N$$

위 예제에서, $P_1 = P_2\cdots = P_N$ (같은 확률 따라서 움직임 가정)

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty}dk\cdot e^{+ikX}\left(\tilde{P}(k)\right)^N$$ 이다. ← $P(X)$의 $\tilde{P}(k)$ 형태 표현

(eg) 예시 상황의 Probability Distribution을 구해보자. (p for $+l$. q for $-l$. after N step, distribution?)

(P.D.F) $p(x) = p\cdot\delta(x-l) + q\delta(x+l)$ 이다.



$(\because P(+l-\varepsilon, +l+\varepsilon) = \int_{l-\varepsilon}^{l+\varepsilon}P(x)\,dx = p.)$

Then, $\left(\tilde{P}(k)\right)^N = \left(\langle e^{-ikx}\rangle\right)^N = \left(e^{-ikl}\cdot p + e^{ikl}\cdot q\right)^N$ → Binomial Polynomial

$$= \sum_{n=0}^{\infty}\binom{N}{n}p^n\cdot q^{N-n}\cdot e^{\boxed{-n\cdot ikl + (N-n)ikl}} = (N-2n)ikl$$

따라서, 위 식 대입

$$P(X) = \frac{1}{2\pi}\int_{-\infty}^{\infty}dk\cdot e^{+ikX}\cdot\sum_{n=0}^{\infty}\binom{N}{n}p^n q^{N-n}\cdot e^{-(2n-N)ikl}$$

$$= \underline{\frac{1}{2\pi}}\cdot\sum_{n=0}^{\infty}\binom{N}{n}p^n q^{N-n}\cdot\underbrace{\int_{-\infty}^{\infty}dk\cdot e^{+ik[X-(2n-N)l]}}_{} = \delta[X-(2n-N)l]$$

$$\therefore P(X)\,dX = \sum_{n=0}^{\infty} \binom{N}{n} p^{n} q^{N-n} \cdot \delta[X-(2n-N)\ell]\,dX$$

$n=0 \quad X = -N\ell$

$\vdots$

$n=N \quad X = N\ell$

$\Rightarrow X = (2n'-N)\ell$ 이 될 확률 $P(X=(2n'-N)\ell) = \int_{X=(2n'-N)\ell-\varepsilon}^{X=(2n'-N)\ell+\varepsilon} P(X)\,dX$

$$= \binom{N}{n'} p^{n'} q^{N-n'} \cdot \quad (n' : \text{Dummy index})$$

$$\therefore P((2n-N)\ell) = \binom{N}{n} p^{n} q^{N-n}$$ for otherwise, $P = 0$.

(ex: $X = (2n-N)\ell + \frac{\ell}{2}$).

(*) Central Limit Theorem ($N \gg 1$)

Consider $X = \sum_{i=1}^{N} x_i$ then, for random variable X, Characteristic function

$$\tilde{p}_X(k) = \langle e^{-ikX} \rangle = \langle e^{-ik\sum_i x_i} \rangle = \langle e^{-ikx_1} \cdot e^{-ikx_2} \cdots e^{-ikx_N} \rangle$$

$$= \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle X^n \rangle$$

$$\ln \tilde{p}_X(k) = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle X^n \rangle_c = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle (x_1+x_2+\cdots x_N)^n \rangle_c$$

Let's assume that x_i are statistically independent. Then, in the cumulant formula, cross terms should disappear(why?)

$$\langle X^n \rangle_c = \langle x_1^n \rangle_c + \langle x_2^n \rangle_c + \cdots + \langle x_N^n \rangle_c = \sum_{i=1}^{N} \langle x_i^n \rangle_c$$

⇒ (Sum of random variables 의 Cumulant) = (random variable의 Cumulant 의 Sum)

Independent and Identical distribution

⇒ 여기에, $x_1, \cdots, x_n$ 이 Identical distribution을 가진다고 하자.

⇒ 이 조건과 Statistically Independent 조건을 묶어서 함께 I.I.D 라고 부른다.

Then, $\langle X^n \rangle_c = N \cdot \langle x^n \rangle_c$ 가 된다.

$$\downarrow$$

$$P(X_1, \cdots, X_n) = P_1(x_1)P_2(x_2)\cdots P_N(x_N)$$
$$= P(x_1)P(x_2)\cdots P(x_N)$$

Now, Let's introduce $y = \dfrac{X - \langle X \rangle_c}{\sqrt{N}} = \dfrac{X - N\langle x \rangle_c}{\sqrt{N}} = \dfrac{X - N\cdot\langle x \rangle}{\sqrt{N}}$.

It is the Linear transformation of variable X. so, If we calculate Cumulant of y,

$$\langle y^1 \rangle_c = \frac{\langle X^1 \rangle_c - \langle X^1 \rangle_c}{\sqrt{N}} = 0 \cdots ①$$

$$\langle X^2 \rangle_c - \cancel{2N\langle X \rangle_c \langle x \rangle + N^2\langle x \rangle^2}$$
$$\underbrace{- N^2 \langle x \rangle^2}$$
$$\langle x \rangle = 0 \,?$$

$$\langle y^2 \rangle_c = \frac{\langle X^2 \rangle_c}{N} = \frac{N\langle x^2 \rangle_c}{N} = \langle x^2 \rangle_c \longrightarrow \sigma^2 \cdots ②$$

? :

→ Intuition : Linear transform 이니, 뒤팡 즉시가능. 계산 해도 쉬울걸다.

$$\langle y^m \rangle_c = \frac{\langle X^m \rangle_c}{N^{\frac{m}{2}}} = \frac{N\cdot\langle x^m \rangle_c}{N^{\frac{m}{2}}} \sim N^{1-\frac{m}{2}} \longrightarrow 0 \quad \left(\begin{array}{c}\text{for } m > 2 \\ N \to \infty\end{array}\right)$$

즉, $N \ggg 1 \to \infty$ 인 때, $m > 2$ 인 $\begin{cases} \langle y^m \rangle_c = 0 \\ \langle y^1 \rangle_c = 0 \\ \langle y^2 \rangle_c = \sigma^2 \end{cases}$ 이므로

이 조건에서 y의 확률분포는 $N(0, \langle x^2 \rangle_c)$ 인 Gausian distribution이다.

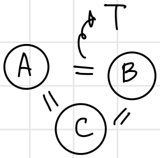
$$P(y) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{y^2}{2\langle x^2 \rangle_c}} \longrightarrow N \text{과 관계 X}.$$

따라서, $P(x)$가 무엇이든지, $N \to \infty$ 이면 single variable gausian으로 변환 가능하다.

$\therefore \left(\begin{array}{c} N \gg 1 \\ \text{I.I.D} \end{array}\right) \Rightarrow$ N의 정확한 값을 몰라도 통계적 분석 가능하다.

II. Classical Thermodynamics

1. The 0th & 1st Law of Thermodynamics



1) 0th Law : The abstract definition of temperature

⇒ If two systems are in thermal equilibrium with a third, the two systems should be in thermal equilibrium each other

definition

⇒ Thermal Contact for a sufficiently long time, and no "net energy" transfer in the stationary state. Then they should have the same physical quantity, specially named : Temperature

definition of thermal contact.

⇒ When the two systems are able to exchange energy while keeping external parameters, they are said to be in thermal contact.

$$\left(\begin{cases} T_A = T_C \\ T_B = T_C \end{cases} \Rightarrow T_A = T_B \right)$$

↪ the definition of temperature : Ambiguity

Q. How can we define temperature "Rigorously"?

↓

2) Statistical Definition of Temperature.

· We will define the temperature through Ω, the number of microstates.

(*) Microscopic states (μ-states)

N = 100

H T H H T T ··· H T

⋮

T H H T T H ··· H H

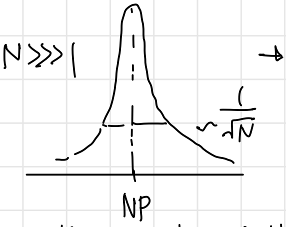
} Sequences

For unbiased, equally probable

Number of possible configuration = $2^{100} \sim 10^{30}$

All possible μ-states are equally likely.

(*) Macroscopic states (M-states)



→ Sharp Peak shape

Interested in k = number of H = Composition

$$\Rightarrow P_N(k) = \binom{N}{k} \cdot p^k \cdot q^{N-k}$$

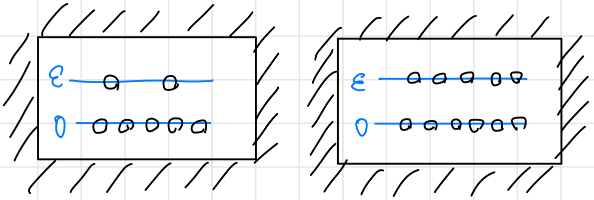
$= \Omega_N(k)$ = Multiplicity = Density of state

(ex) $\frac{P_{1000}(400)}{P_{1000}(500)} \sim 10^{-9}$: Huge difference because of Ω

⇒ From this, we can get the following (Powerfull) Postulate, which is true from now on.

- For a system of large N, there is a strong tendency that the system tends to be in Macroscopic State that maximizes the number of microstates ($=\Omega$) belonging to that macrostate in thermal equilibrium

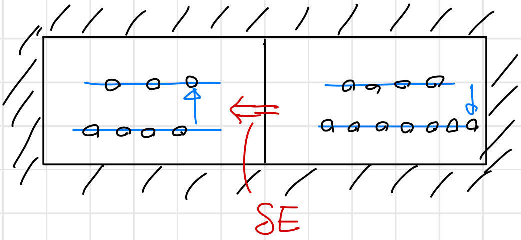
(*) 이제, 간단한 상황을 통해 Ω의 성질을 확인하고, 이를 통해 온도를 엄밀하게 정의하자.



(E_1^0, N_1, V_1) (E_2^0, N_2, V_2)

- Two M-State systems initially isolated
- For simplicity, only 2-energy level available

make these two thermal contact for sufficiently long time
⇒ Thermal equilibrium



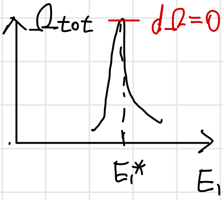
$(E_1, \underbrace{N_1, V_1}_{\text{fixed}})$ $(E_2, \underbrace{N_2, V_2}_{\text{fixed}})$

- What value is E_1?
  ⇒ We should know $E = k \cdot \varepsilon$.
  Where k = number of particles in the excited state.
- Then, the multiplicity of the system

$$\Omega_N(k) \xrightarrow{\text{Macrovariable}} \Omega_N(E, \cancel{V, N})$$

N, V fixed

$= \Omega(E)$ where $E_{tot} = E_1^0 + E_2^0 = E_1 + E_2 = \text{Const.}$



⇒ By the postulate we have seen, $\Omega_{tot}(E_{tot})$ should be maximized.

⇒ $\Omega_{tot}(E_{tot}) = \Omega_1(E_1) \times \Omega_2(E_2)$ ($\because$ Two independent system, think about the multiplicity : composition)

$= \Omega_1(E_1) \times \Omega_2(E_{tot} - E_1)$

Now, we are to find E_1^*, where $\boxed{d\Omega_{tot} = 0}$.

$$\Rightarrow d\Omega_{tot} = \Omega_2(E_2) \times \frac{\partial \Omega_1(E_1)}{\partial E_1} \cdot dE_1 + \Omega_1(E_1) \times \frac{\partial \Omega_2(E_2)}{\partial E_2} \cdot dE_2$$

$$= \Omega_1(E_1) \cdot \Omega_2(E_2) \cdot \left(\frac{1}{\Omega_1} \cdot \frac{\partial \Omega_1}{\partial E_1}\bigg|_{E_1 = E_1^*} - \frac{1}{\Omega_2} \cdot \frac{\partial \Omega_2}{\partial E_2}\bigg|_{E_2 = E_2^*} \right) dE_1 = 0.$$

So, 임의의 E_1에 대해 항상 이 식이 참이기 위해서 $(\because dE_1 + dE_2 = 0)$

$$\therefore \frac{1}{\Omega_1} \cdot \frac{\partial \Omega_1}{\partial E_1}\bigg|_{E_1 = E_1^*} = \frac{1}{\Omega_2} \cdot \frac{\partial \Omega_2}{\partial E_2}\bigg|_{E_2 = E_2^*}$$

식을 ln의 미분형으로 표현하면,

$$\boxed{\frac{\partial}{\partial E_1} \cdot \ln \Omega_1(E_1)\bigg|_{E = E_1^*} = \frac{\partial}{\partial E_2} \cdot \ln \Omega_2(E_2)\bigg|_{E = E_2^*}}$$

이다. 이는 간단하지만 강력한, 위의 가설에서 유도된 식이다.

Condition of thermal equilibrium

⇒ 이 때, 이 조건식의 차원을 살펴보자. $\ln \Omega$는 number이고, E에 대해 미분하니 $[E^{-1}]$의 차원을 가진다. 또한, 0th Law를 보면 이 열평형 조건에서 온도가 정의된다는 사실을 알 수 있다. 따라서, 적절한 상수를 통해 아래와 같이 정의식을 만든다.

$$\boxed{\frac{1}{k_B \cdot T} = \frac{\partial}{\partial E} \cdot \ln \Omega(E)}$$

k_B : Boltzmann Constant [J/K]

⇒ 이는, "macrostate observable T"와 statistic (Probability) origin을 관계하는 관계식이다!

⇒ 따라서, 계의 엔트로피 (Entropy) S를 $S = k_B \cdot \ln \Omega(E)$로 정의한다면, 아래와 같은 관계식을 얻고, 이는 fundamental definition of Temperature 이다. (absolute temperature)

$$\boxed{\frac{1}{T} = \frac{\partial}{\partial E} \cdot k_B \cdot \ln \Omega(E) = \frac{\partial S(E)}{\partial E}}$$

⇒ Thus, by using this equation, Condition of thermal equilibrium is,

$$\boxed{\frac{1}{T_1} = \frac{1}{T_2}}$$

(*) 이제, 열평형 조건식과, 이를 통해 온도를 엄밀하게 정의했으니, Direction of heat flows를 알아보도록 하자. 주어진 조건에서,

$$(E_1^{\circ}, E_2^{\circ}) \xrightarrow[\text{equilibrium}]{} (E_1^*, E_2^*)$$ 이다.

이 때, 평형을 이루는 지점에서 Ω_{tot} 가 최대이므로, 아래 식은 참이다.

$\Omega_1(E_1^*)\,\Omega_2(E_2^*) \geq \Omega_1(E_1^0)\,\Omega_2(E_2^0)$ 양변에 ln을 씌우고 정리하면 (∵ ln 증가함수)

$\Rightarrow \ln\Omega_1(E_1^*) + \ln\Omega_2(E_2^*) \geq \ln\Omega_1(E_1^0) + \ln\Omega_2(E_2^0)$ k_B 곱해서 정리

$\Rightarrow S_1(E_1^*) + S_2(E_2^*) \geq S_1(E_1^0) + S_2(E_2^0)$

$\therefore \Delta S_{tot} = \Delta S_1 + \Delta S_2 \geq 0$: For isolated system, total entropy should be increased

Clausiu's Statement of 2nd Law

For small $\delta S = S_1(E_1^*) - S_1(E_1^0) + S_2(E_2^*) - S_2(E_2^0)$, Energy of system can be described as

$$\begin{cases} E_1^* = E_1^0 + \delta E_1 \\ E_2^* = E_2^0 + \delta E_2 \end{cases}$$

And, by upper statement, $\delta S = \left(\frac{\partial S}{\partial E_1}\cdot\delta E_1 + \frac{\partial S}{\partial E_2}\cdot\delta E_2\right)$

$$= \left(\left.\frac{\partial S}{\partial E_1}\right|_{E_1^0} - \left.\frac{\partial S}{\partial E_2}\right|_{E_2^0}\right)\delta E_1$$

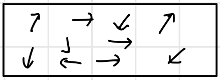
$$= \left(\frac{1}{T_1^0} - \frac{1}{T_2^0}\right)\delta E_1 \geq 0.$$

$\Rightarrow$ This means if $T_2^0 > T_1^0$, $\delta E_1 > 0$. Energy flows from high temperature to low temperature.

3) The first Law of Thermodynamics

< Micro states >

- 6N variables $\{\vec{p}_i, \vec{q}_i\}$



< Macro states >

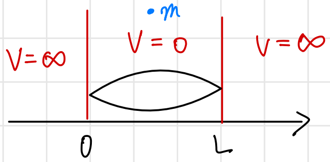
- A few macroscopic observables (variables)
  ex) E, N, V, T, P · · ·

$\Rightarrow$ In thermal equilibrium, the macroscopic properties of system are characterized by a set of functions of states (state variables, 상태함수)

$\Rightarrow$ Macroscopic observables do not change (fixed value) under time evolution or privious history, because they are "functions of states"

↪ If not, 0th Law 위반한다.

(Ex) 약간의 양자역학이 가미된, Infinite Potential well을 고려해보자. (1-D)



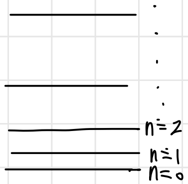
$\hat{H}\cdot\psi(x) = E\cdot\psi(x)$. for this case, $\hat{H} = -\frac{\hbar^2}{2m}\cdot\frac{d^2}{dx^2}$.

$\psi \sim e^{ikx}$ 이고, $\psi(0) = \psi(L) = 0$ 이므로

$\therefore \psi(x) = C\cdot\sin kx$. $k_n = \frac{n\pi}{L}$ 이식을 풀면

$$E_n = \frac{\hbar^2\cdot k_n^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}n^2.$$ → Quantized energy level, discrete value.

$(n = 0, 1, 2 \cdots)$



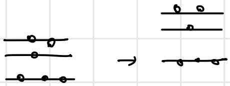
$H(\underbrace{x_1, x_2, x_3, \cdots}_{})$

Internal Parameter.

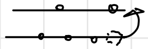
- If $L \to L + \delta L$, E_n shifted, energy changes (External Parameter)
- If $n = i \to j$, Energy changes (Internal Parameter)

⇒ 이처럼, 계의 에너지에 영향을 주는 변화 인자를 구분할 수 있다. 여기서, 아래의 정의가 유래한다.

(i) Work : Energy changes induced by variation of External parameters
(= due to the changes of energy level)
$\Delta E = W$ (Naturally, 계에 가해진 일 개념이다)



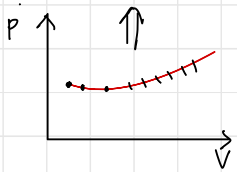
(ii) Heat : Energy changes when all the external parameters remain fixed
$\Delta E = Q$. (계에 흡수된 열)



(iii) Combine (i), (ii) together ⇒ $\boxed{\Delta E = W + Q}$ … The 1st Law of Thermodynamics

⇒ Note that
- ΔE : Energy의 "변화량"
- W, Q Should be defined only through the process (= Energy in transit)

All of these discussions are valid during thermal equilibrium.



System go through the points that all satisfy thermal equilibrium, at every instant moments, So Ω is maximized

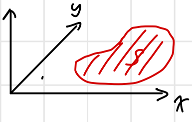
⇒ For infinitesimal process, $dE = đQ + đW$ (or $\delta Q + \delta W$)
↳ Inexactive differential, which means Path-dependent.

(*) Exact vs Inexact.

- Exact is, for $z = f(x,y)$, $df = f(x+dx, y+dy) - f(x,y) = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

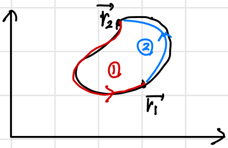
$$\Rightarrow \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y. \qquad = A(x,y)\,dx + B(x,y)\,dy$$

in this case, $\int_a^b df = f(b) - f(a)$ (Path independency)



Pf) $\vec{F} = \left(A(x,y), B(x,y) \right)$ then, $\oint_{\partial S} \vec{F}\cdot d\vec{x} = \int_S d\vec{S}\cdot(\nabla\times\vec{F})$ 여기서는 $\hat{z}$ 방향이니

$(\nabla\times\vec{F})_z = \left(\left(\frac{\partial B}{\partial x}\right)_y - \left(\frac{\partial A}{\partial y}\right)_x \right) \underset{\text{if}}{=} 0$ 이라면, $= 0$ 이므로



$\left(\int_{\vec{r_1}}^{\vec{r_2}} \vec{F}\cdot d\vec{x} \right)_{①} + \left(\int_{\vec{r_2}}^{\vec{r_1}} \vec{F}\cdot d\vec{x} \right)_{②} = 0$. So, $\left(\int_{\vec{r_1}}^{\vec{r_2}} \underbrace{\vec{F}\cdot d\vec{x}}_{=df} \right)_{①} = \left(\int_{\vec{r_1}}^{\vec{r_2}} \underbrace{\vec{F}\cdot d\vec{x}}_{df} \right)_{②}$

즉, 이것의 필요 조건이 df가 exact differential 이다. ⟺ Path Independence

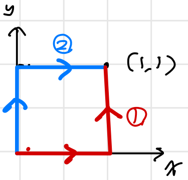
- Inexact differential : naturally path-dependent property.

ex) Let $\text{đ}f = xy\cdot dx + x^2\cdot dy$.

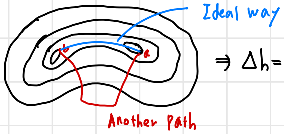
$\int_{(0,0)\,①}^{(1,1)} \text{đ}f = 0 + \int_{y=0}^{y=1} 1^2\cdot dy = 1$

$\neq$

$\int_{(0,0)\,②}^{(1,1)} \text{đ}f = 0 + \int_0^1 xy\,dx = \frac{1}{2}$.



(cf) Contour map



$\Rightarrow \Delta h = h(\vec{r_b}) - h(\vec{r_a})$

4) Heat Capacity

< 1st Law : $\text{đ}Q = dE - \text{đ}W$ >

Question : How much heat should be added to the system, to increase the temperature?

⇒ The answer comes from new definition, Heat Capacity $C \equiv \left(\frac{dQ}{dT}\right)$

이 때, Energy of the system을 T, V의 함수로 간주하자.

(과연 이래도 충분한가? 그렇다!) $E = E(T,V)$

$$\Rightarrow dE(T,V) = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = \text{đ}Q + \text{đ}W.$$

$$\Rightarrow \text{đ}Q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV - \text{đ}W.$$

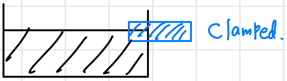
이 때, System이 quasi-static process (slowly enough to remain in thermodynamic equilibrium) 을 따른다고 하면, $\text{đ}W = -PdV$ 이다.

$$\Rightarrow \boxed{\text{đ}Q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] dV}$$

이제, 이 식을 이용해 Heat Capacity under certain condition을 구하자.

① Constant Volume, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$

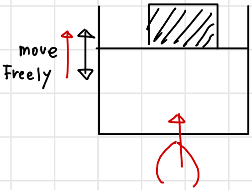
$(dV = 0)$



⇒ 이 때, (Amount of heat) = (Amount of Internal energy change), 외부에서 가해진 heat가 모두 energy로 전환된다.

② Constant Pressure. $C_P = \left(\frac{dQ}{dT}\right)_P = \underbrace{\left(\frac{\partial E}{\partial T}\right)_V}_{= C_V} + \left[\left(\frac{\partial E}{\partial V}\right)_P + P\right]\left(\frac{\partial V}{\partial T}\right)_P$

$(dP = 0)$



$$\Rightarrow C_P - C_V = \left[\left(\frac{\partial E}{\partial V}\right)_P + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

→ extra relation이 더해지면 정리 가능.

(like ideal gas etc...)

↓

In general, we can say this using entropy.

$\left(C_P - C_V = \frac{\alpha^2}{\kappa} V ?\right)$

$\boxed{\therefore C_P > C_V.}$

$\Rightarrow \gamma \equiv \frac{C_P}{C_V} > 1.$ (Adiabatic index)

2. The Ideal Gas

2.1) The equation of State

(*) The Empirical statement of gas

Boyle's Law : $P \propto \frac{1}{V}$ at constant Temperature

Charles's Law : $V \propto T$ at Constant Pressure

$P \propto T$ at Constant Volume.

$P \propto N$

⇒ Empirical Laws combined into one formula:

$$\boxed{PV = Nk_BT}$$ ... The equation of state.

⇒ These Laws were found experimentally, so physicists wanted how to explain this theorically.

To explain this, they made a few assumptions.

(*) Assumptions

a) No inter-molcular interactions

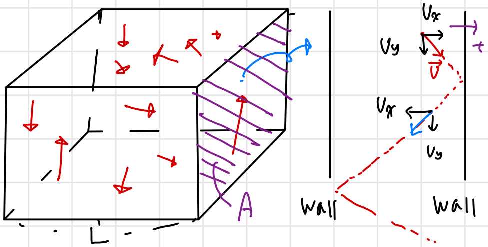
b) Point-like Particles

c) Randomly moving.

d) Elastic collisions 'with the wall': No collisions between Particles because of a).

With these assumptions, Let's use kinetic theory.

⟨N particles in Rectangular box⟩



Before & After the collision of a particle, momentum changes

$|\Delta P_i| = 2mv_x = mv_x - (-mv_x)$

$\Rightarrow F_i = \frac{\Delta P}{\Delta t} = \frac{mv_x^2}{L}$ $\left(\because \Delta t = \frac{2L}{v_x},\right.$ Because no inter-molecular collision$\left.\right)$

So, the force acting on the wall by N particles is

※ $(\Sigma v^2) = (\langle v^2 \rangle) \times N$

$$F = \sum_i F_i = \frac{m}{L}\cdot\sum_i (v_{i,x})^2 \Rightarrow p = \frac{F}{A} = \frac{m}{\underbrace{A\cdot L}_{=V}} \sum_i \overset{\frac{1}{3}v^2}{(v_{i,x})^2}$$

이 때, moment의 정리에 의해, $\langle v_x^2 \rangle = \dfrac{\sum_i (v_{i,x})^2}{N}$ 이므로,

$$\Rightarrow p = \frac{m}{V}\cdot N\cdot\langle v_x^2\rangle = \frac{mN}{3V}\langle v^2\rangle \quad (\because \text{축 방향 구분 의미 X})$$

$v^2 = v_x^2 + v_y^2 + v_z^2$

$$= \frac{2N}{3V}\cdot\left(\frac{1}{2}m\langle v^2\rangle\right) = \frac{Nk_BT}{V} \quad (\because \text{The equation of state})$$

$$\therefore \langle K \rangle = \underbrace{\frac{1}{2}m\langle v^2\rangle}_{\text{microscopic}} = \underbrace{\frac{3k_BT}{2}}_{\text{Macroscopic}}$$

$\Rightarrow$ So, we can get the relation between v^2 and T like this.

$\langle K \rangle = \left\langle \boxed{\frac{1}{2}mv^2} \right\rangle = \frac{1}{2}m\langle v^2\rangle$

cf) $Nk_B = n\cdot N_A\cdot k_B = nR. \Rightarrow PV = nRT.$

2.2) Maxwell-Boltzmann Distribution

- 기체 분자의 속도 분포에 대한 확률 밀도 함수를 유도해보자. 여기서, 우리는 속도의 크기에 대해 분석하고 싶으니 v^2에 대한 확률밀도 함수 $f(v^2)$을 찾고, 이 때 $v^2 = v_x^2 + v_y^2 + v_z^2$, where v_x, v_y, v_z are independent 이므로 아래와 같다.

$\Rightarrow f_t(v^2) = f(v_x^2)f(v_y^2)f(v_z^2)$ (In thermal equilibrium, v_x^2, v_y^2, v_z^2 의 확률 분포는 같다)

이를 만족하는 함수는 지수함수이므로, f를 아래와 같이 표현가능하다.

?

$\Rightarrow f(v_x^2) = C\cdot e^{-av_x^2}$ (사실, boltzmann distribution $e^{-\beta E}$ 에 비례함을 통해 직관적 유도 가능)

$$\Rightarrow \int_{-\infty}^{\infty} dx\cdot f(v_x^2) = C\int_{-\infty}^{\infty} dx\cdot e^{-av_x^2} = 1 \quad \text{(Normalization Condition)}. \quad C\cdot\sqrt{\frac{\pi}{a}} = 1. \quad \therefore C = \sqrt{\frac{a}{\pi}} \quad \cdots ①$$

$\Rightarrow$ Let's use the consequence of the ideal gas : $m\langle v_x^2\rangle = k_BT$. with Probability density $f(v_x^2)$,

$$\Rightarrow m\langle v_x^2\rangle = m\cdot\int_{-\infty}^{\infty} dv_x\left(v_x^2\cdot\sqrt{\frac{a}{\pi}}\,e^{-av_x^2}\right) = k_BT \Rightarrow 2m\sqrt{\frac{a}{\pi}}\cdot I = k_BT,\ , \quad I = \int_0^{\infty} dv_x\left(v_x^2\, e^{-av_x^2}\right)$$

$$I = \int_0^{\infty}\frac{dt}{2av_x}\cdot v_x^2\cdot e^{-t} = \frac{1}{2a\sqrt{a}}\int_0^{\infty}\sqrt{t}\cdot e^{-t}\,dt \quad \left(\text{To calculate integral, } t = av_x^2.\ dt = 2av_x\,dv_x\right)$$

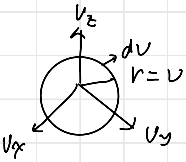
$$= \frac{1}{2a\sqrt{a}}\Gamma\left(\frac{3}{2}\right) = \frac{1}{2a\sqrt{a}}\,\frac{1}{2}\,\Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{4a\sqrt{a}} \quad \left(\because \Gamma(n+1) = n\Gamma(n),\ \Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi}\right)$$

$$\therefore \frac{m}{2a} = k_BT, \quad a = \frac{m}{2k_BT} \quad \cdots ②$$

So, in ①, ② we know C, a.

Finally, we can get the result.

$$f_t(\vec{v}^2) = f(v_x^2)f(v_y^2)f(v_z^2) = C^3 e^{-av^2} = \left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}$$



For conventional purpose, we use final representation.

$$\boxed{f(v) = \left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}}$$

… Maxwell-Boltzmann Distribution.

$\Rightarrow$ If we want to change this into the familiar form, be carefull when you integrate! You need to integrate in d^3v, that is, $d^3v\cdot f(v) = (4\pi v^2 dv)f(v)$.

What we know, $4\pi v^2 f(v)$, is very familiar form.

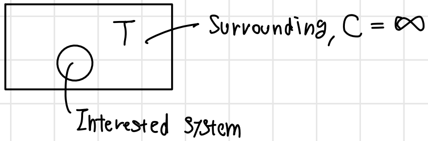
2.3) Equipartition Theorem

- In the Canonical Ensemble, we can show this statement.

$\boxed{P(E) \propto e^{-\beta E}, \ \beta = \frac{1}{k_B T}}$ ↪ In this level, we just adopt this is true.

... Boltzmann Distribution

cf) Canonical Ensemble (T fixed ensemble)



Probability theory 이용, $P \sim W = \frac{N!}{n_1! \cdots n_s!} \Rightarrow P \sim e^{-\beta E}$

Then, total energy of the system is the sum of "each degree of freedom energy".

$E_{tot} = \sum_i \varepsilon_i(x_i) = \varepsilon_1(x_1) + \varepsilon_2(x_2) + \cdots + \varepsilon_n(x_n)$ 이다. 따라서,

Where, $\langle \varepsilon_i \rangle = \int d_n x \cdot \varepsilon_i \, P(E) = \dfrac{\int dx_1 dx_2 \cdots dx_n \cdot \varepsilon_i \cdot e^{-\beta \cdot (\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_n)}}{\int dx_1 dx_2 \cdots dx_n \, e^{-\beta(\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_n)}}$ ↪ Normalization

$$= \frac{\left(\int dx_i \, \varepsilon_i e^{-\beta \varepsilon_i}\right) \prod_{j \neq i} dx_j \, e^{-\beta \varepsilon_j}}{\int dx_i \, e^{-\beta \varepsilon_i} \cdot \prod_{j \neq i} \cdot \int dx_j \, e^{-\beta \varepsilon_j}}$$

$$= \frac{\int dx_i \, \varepsilon_i \, e^{-\beta \varepsilon_i}}{\int dx_i \, e^{-\beta \varepsilon_i}} = -\frac{\partial}{\partial \beta} \cdot \ln\left[\int_{-\infty}^{\infty} dx_i \cdot e^{-\beta \varepsilon_i}\right]$$

⇒ 여기서, 물리적 직관을 발휘해야 한다.

Let $\varepsilon_i(x_i) = \alpha \cdot x_i^2$.

$$\Rightarrow \langle \varepsilon_i \rangle = -\frac{\partial}{\partial \beta} \ln\left[\int_{-\infty}^{\infty} dx_i \, e^{-\alpha \beta x_i^2}\right] = -\frac{\partial}{\partial \beta} \cdot \frac{1}{2} \ln\left[\frac{\pi}{\alpha \beta}\right] = -\frac{1}{2} \cdot \frac{\partial}{\partial \beta}\left[\ln \pi - \ln \alpha - \ln \beta\right]$$

$\boxed{\langle \varepsilon_i \rangle = \frac{1}{2\beta} = \frac{k_B T}{2}}$ (β의 definition : $\beta = \frac{1}{k_B T} = \frac{\partial \ln \Omega(E)}{\partial E}$)

... Equipartition thm

⇒ Single degree of freedom에 해당하는 에너지은 $\langle \varepsilon_i \rangle = \frac{k_B T}{2}$ 이다.

(ex) For $n = 3, (x_1, x_2, x_3) \Rightarrow K = \sum_1^3 \langle \varepsilon_i \rangle = \frac{3 k_B T}{2}$ ... 이는 2.1) 에서 검증한 식이다.

Q. In Quantum mechanics, energy is discrete value... why integral is ok?

→ $\Delta E \ll k_B T$, It works well in our region!

2.4) Specific Heats

- We can define specific heat of the system like this :

$$\left.\begin{aligned} c_v &= \frac{C_v}{N} \text{ or } \frac{C_v}{n} \\ c_p &= \frac{C_p}{N} \text{ or } \frac{C_p}{n} \end{aligned}\right] \text{where Large } C \text{ means heat capacity.}$$

- Now, ideal gas 의 경우에는, $E = \frac{3}{2} N k_B T$ 이므로 다음과 같다. (In monoatomic case)

(i) $c_v = \frac{1}{N}\left(\frac{đQ}{dT}\right) = \frac{1}{N}\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} k_B ;\ (\because dV = 0)$

(ii) For constant pressure,

$$c_p = \frac{1}{N}\cdot\left(\frac{đQ}{dT}\right) = \frac{1}{N}\cdot\left[\frac{dE - đW}{dT}\right]_P \xrightarrow{} = \frac{1}{N}\left[\left(\frac{\partial E}{\partial T}\right)_V + \left\{\cancel{\left(\frac{\partial E}{\partial V}\right)_T} + P\right\}\left(\frac{\partial V}{\partial T}\right)_P\right]$$

E 는 T만의 함수, 아래에서 엄밀하게 보이겠다.

For quasi-static process $\left[\begin{array}{l} P \text{ definable} \\ W = -P\,dV \end{array}\right.$

$$= c_v + \frac{\cancel{P}}{\cancel{N}}\cdot\frac{\cancel{N}k_B}{\cancel{P}}$$

$$= c_v + k_B. = \frac{5}{2} k_B \quad (\text{For 자유도} = 3).$$

$$\boxed{\gamma \equiv \frac{c_p}{c_v} = \frac{5}{3}} \ \ldots \text{adiabatic exponent}$$

(*) E가 ideal gas인 경우, T 만의 함수임을 보이겠다. 여기서 우리가 필요한 가정은 "quasi-static" 뿐이다.

- Let $E = E(T, V)$ then, $dE(T,V) = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = đQ + đW$
- In quasi static, $đW = -P\,dV$.

$\Rightarrow$ As we will see later, enthropy can be related to the heat with temperature : $đQ = T\,dS$

$\Rightarrow$ $T\,dS = dE - đW = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + P\,dV$. T로 나누고, 정리해서 dS에 대한 항등식 구하면,

$$\Rightarrow dS = \underbrace{\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V}_{①} dT + \underbrace{\left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{P}{T}\right]}_{②} dV = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{①'} dT + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{②'} dV.$$

$\Rightarrow$ This is true for all condition of (T, V) so we can say ① = ①′, ② = ②′

$$\left(\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V \quad \cdots ⓐ \\ \left(\frac{\partial S}{\partial V}\right)_T &= \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{P}{T} \quad \cdots ⓑ \end{aligned}\right.$$

이제, S는 상태함수이므로 $S_{TV} = S_{VT}$ 이다. 이를 $\frac{\partial}{\partial V}\cdot ⓐ = \frac{\partial}{\partial T}\, ⓑ$ 로 정리하면

$$\Rightarrow \underbrace{\frac{1}{T}\cdot\frac{\partial^2 E}{\partial V \partial T}}_{①} = -\frac{1}{T^2}\cdot\left(\frac{\partial E}{\partial V}\right)_T + \underbrace{\frac{1}{T}\cdot\frac{\partial^2 E}{\partial T \partial V}}_{①'} + \overset{0}{\overset{\|}{\cancel{\frac{\partial}{\partial T}\left[\frac{N k_B}{V}\right]}}}$$

⇒ E도 상태함수이므로, $E_{VT} = E_{TV}$ 이다. (미분 순서 상관X) 즉, ① = ①' 이므로 위 식을 정리하면,

$\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T = 0$ for all T. 따라서, $\boxed{\left(\frac{\partial E}{\partial V}\right)_T = 0}$ ··· $\boxed{\text{E is not the function of V.}}$

∴ In Ideal gas system, E only depends on the temperature.

3. The 2nd Law

- The only way to tell the direction of time flows.
- Before we go further, let's talk about thermodynamic process.

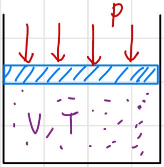
Thermodynamic Process : Transformation, changes of thermodynamic states.

3.1) Quasi-Static Process

→ So slowly performed that the system is in the thermal equilibrium at every moment. $\xrightarrow{\text{Related}}$ 'Reversible process'

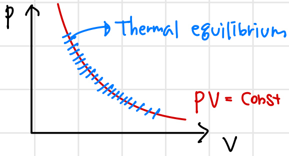
→ Pressure is measured (definable) at every moment : $đW = -PdV$ can be used. Otherwise, you cannot use it.

(ex1)



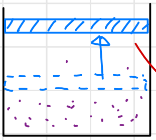
For ideal gas $PV = Nk_BT$, during Quasi-Static Process, we can see that :

$$\begin{cases} P \to P' = P + \delta P \to P'' \to \cdots \\ V \to V' = V + \delta V \to V'' \to \cdots \\ T \to T' = T + \delta T \to T'' \to \cdots \end{cases}$$



Thermal equilibrium at every moment.

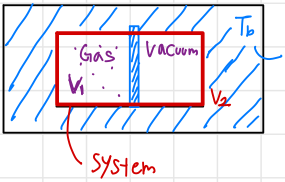
(ex2)



Sudden expansion for very small time interval

Nearly vacuum, molecules not yet reach, Cannot find P.

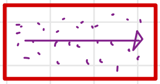
(*) Isothermal expansion.



Heat bath (Reservoir) : T_b is fixed, because heat capacity $C \to \infty$

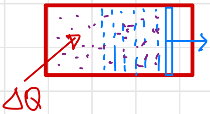
⇒ In thermal equilibrium, $T_b = T_s$.

a) Free expansion : 칸막이 중간 가림판 제거, Non quasi-static process



- $\Delta T = 0 \Rightarrow \Delta E = 0$ for ideal gas
- $\Delta W = 0 \Rightarrow$ No pushing material, no work !
- $\Delta Q = \Delta E - \Delta W = 0 - 0 = 0$. No heat exchange.

b) Quasi-static isothermal expansion (Reversible?)



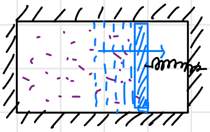
- Pressure can be defined always : $đW = -PdV$.
- $\Delta T = 0 \Rightarrow \Delta E = 0$
- $\Delta W = \int_1^2 đW = -\int_1^2 PdV = -\int_{V_1}^{V_2} \frac{Nk_BT}{V} dV = -Nk_BT \cdot \ln\left(\frac{V_2}{V_1}\right)$

$\cdot\ \Delta Q = \Delta E - \Delta W = -\Delta W$.

$V_2 > V_1$ (Expansion) : $\Delta W < 0 \quad \Delta Q > 0$

$V_2 < V_1$ (Compression) : $\Delta W > 0 \quad \Delta Q < 0$

(*) Adiabatic expansion. : Thermally insulated & Quasi-static



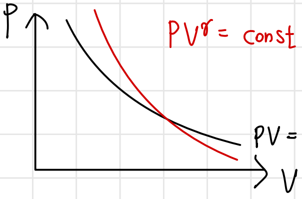
$\cdot\ đQ = 0 = dE - đW$

- $C_V = \left(\frac{\partial E}{\partial T}\right) = \left(\frac{dE}{dT}\right)$ (Ideal gas condition)
- $đW = -PdV$

$\Rightarrow C_V dT + PdV = 0$ dT를 P, V에 대해 정리하면 아래와 같다.

$\Rightarrow C_V \cdot \left[\frac{PdV + VdP}{Nk_B}\right] + PdV = 0. \Rightarrow \underbrace{(C_V + Nk_B)}_{= C_P} PdV + C_V \cdot VdP$ 양변을 C_VVP로 나누고 적분하면 $\gamma = \frac{C_P}{C_V}$ 이므로

$\Rightarrow \int \frac{\gamma}{V} dV + \int \frac{dP}{P} = 0. \Rightarrow \ln PV^\gamma = C.$ $\boxed{\therefore PV^\gamma = \text{Const}}$ … state equation of adiabatic expansion.



$PV^\gamma = $ const. : more steep because $\gamma > 1$

$PV = $ const : Isothermal expansion

3.2) The Second Law (Statement based on the observation)

- Clausius's statement. (= No perfect refrigerator)

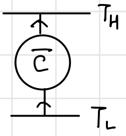
  ⇒ No process is possible whose sole effect is the transfer of heat from a colder to hotter body.

  = with no other effect. (여타의 효과)

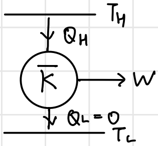
- Kelvin's statement (= No perfect engine)

  ⇒ No process is possible whose sole effect is the complete conversion of heat into work.

Equivalence!



⟨Clausius violater⟩

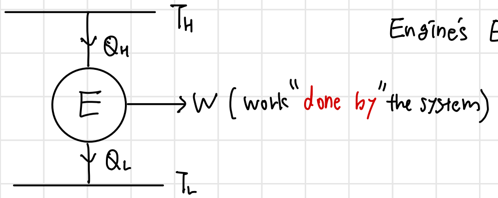


⟨Kelvin violater⟩

Q. How about isothermal expansion? Its $\Delta E = 0$. So, $\Delta Q + \Delta W = 0$. Isn't it Kelvin violater?

A. No! why?

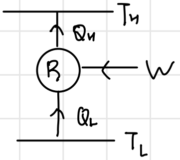
- Engine : A system operating a cyclic process that converts heat into work.



Engine's Efficiency $\eta \equiv \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \leq 1$

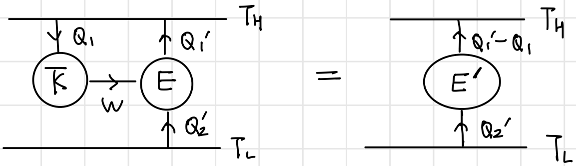
where $Q_H, Q_L > 0$ in this diagram.
(arrow indicate the sign).

cf) Refrigerator



(*) Proof of the equivalence of Kelvin & Clausius's statement.

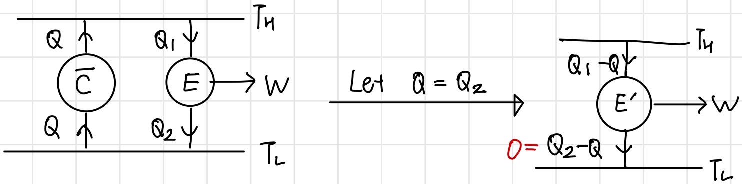
(i) $K \to C$: Let's assume we have Kelvin violator $\overline{K}$.



$$Q_1' - Q_1 = W + Q_2' - Q_1$$
$$= Q_2' \quad (\because W = Q_1)$$

So, $(Q_1' - Q_1) = Q_2'$ 이므로,
외부에서 일 없이 T_L에서 T_H로 Heat transfer가 발생한다. ⇒ E' = Clausius violator $\overline{C}$

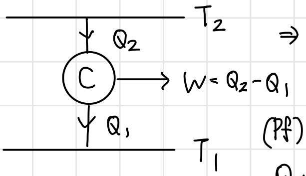
(ii) $C \to K$: Let's assume we have $\overline{C}$.



∴ E' = Kelvin violator $\overline{K}$

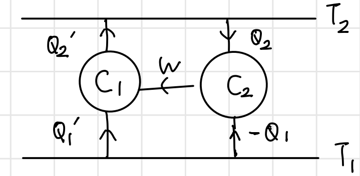
3.3) The Carnot Engine.

Def) Any reversible engine working between two given temperatures. (Based on Carnot's assumption)



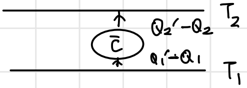
⇒ If we think the diagram like this, we can say one strong argument.
"If $W > 0$, Q_1 and Q_2 are also positive".

(Pf) 우선, $Q_1 \neq 0$ 이다. (Kelvin 2nd Law)
$Q_1 < 0$ 이라고 해보자. 정의에 의해, $Q_1' > 0$ 이다. 그러면 다음과 같이 카르노 엔진 연결이 가능하다.
(∵ Reversible engine!)



$$\overset{+}{\underbrace{W}} = \overset{\therefore +}{\underbrace{Q_2}} - \overset{+}{\underbrace{Q_1}}, \quad Q_2' = W + Q_1' \text{이다.} \Rightarrow \overset{+}{\underbrace{Q_2'}} = \overset{+}{\underbrace{Q_2}} \overset{+}{\underbrace{-Q_1}} + \overset{-}{\underbrace{Q_1'}}.$$

∵ 전제 조건에 의해, $W > 0$ 이다. (C_2로 분석) $> Q_2$.
따라서, $Q_2' - Q_2 > 0$ 이고, $Q_1' - Q_1 > 0$ 이다.
이는, 알짜 열기관이 Clausius violator가 되므로 불가능하다.

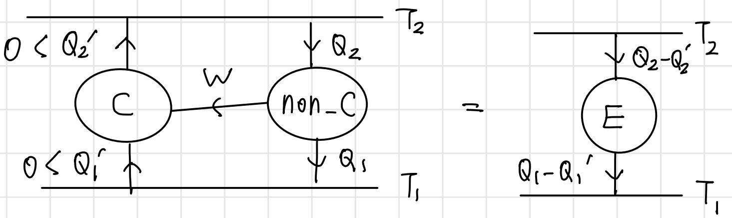


따라서, 전제가 틀렸다. ∴ $W > 0$ 일 때 $Q_1 > 0$. $Q_2 = Q_1 + W > 0$.

중요한 정리인 카르노 정리를 알아보자.

(*) Carnot's theorem : No engine operating between the two temperatures is more efficient than the Carnot engine.

Pf) Let's assume the following situation



Clausius's

$W = Q_2 - Q_1 = Q_2' - Q_1' \Rightarrow Q_2' = (Q_1' - Q_1) + Q_2$, 이때, By 2nd Law, $Q_2 \geq Q_2'$
$Q_1 \geq Q_1'$.

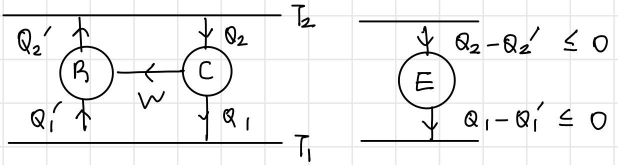
Then, we can now see, $\eta_{nc} = \frac{W}{Q_2}$. $\eta_c = \frac{W}{Q_2'} \Rightarrow \eta_{nc} \leq \eta_c$.

If $\eta_{nc} = \eta_c$, then $Q_2 = Q_2'$. $Q_1 = Q_1'$. so, now non_c is Carnot engine! ■

(*) Corollary

① All reversible engine have the same efficiency.

Pf) We know $\eta_B \leq \eta_c \Rightarrow \frac{W}{Q_2'} \leq \frac{W}{Q_2} \Rightarrow Q_2' \geq Q_2$.



Not to violate Clausius's 2nd Law,

We have $\left.\begin{array}{l} Q_2 = Q_2' \\ Q_1 = Q_1' \end{array}\right] \Rightarrow \eta_B = \eta_c$.

∴ So, any reversible engine has the same efficiency!

⇒ Based on these statements ($\eta \leq \eta_c$, $\eta_B = \eta_c$) we can think the simplest condition.

Let's think reversible, idle-gas working, frictionless idealized engine.

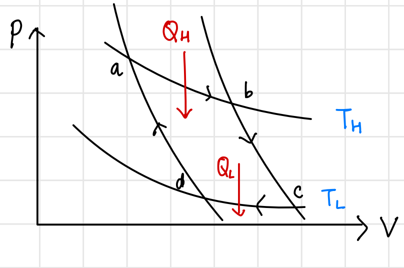
⇒ From reversible, during heat transfer, no Temperature of system change!
(온도가 바뀐다면; 어느 한방향에서는 열이 낮→높이 되어서 클라우시우스 2법칙 위배)

⇒ T_H, T_L 두 온도의 가역기관에서, 각각의 온도와 같을 때만 heat transfor 가능 (실제로는 불가능)

⇒ Then, engine이 $T_H \longleftrightarrow T_L$일 때는 열교환 X : Adiabatic process!

애매...

- 이제, 이러한 배경을 바탕으로, 간단한 Carnot cycle 분석하자.



Engine : Cyclic process, Converts heat into work.

(i) ab (Isothermal Expansion)

$\Delta T = 0,\ \Delta E = 0 = \Delta Q_1 + \Delta W_1.$

$\Rightarrow \Delta Q_1 = -\Delta W_1 = \int_{V_a}^{V_b} P\,dV = Nk_BT_H \cdot \ln \frac{V_b}{V_a} > 0.$

이때, $P_aV_a = P_bV_b$ 이다.

(ii) bc (Adiabatic expansion)

$PV^{\gamma} = \text{Const} \Rightarrow V^{\gamma-1} \cdot T = \text{Const}.$ ($\because$ ideal gas equation)

$\Rightarrow \left(\frac{V_b}{V_c}\right)^{\gamma-1} = \frac{T_L}{T_H}$ $\quad \Delta Q_2 = 0$ 이다, $\Delta W_2 = \Delta E_2 = C_V \Delta T = C_V (T_L - T_H)$

(iii) cd (Isothermal Compression)

$\Delta T = 0.\ \Delta E_3 = 0.\ \Delta Q_3 = -W_3 = Nk_BT_L \ln\left(\frac{V_d}{V_c}\right) < 0$

(iv) da (Adiabatic Compression). $\Delta Q_4 = 0.$ $\quad \left(\frac{V_a}{V_d}\right)^{\gamma-1} = \frac{T_L}{T_H}$

$\Delta W_4 = \Delta E_4 = C_V(T_H - T_L).$

$\Rightarrow \Delta E_{tot} = (\Delta E_1 + \Delta E_3) + (\Delta E_2 + \Delta E_4) = 0$ also, $\frac{V_b}{V_c} = \frac{V_a}{V_d}. \Leftrightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d}.$

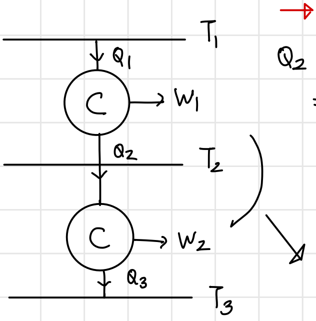
$\Rightarrow \frac{Q_L}{Q_H} = \frac{-\Delta Q_3}{\Delta Q_1} = \frac{Nk_BT_L \ln\left(\frac{V_c}{V_d}\right)}{Nk_BT_H \cdot \ln\left(\frac{V_b}{V_a}\right)} = \frac{T_L}{T_H}$ 이므로 $\boxed{\eta_c = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}}$

$\therefore$ 모든 reversible engine에 $\eta = \eta_c = 1 - \frac{T_L}{T_H}$ 이다. $\quad ; \eta(T_L, T_H)$

지금까지 Temperature의 정의는
- 0th law → not rigorous
- Ideal gas Law
  - → only for ideal gas
  - → gas property dependent

(*) Defining temperature scale using Carnot engine efficiency.

→ Universal way to define temperature scale



$Q_2 = Q_1 - W_1.$

$= Q_1 - \eta Q_1$

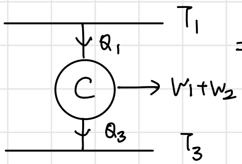
$= [1 - \eta(T_1, T_2)]\, Q_1 \longrightarrow$

$Q_3 = Q_2 - W_2.$

$= Q_2 - \eta(T_2, T_3)\, Q_2$

$= Q_2\,(1 - \eta(T_2, T_3))$

$= [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)]\, Q_1.$



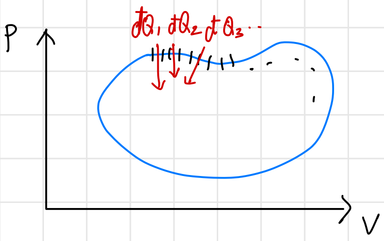
$\Rightarrow Q_3 = Q_1\,(1 - \eta(T_1, T_3))$

$\therefore 1 - \eta(T_1, T_3) = (1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3))$

Let's guess $1 - \eta = \frac{f(T_3)}{f(T_1)} = \frac{f_3 \sim \alpha T_3}{f_1 \sim \alpha T_1} = \frac{T_3}{T_1}.$

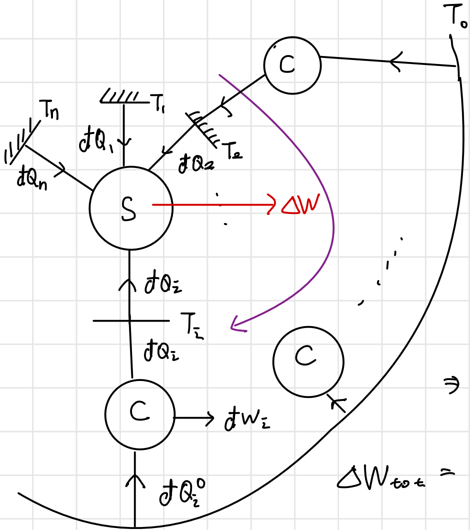
↳ Linear eg

3.4) Clausius's theorem



$\Rightarrow$ In the real world, cycle is not that simple and beautiful.

(*) Let's think about the situation below.



$\text{đ}Q_i > 0$: System S absorbs heat

$\Rightarrow \Delta W = \sum_i \text{đ}Q_i$.

Because of the carnot engine property, we know

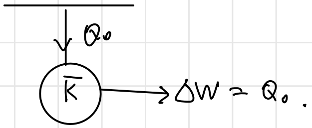
$$\left\{ \frac{\text{đ}Q_i}{\text{đ}Q_i^0} = \frac{T_i}{T_0} \Rightarrow \frac{\text{đ}Q_i}{T_i} = \frac{\text{đ}Q_i^0}{T_0} \right.$$

where $\text{đ}Q_i^0 = \text{đ}W_i + \text{đ}Q_i$.

$$\Rightarrow \text{đ}Q_i^0 = \left(\frac{T_0}{T_i}\right) \cdot \text{đ}Q_i \quad Q_i^0 = \sum \text{đ}Q_i^0 = T_0 \cdot \sum_i \left(\frac{\text{đ}Q_i}{T_i}\right)$$

$$\Delta W_{tot} = \Delta W_s + \Delta W_C = \Delta W + \sum_i \text{đ}W_i.$$

$$= \Delta W + \sum_i \left(\text{đ}Q_i^0 - \text{đ}Q_i\right) = \sum_i \text{đ}Q_i^0 = T_0 \cdot \sum_i \left(\frac{\text{đ}Q_i}{T_i}\right) = Q_0.$$

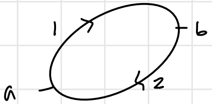


If $Q_0 > 0$. $\Rightarrow Q_0 \leq 0. \Rightarrow T_0 \cdot \sum_i \left(\frac{\text{đ}Q_i}{T_i}\right) \leq 0$.

Clausius's violator!

$\therefore \sum_i \frac{\text{đ}Q_i}{T_i} \leq 0$. if $\text{đ}Q_i$ infinetisimal value, $\oint \frac{\text{đ}Q}{T} \leq 0$.

$\Rightarrow$ For any cycle, $\oint \frac{\text{đ}Q}{T} \leq 0$. The equality holds for the reversible process.



3.5) Entrophy

$\int_a^b \frac{\text{đ}Q_{rev}}{T}$ 를 고려하자. For reversible process, $\oint \frac{\text{đ}Q_{rev}}{T} = \left[\int_a^b \frac{\text{đ}Q}{T}\right]_1 + \left[\int_b^a \frac{\text{đ}Q}{T}\right]_2 = 0$

$$\Rightarrow \left[\int_a^b \frac{\text{đ}Q_{rev}}{T}\right]_1 = \left[\int_a^b \frac{\text{đ}Q_{rev}}{T}\right]_2 \qquad \boxed{\therefore \int_A^B \frac{\text{đ}Q_{rev}}{T} \equiv S(B) - S(A)} \qquad \left(dS \equiv \frac{\text{đ}Q_{rev}}{T}\right)$$

... Path independence

⇔ Exact differential

(*) Property

ⓐ For arbitary process, There is upper bound of heat exchange

Pf) $\oint \frac{\text{đ}Q}{T} = \int_A^B \frac{\text{đ}Q}{T} + \int_B^A \frac{\text{đ}Q_{rev}}{T} \le 0.$ $\quad \int_A^B \frac{\text{đ}Q}{T} \le \int_A^B \frac{\text{đ}Q_{rev}}{T} = S(B) - S(A)$

or, $\frac{\text{đ}Q}{T} \le \frac{\text{đ}Q_{rev}}{T} = dS \qquad \therefore \text{đ}Q \le \text{đ}Q_{rev} = TdS.$

... upper bound of heat exchange.

ⓑ For thermally isolated system, $\text{đ}Q = 0. \Rightarrow T \cdot dS \ge 0.$ $\boxed{\therefore dS \ge 0}$

⇒ 열적 고립계의 엔트로피는 감소하지 않는다.

⇒ 평형상태에서 S가 maximized.

... Another form of 2nd Law of thermodynamics

Holds for both Rev & Irrev process

- For reversible (quasi-static) process, $\text{đ}Q = TdS.$ $\text{đ}W = -PdV + \sum_i f_i\, dx_i$

(Volume work) generalized force displacement

$$dE = \text{đ}Q_{rev} + \text{đ}W_{rev}$$
$$= TdS - PdV + \mu dN + \cdots \quad = dE(S, V, N, \cdots)$$
$$= \text{đ}Q_{irrev} + \text{đ}W_{irrev} \quad \Rightarrow \text{đ}Q_{irr} \le \text{đ}Q_{rev} = TdS.$$

이고, $\text{đ}W_{irr} \ge \text{đ}W_{rev} = -PdV$

Natural variables (extensive)

↪ T, P도 generalized force, dS, dV가 displacement

(ex) $\mu \cdot dN$

(chemical potential) × (number of particle)

T가 달라지면, dS가 flow

= P가 달라지면, dV가 flow

= μ가 달라지면, dN이 flow ...

ex) Compression $\quad \text{đ}W_{irr} \ge \text{đ}W_{rev} > 0$

$dV < 0$

$dV > 0.$

expansion $\quad \text{đ}W_{irr} \ge \text{đ}W_{rev}$

(System이 한 일) $\quad -\text{đ}W'_{irr} \ge -\text{đ}W'_{rev}$

$\text{đ}W'_{irr} \le \text{đ}W'_{rev}$

⇒ 이제, dE(S,V,N)은 다음과 같이 표현될 수 있다.

$$dE = TdS - PdV + \mu dN$$
$$= \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN \Rightarrow \left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \left(\frac{\partial E}{\partial V}\right) = -P, \left(\frac{\partial E}{\partial N}\right) = \mu$$

$$\Rightarrow \frac{P}{T} = \frac{-\left(\frac{\partial E}{\partial V}\right)_S}{\left(\frac{\partial E}{\partial S}\right)_V}$$ (where N is fixed)

(*) Mathmatical Skills of Partial derivatives

In $x(y,z)$, $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$, where $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$.

$$\Rightarrow dx = \left(\underbrace{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y}_{=1}\right) dx + \left[\underbrace{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x + \left(\frac{\partial x}{\partial y}\right)_z}_{=0}\right] dy = 0 \quad \text{for} \quad \forall\, x(y,z)$$

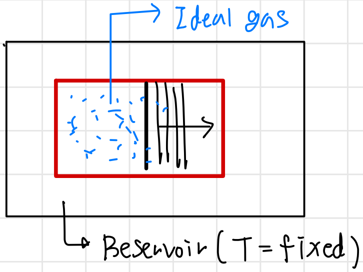
$$\therefore \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} \cdots ①, \quad \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = -1 \cdots ②$$ 이제, 이를 이용하자.

$$\frac{P}{T} = -\left(\frac{\partial E}{\partial V}\right)_S \Big/ \left(\frac{\partial E}{\partial S}\right)_V = -\left(\frac{\partial E}{\partial V}\right)_S \cdot \left(\frac{\partial S}{\partial E}\right)_V \quad (\because ①)$$

$$\Rightarrow \frac{P}{T} \cdot \left(\frac{\partial V}{\partial S}\right)_E = -1 \times -1 = 1. \quad (\because ②) \qquad \boxed{\therefore \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E}$$

3.6) Examples

① Reversible isothermal expansion ($\Delta T = 0$)



For ideal gas, we know $E = E(T)$. $\Rightarrow \Delta E = \Delta Q + \Delta W = 0$

$$\Rightarrow \Delta Q = -\Delta W = N k_B T \cdot \ln\left(\frac{V_2}{V_1}\right)$$

- How about Entropy ?

$$\Rightarrow \Delta S = \int_1^2 dS = \int_1^2 \frac{đQ_{rev}}{T} = \frac{\Delta Q}{T} \quad (\because T = \text{fixed})$$

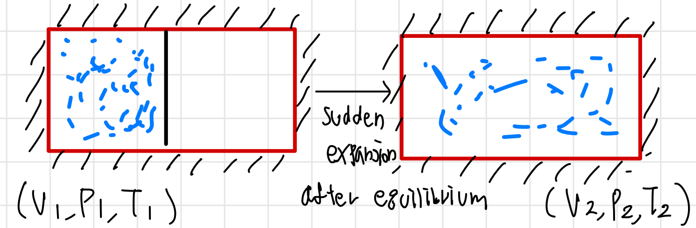
(i) $$(\Delta S)_{sys} = \frac{\Delta Q}{T} = N k_B \ln\left(\frac{V_2}{V_1}\right) > 0$$

(ii) $$(\Delta S)_{bath} = \frac{-\Delta Q}{T} = -N k_B \ln\left(\frac{V_2}{V_1}\right) < 0.$$

$$(\Delta S)_{tot} = (\Delta S)_{sys} + (\Delta S)_{bath} = \underline{\underline{0}}$$

$(\because$ reversible$)$

② Joule's expansion (Irreversible)



$\Delta Q = 0$ $(\because$ Adiabatic process$)$

$\Delta W = 0$ $(\because$ Free expansion$)$

$$\Rightarrow \Delta E = \Delta Q + \Delta W = 0 = \Delta E(T).$$

$$\therefore T_1 = T_2.$$

- How about Entropy ? → It is irreversible, so we cannot say directly "ΔS"

⇒ Instead, Let's consider reversible path from $(V_1, P_1, T_1) \rightarrow (V_2, P_2, T_2)$

(∵) 가역과정/비가역과정 모두, initial → Final state가 동일하면, ΔS가 가역과정으로 구해진다.
→ 엔트로피는 상태함수이기 때문.

(Assume Isothermal reversible process)

$$\Rightarrow TdS = \text{đ}Q_{rev} = \overset{0}{\cancel{dE}} + PdV \Rightarrow N \cdot k_B T \cdot \ln\left(\frac{V_2}{V_1}\right) = \int TdS. \quad \therefore \Delta S = Nk_B \ln\left(\frac{V_2}{V_1}\right)$$

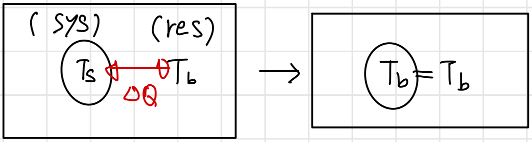
$$\Rightarrow \therefore (\Delta S)_{sys} = Nk_B \ln\left(\frac{V_2}{V_1}\right) > 0.$$

$$\Rightarrow (\Delta S)_{bath} = 0 \quad (\because \text{No heat exchange}).$$

$$\Delta S_{tot} = Nk_B \ln\left(\frac{V_2}{V_1}\right) > 0.$$

$(\because$ Irreversible$)$

(*) How to get $(\Delta S)_{tot}$ only using system variables



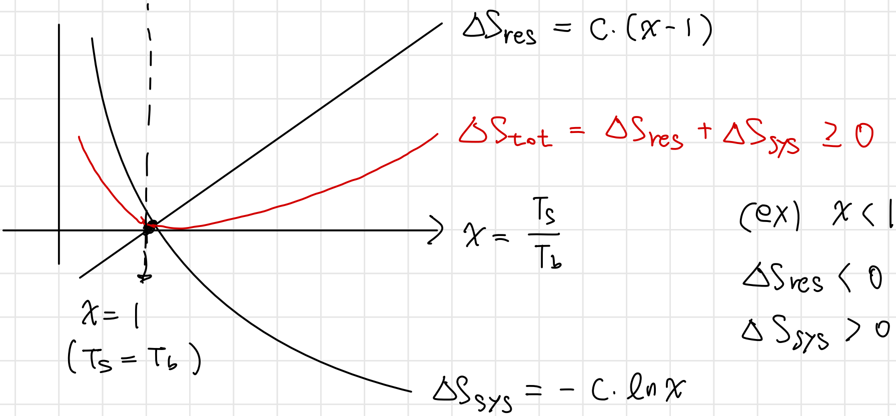
$$\left(\begin{array}{l}\Delta Q = C \cdot (T_b - T_s) \quad (C: \text{비열}) \\ (\Delta S)_{res} = \int \frac{\text{đ}Q}{T} = -\frac{\Delta Q}{T_b}\end{array}\right.$$

$$\Rightarrow (\Delta S)_{res} = C \cdot \left(\frac{T_s}{T_b} - 1\right)$$

$$(\Delta S)_{sys} = \int \frac{\text{đ}Q_{rev}}{T} = \int \frac{C\,dT}{T}$$

$$= C \cdot \ln\left(\frac{T_b}{T_s}\right) \quad (C: \text{constant})$$

$$\Rightarrow (\Delta S)_{tot} = (\Delta S)_{sys} + (\Delta S)_{res} = C \cdot \left[-\ln x + x - 1\right] \geq 0 \qquad \left(x \equiv \frac{T_s}{T_b}\right)$$



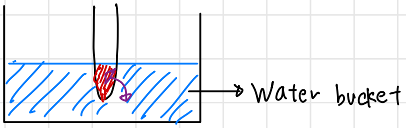
(ex) $x < 1 \; (T_s < T_b)$

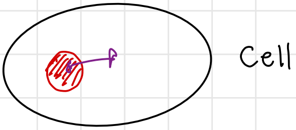
$$\left.\begin{array}{l}\Delta S_{res} < 0 \\ \Delta S_{sys} > 0\end{array}\right] \Delta S_{tot} > 0$$

(*) Limitation of $\Delta S \geq 0$

(i) System should be isolated in order to apply $\Delta S \geq 0$

⇒ Example case : Test tube, Cell





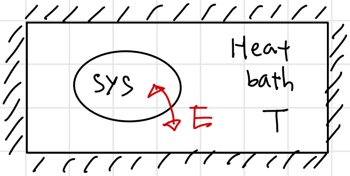
⇒ The red area (System) is the region we are interested in, which is interacting with the surrounding. (Non-isolated system)

(ii) Measurable / Controllable : $S(E, V, N)$

4. Thermodynamic Potentials

4.1) Extremum principles

관심있는 system을 외부의 이상적인 heat bath가 둘러싸고 있다고 가정하자.



- $E_{res} \gg \Delta E$: Assume E_{res} is constant (ideal reservoir)

  ⇒ T of reservoir is constant.

★ ↪ Thermal contact with the system long enough time
↪ The role of reservoir : To fix T.

System temperature → T

$$\frac{(S)}{\text{non-isolated}} \qquad \frac{(S)+(B)}{\text{isolated}} \Rightarrow \Delta S \geq 0.$$

- $\Delta S_{tot} = (\Delta S)_{sys} + (\Delta S)_{bath}$ where $(\Delta S)_{bat} = \int \frac{\text{đ}Q_{rev}}{T} = \frac{\Delta Q_{bath}}{T} = -\frac{\Delta Q_{sys}}{T}$

$$= \left[(\Delta S)_{sys} - \frac{\Delta E_{sys} - \Delta W_{sys}}{T}\right]$$

→ 이는 모두 system quality 이므로, 이제 Reservoir의 detailed information이 필요 없다. "Sys" subscript를 drop하자.

$$= \frac{1}{T}\left[T\Delta S - \Delta E + \Delta W\right] \geq 0$$

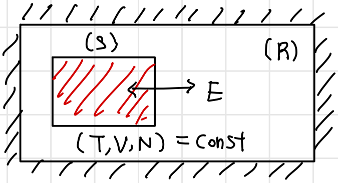
$$\boxed{\therefore \Delta E - T\Delta S \leq \Delta W}$$

... System information 에 의한 식

⇒ T가 충분히 오랜 시간이 지난 뒤 열평형에서 system의 온도이고 $\Delta E, \Delta S, \Delta W$는 각각 system의 내부에너지 변화 / 엔트로피 변화 / system에 해준 일의 변화 이다.

- 이제, 이 식을 기반으로 여러 주어진 상황에서 계의 Potential을 나타내는 물리량을 정의해보자.

(*) Helmholtz Free energy



- T, V, N이 일정하게 유지되면서 E 교환이 가능한 System이 주어졌다.
- 이는 isothermal process (?) including no mechanical work

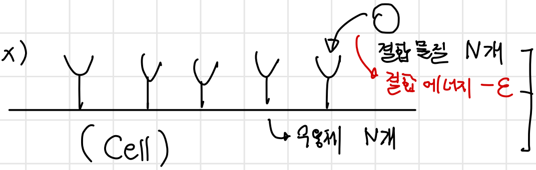
⇒ 위식을 ($\Delta E - T\Delta S \le \Delta W$) 미소 변화량에 대해 보면,

$$\Rightarrow d(\underbrace{E - TS}_{\equiv F\text{ (Helmholtz free energy)}}) \le \text{đ}W \qquad (\because dT = 0)$$

⇒ No mechanical work, $\boxed{dF \le 0}$ → In equilibrium, $dF = 0$, $F \to F_{min}$.

(i) Described by Itself (System)
(ii) Reservoir only fixes Temperature : Don't need to consider detailed informations
(iii) New Extremum Principle : upper bound exist.
(iv) "Balance" between $dE \le 0$ and $dS \ge 0$.

(ex)

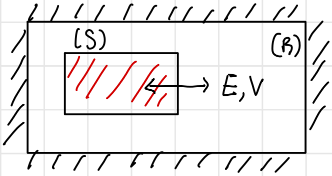


최저 에너지 되려면 모두 결합해야 한다. ⇒ $E = -N \cdot \varepsilon$

→ Impossible!

dE 가 아닌, dF 가 최소. 따라서, 몇몇 분자는 결합 X. Balance Point에서 평형.

(*) Gibbs Free energy

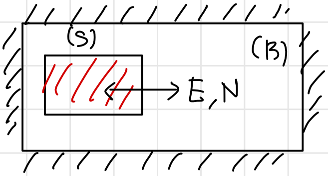


- 이번에는, E와 V가 변화 가능하고 (T, P, N)이 Constant.
  (P가 일정하니 V가 변화)
- Isothermal and isobaric involving mechanical work.
- $\text{đ}W = \underbrace{-PdV}_{\text{Volume work}} + \text{đ}W_{other}$

$$\Rightarrow dE - TdS + PdV = d(\underbrace{E - TS + PV}_{\equiv G\text{ (Gibbs Free energy)}}) \le \text{đ}W_{other}.$$

⇒ If no other work (⇔ $\text{đ}W_{other} = 0$), $\boxed{dG \le 0}$. → In equilibrium, $dG = 0$, $G \to G_{min}$

(*) Grand Potential



· 이번에는 E와 N이 교환 가능하고, $(T, V, \underbrace{\mu}_{\to \text{Potential}})$ 가 constant.

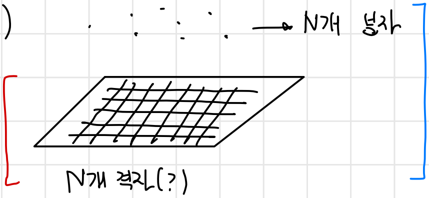
$\Rightarrow \bar{d}W = \underbrace{\mu dN}_{\text{Chemical work}} + \bar{d}W_{other}$ 이면, 마찬가지 방식으로

$$\Rightarrow d(\underbrace{E - TS - \mu N}_{\equiv \Phi\ (\text{Grand Potential})}) \le \bar{d}W_{other}$$

$\Rightarrow$ If no other work $(\bar{d}W_{other} = 0)$, $\boxed{d\Phi \le 0}$ $\to$ In equilibrium, $d\Phi = 0$, $\Phi \to \Phi_{min}$

$\Rightarrow$ 이 3가지 상황에서 정의된 계의 Potential은, 계를 무엇으로 잡느냐에 따라 사용해야 하는게 달라진다.

(Ex)



(T, V, N) 일정, E만 변화 $\Rightarrow dF = 0$.

$\Rightarrow$ Depending on the picture, different potential

$\Rightarrow$ But, answer must be same!

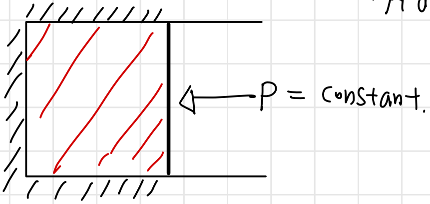
N, E 변화. T, V, μ 일정

$\Rightarrow d\Phi = 0$

(*) Entalpy

+ Isobaric

· Adiabatic involving mechanical work



$$\Rightarrow \bar{d}Q = 0. \quad dE = \cancel{\bar{d}Q} + \bar{d}W^{rev} = -PdV + \bar{d}W^{rev}_{other}$$

$$\Rightarrow (dE + PdV) = d(\underbrace{E + PV}_{\equiv H\ (\text{Entalpy})}) = \bar{d}W^{rev}_{other} \le \bar{d}W^{irr}_{other}$$

$\Rightarrow$ If no other work $(\bar{d}W_{other} = 0)$, $\boxed{dH \le 0}$ $\to$ In equilibrium, $dH = 0$, $H \to H_{min}$

(*) What kind of Constraint Condition is given in the Problem?

문제 풀기 전

Check point.

4.2) Legendre Transformation

- $dE = TdS - PdV + \underset{\text{Particle exchange}}{\underline{\mu dN}} = dE(S,V,N) \longrightarrow S(E,V,N)$

External Parameter : S, V, N

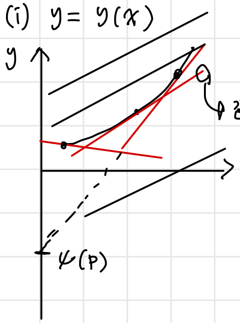
$\updownarrow \; \updownarrow \; \updownarrow$

Internal Parameter : T, P, μ

$\downarrow$ more easy to control / measure.

$\Rightarrow$ Let $y = y(x_1, x_2, \cdots, x_n)$ then $P_i \equiv \dfrac{\partial y}{\partial x_i}$. y를 P_i의 function으로 표현하자.

(i) $y = y(x)$



→ Tangent slope family for every point : $P = \dfrac{dy}{dx}$.

↳ 같은 기울기 가져도, 이 slope만 진짜 함수의 정보를 대변한다.

$$\Rightarrow \frac{y - \psi}{x - 0} = P. \qquad \therefore \psi = y(x) - xP.$$

이제, $y'(x) = P$. $x = y'^{-1}(P)$ 이므로

$$\boxed{\therefore \psi = y\left(y'^{-1}(P)\right) - y'^{-1}(P) \cdot P = \psi(P).}$$

Now, we have $y = y(x) \Leftrightarrow \psi = \psi(P)$. $\qquad dy = Pdx \longleftrightarrow d\psi = -xdP$

$$d\psi(P) = \underbrace{dy - Pdx}_{=0} - xdP = -xdP$$

① Entalpy : we now use $(V \rightarrow P)$

$$H \equiv E + PV \Rightarrow dH = dE + d(PV) = TdS - PdV + \overset{\text{입자 무시 가정}}{\cancel{\mu dN}} + PdV + VdP = TdS + VdP$$

$$\Rightarrow dH(S,P) = TdS + VdP. = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\boxed{\therefore \left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V}$$

② Helmholtz Free Energy $(S \rightarrow T)$

- $F = E - TS$

$$\Rightarrow dF = dE - d(TS) = TdS - PdV - TdS - SdT = \underbrace{-(PdV + SdT)}_{= \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV}$$

$$\boxed{\therefore S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T.}$$

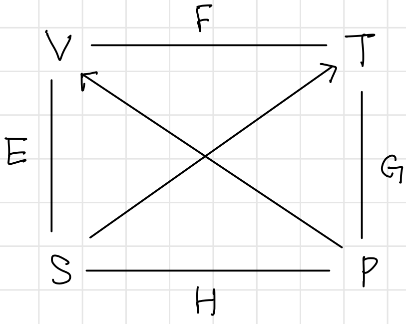
③ Gibbs Free Energy ($S \to T$, $V \to P$)

$$G = E - TS + PV$$

$$\Rightarrow dG = dE - d(TS) + d(PV) = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\boxed{\therefore\ S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T}$$

(*) Thermodynamic Rectangle.



- (T, S) (P, V) conjugate.
- Arrow 방향은 + sign.
-

ex) $\left(\frac{\partial E}{\partial V}\right)_S = -P.$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

4.3) Maxwell's relation

- $dE = TdS - PdV$ ⟶ 4가지가 각각 독립이 아니라, 연관되어있음. $dE(S, V)$

$$\Rightarrow \left(\frac{\partial}{\partial V}\right)_S \underbrace{\left(\frac{\partial E}{\partial S}\right)_V}_{=T} = \left(\frac{\partial}{\partial S}\right)_V \underbrace{\left(\frac{\partial E}{\partial V}\right)_S}_{-P} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

- $dH(S, P)$ 는?

$$\Rightarrow \left(\frac{\partial}{\partial P}\right)_S \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial}{\partial S}\right)_P \left(\frac{\partial H}{\partial P}\right)_S \qquad \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

- $dF(T, V)$ 는?

$$\Rightarrow \left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T. \qquad \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

- $dG(T, P)$ 는?

$$\left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial P}\right)_T \qquad \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P.$$

의 rectangle 확인 가능.

(*) General relationship between C_V and C_P through Maxwell relation.

- $đE = đQ + đW = TdS - PdV$
- $đQ|_V = TdS = C_V dT \quad (dV = 0)$
- $đQ|_P = dE + PdV = d(E + PV) = dH|_P = C_P dT \quad (dP = 0)$

$$\left[\begin{array}{l} C_P = T\left(\frac{\partial S}{\partial T}\right)_V \\ C_V = T\left(\frac{\partial S}{\partial T}\right)_P \end{array}\right. \Rightarrow đQ = TdS(T,P)$$

$$= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_P}_{C_P} dT + T\left(\frac{\partial S}{\partial P}\right)_T \underbrace{dP(T,V)}_{}$$

$$= \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\therefore đQ = \left[C_P + T\cdot\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\right]dT + T\cdot\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_T dV$$

if $dV = 0$, $đQ = C_V dT$. $\Rightarrow$ $C_V = C_P + T\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$

→ But, $\frac{\partial S}{\partial P}$ 같은 항은 다루기 어려움. Maxwell relation 이용하자.

we know, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$. $\boxed{\alpha \equiv \frac{1}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_P}$ … Isobaric expansion coefficient

$\left(\frac{\partial P}{\partial T}\right)_V$ 도, T가 늘어남에 따라 P가 증가, 측정 쉽지 않음. (꽉 막은 실린더 가열!)

지금 조건에서, $dV = 0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{-\alpha V}{-\kappa V} = \frac{\alpha}{\kappa}. \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

… Isothermal Compressibility

$$\boxed{\therefore C_P - C_V = VT\cdot\frac{\alpha^2}{\kappa}} \qquad (\because T\cdot -\alpha V\cdot\frac{\alpha}{\kappa})$$

→ For any material

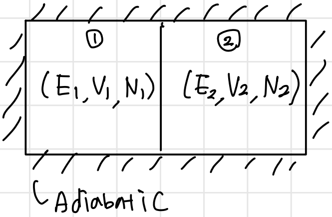
(eg) $PV = Nk_BT$ (Ideal gas), $V = \frac{Nk_BT}{P}$ 이므로

$$\left[\begin{array}{l} \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk_B}{PV} = \frac{1}{T} \\ \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V}\frac{Nk_BT}{P^2} = \frac{1}{P} \end{array}\right.$$

$$\Rightarrow C_P - C_V = VT\left[\frac{1}{\left(\frac{1}{P}\right)}\right] \times \frac{1}{T^2} = \frac{PV}{T} = Nk_B$$

$\therefore C_P - C_V = Nk_B$.

4.4) Equilibrium Conditions



- 초기 각각 분리된 평형에서, Partition 통해 E, V, N 변화. .
- In Final, equilibrium,

$$\delta S_{tot} = \delta S_1 + \delta S_2 (E_2, V_2, N_2)$$

$$= \left(\frac{\partial S_1}{\partial E_1}\delta E_1 + \frac{\partial S_1}{\partial V_1}\delta V_1 + \frac{\partial S_1}{\partial N_1}\delta N_1\right) + \left(\frac{\partial S_2}{\partial E_2}\delta E_2 + \frac{\partial S_2}{\partial V_2}\delta V_2 + \frac{\partial S_2}{\partial N_2}\delta N_2\right)$$

where $\delta S_1 = -\delta S_2$, $\delta V_1 = -\delta V_2$, $\delta N_1 = -\delta N_3$

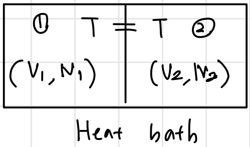
대입해서 $\delta E_1, \delta V_1, \delta N_1$으로 묶고 정리하면

$$\Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\delta N_1 \geq 0.$$

- If $T_1 > T_2$, $\delta E_1 < 0 \Rightarrow T_1 = T_2$ ... Thermal equilibrium
- If $P_1 > P_2$, $\delta V_1 > 0$. $\Rightarrow P_1 = P_2$ ... mechanical equilibrium
- If $\mu_1 > \mu_2$, $\delta N_1 < 0 \Rightarrow \mu_1 = \mu_2$ ... Chemical equilibrium

(*) Helmholtz energy로 eq condition 구해보자.

⇒ Isothermal condition.



$$\delta F_{tot} = \delta F_1 + \delta F_2$$

$$= \left(\frac{\partial F_1}{\partial V_1}\cdot\delta V_1 + \frac{\partial F_2}{\partial V_2}\delta V_2\right) = -(P_1 - P_2)\delta V_1 \leq 0.$$

If $P_1 > P_2$, $\delta V_1 > 0$. $\longrightarrow P_1 = P_2$

4.5) Euler's equation

- $dE = TdS - PdV + \mu dN \Rightarrow E(S, V, N)$

if we change the size of the system : $E(\alpha S, \alpha V, \alpha N) = \alpha E$.

$$\Rightarrow E((1+\varepsilon)S, (1+\varepsilon)V, (1+\varepsilon)N) = E(S,V,N) + \frac{\partial E}{\partial S}\varepsilon S + \frac{\partial E}{\partial V}\varepsilon V + \frac{\partial E}{\partial N}\varepsilon N$$

$$= E(S,V,N) + \varepsilon(TS - PV + \mu N) = (1+\varepsilon)E.$$

$$\boxed{\therefore E = TS - PV + \mu N}$$ ... Euler's equation

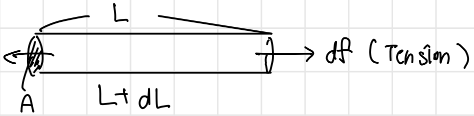
$$\xrightarrow{\text{derivative}} dE = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

So, $\boxed{SdT - VdP + Nd\mu = 0}$ … Gibb's Dahem relation (?)

→ Not independent, somehow related (?)

4.6) Examples

#1. Elastic rod



at constant T.

- Young's modulus

$$\Upsilon = \frac{\sigma}{\varepsilon} = \frac{\frac{df}{A}}{\frac{dL}{L}} = \frac{L}{A}\left(\frac{\partial f}{\partial L}\right)_T$$

- We know α (expansion coefficient at constant f) $\updownarrow$ P

$$\alpha_f = \frac{1}{L}\cdot\left(\frac{\partial L}{\partial T}\right)_f$$

→ Isothermal expansion 으로 분석해보자.

- $dE = TdS + \underbrace{fdL}_{} \rightarrow dW_{other}$

- Isothermal 이니 $dF = d(E-TS) \Rightarrow dF(T,L) = -SdT + fdL$

$$= \left(\frac{\partial F}{\partial T}\right)_L dT + \left(\frac{\partial F}{\partial L}\right)_T dL$$

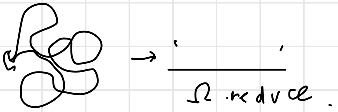
$$\therefore S = -\left(\frac{\partial F}{\partial T}\right)_L \quad f = \left(\frac{\partial F}{\partial L}\right)_T.$$

$$\xrightarrow[\text{Maxwell relation}]{} \left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L = \left(\frac{\partial f}{\partial L}\right)_T\left(\frac{\partial L}{\partial T}\right)_f = \left(\frac{YA}{L}\right)\left(L\alpha_f\right) = YA\alpha_f$$

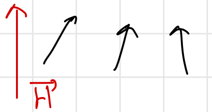
So, $\Delta Q = T\Delta S = T\cdot YA\alpha_f(\Delta L) > 0$ if $\alpha_f > 0$.

< 0 if $\alpha_f < 0$

→ Polymer:



#2 Paramagnetism



(Independent magnetic moment)

$dE = TdS - MdH$ (M= total magnetic moment $= mV$)

$\chi \equiv \lim_{H\to 0}\frac{m}{H}$ (magnetic susceptibility) ⟶ $m = \chi\cdot H$ (small volume)

- Isothermal magnetization. ($H\uparrow$)

$$\Rightarrow dF = d(E-TS) = -SdT - MdH = \left(\frac{\partial F}{\partial T}\right)_H dT + \left(\frac{\partial F}{\partial H}\right)_T dH$$

$$\therefore S = -\left(\frac{\partial F}{\partial T}\right)_H \quad M = -\left(\frac{\partial F}{\partial H}\right)_T.$$

$$\longrightarrow \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial \chi H \underbrace{V}_{\text{Constant (V도, 안변한다)}}}{\partial T}\right)_H = H\cdot V\left(\frac{\partial \chi}{\partial T}\right)_H$$

From Curie's Law, $\chi \propto \frac{1}{T}$. $\Rightarrow \left(\frac{\partial S}{\partial H}\right)_T = HV\cdot \underbrace{\left(\frac{\partial \chi}{\partial T}\right)_H}_{(-)\text{ 이다.}} < 0.$

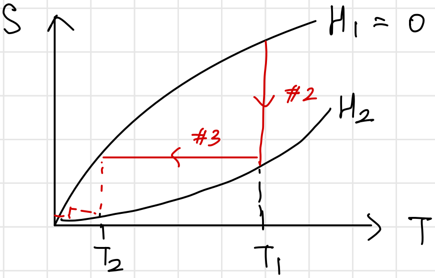
$$\Rightarrow \Delta Q = T\Delta S = HV\cdot\left(\frac{\partial \chi}{\partial T}\right)_H \cdot \Delta H < 0$$

#3. Adiabatic demagnetization

From #2, $dS(T,H) = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH = 0$. (Adiabatic)

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_H} = \frac{-HV\left(\frac{\partial \chi}{\partial T}\right)_H}{\frac{C_H}{T}} = -\frac{THV}{C_H}\left(\frac{\partial \chi}{\partial T}\right)_H > 0$$

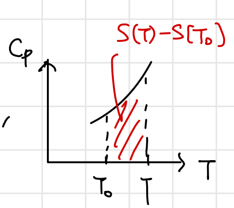
$(\because C_H \equiv \left(\frac{dQ}{dT}\right)_H = T\left(\frac{\partial S}{\partial T}\right)_H)$ $\Rightarrow$ Demagnetization $\longrightarrow$ Cooling.



~ Midterm

4.7) The Third Law

One notices $C_p = T \cdot \left(\frac{\partial S}{\partial T}\right)_p \Rightarrow S(T) - S(T_0) = \int_{T_0}^{T} \frac{C_p(T')}{T'} dT'$



Q. what is reference value? ⟶ Third law : $S(T=0)$ as ref.

$$\left(\begin{array}{l} S = k_B \cdot \ln \Omega(E) \\ E \to E_0 : \underline{\Omega(E_0) = 1} \Leftrightarrow \text{Non-degenerate} \end{array} \right] \Rightarrow \boxed{\text{As } T \to 0,\ S \to 0}$$

(ground state) (Quantum mechanic에서 온 사실)

→ What about degeneracy?

... The Third Law

(cf) $\Delta G = \Delta H - T\Delta S$

Plank : $T \to 0 ; S \to 0$ 득득.

In internal equilibrium

(반론) Nuclear spins : Crystal 생각해보자 $\langle T \sim T_0 \rangle$

$I \to 2I+1$

$\Rightarrow \frac{1}{2} \to 2 \cdot \frac{1}{2} + 1 = 2$. ↑ ⋯ ↓ ⋯ ↓ ⋯ ↑ very weak spin-spin interaction $\Omega = 2^N$, $S_0 = N \cdot k_B \ln 2$ Z오?

⤳ $T \to 0$ 이면 ↑ − ↑ − ↑ − ↑ ⟵ Interaction each other가 강한 영향,
$(T \ll T_0)$

$\Rightarrow$ As $T \to 0+$, $S \to S_0$ (우리가 관심있는 aspect의)
$= 0$

(cf) Simon's 3rd Law Statement.

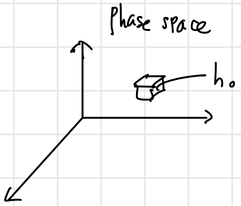
- The contribution to the entropy of a system by each aspect of the system which is in (=different subsystem) the internal thermodynamic equilibrium tends to zero as $T \to 0$

(*) Classical system

$$\Omega = \frac{1}{h_0^N} \int d\vec{P_1}\, d\vec{P_2} \cdots d\vec{P_N} \int d\vec{q_1}\, d\vec{q_2} \cdots d\vec{q_N}$$

$$\Rightarrow S = k_B \cdot \ln \left[\frac{1}{h_0} \int d\vec{P_1} \int d\vec{q_1} \right]^N$$

$$= N k_B \cdot \ln \left[\int d\vec{P} \int d\vec{q} \right] - N \cdot k_B \ln h_0 .$$



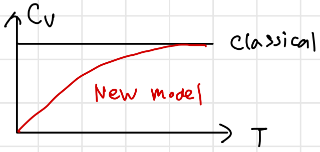
(*) Consequences

i) $S(T=0, X) \to 0$. $\left(\frac{\partial S}{\partial X}\right)_T \to 0$ as $T \to 0$

cf) $C_X = T \cdot \left(\frac{\partial S}{\partial T}\right)_X = \left(\frac{\partial S}{\partial \ln T}\right)_X = 0$
($\ln T \to -\infty$ $S \to 0$)

ii) $S(T, X) - S(T=0, X) = \int_0^T \frac{C_X(T')}{T'} dT'$ $T'=0$ 일때 $\frac{1}{T'}$ diverges, so

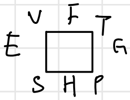
$$\boxed{\therefore \lim_{T \to 0} C_X(T) \to 0}$$



ex) $C_V = \frac{3}{2} N k_B$
in classical model

iii) $\left(\frac{\partial S}{\partial P}\right)_T = 0 \iff \alpha = \frac{1}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_P = 0$ Thermal expansion stops.

at $T \to 0$.



iv) ~~$S = C_v \ln T + R\cdot\ln V + \text{const}$~~ No ideal gas at $T \to 0$

~~$C_p - C_v = R$~~

$C_v \to 0,\ \ln T \to -\infty$

v) Curie's Law ($\chi \propto \frac{1}{T}$)

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H = VH\underbrace{\left(\frac{\partial \chi}{\partial T}\right)_H}_{\sim -\frac{c}{T^2}}$$

⇒ breaks down

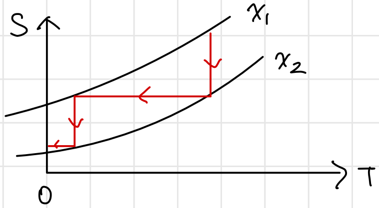
↓ by 3rd Law ↓

0 ⇐ $T \to 0$ ⇒ diverge

$T \to 0$,

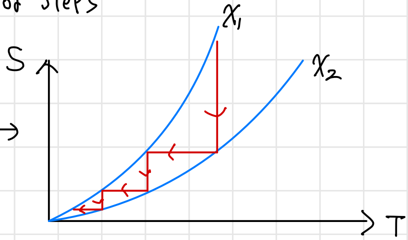
Interaction이 중요해지고 기존의 유효했던 법칙/model이 breaks down.

vi) Never reach $T=0$ in a finite numbers of steps



(but, $T=0$ 일 때 $S \to 0$)

Third Law

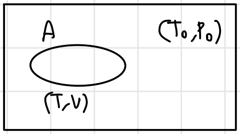


Q. Carnot engine with $T_L = 0$?

$\varepsilon = 1 - \frac{T_L}{T_H} = 1$, Kelvin violation?

⇒ 3법칙은 2법칙과 다른, 독립적인 법칙.

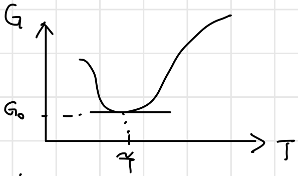
4.8) Stability



N: fixed. (T, V) 변화 가능

$\Rightarrow G = E - T_0 S + P_0 V$

i) $V \to$ fixed. $T \to$ Fluctuates around $\tilde{T}$



$$\Rightarrow G(T) = G_0(\tilde{T}) + \left(\frac{\partial G}{\partial T}\right)_V \Delta T + \frac{1}{2}\left(\frac{\partial G}{\partial T}\right)_V^2 (\Delta T)^2 + \cdots$$

$$\Rightarrow \left.\left(\frac{\partial G}{\partial T}\right)_V\right|_{T=\tilde{T}} = 0 = \left(\frac{\partial E}{\partial T}\right)_V - T_0\left(\frac{\partial S}{\partial T}\right)_V = \left.\left(1 - \frac{T_0}{T}\right)\left(\frac{\partial E}{\partial T}\right)_V\right|_{T=\tilde{T}}$$

$(TdS = dE + PdV)$

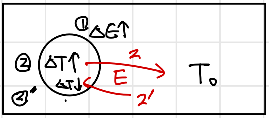
$\boxed{\therefore \tilde{T} = T_0}$ 평형조건

⇝ Either max / min 가능. min으로 정하자. (which mean stability)

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_V \geq 0 \Rightarrow \left[\frac{T_0}{T^2}\left(\frac{\partial E}{\partial T}\right)_V + \cancelto{0}{\left(1-\frac{T_0}{T}\right)\left(\frac{\partial^2 E}{\partial T^2}\right)_V}\right] \geq 0$$

$$\boxed{\therefore \left(\frac{\partial E}{\partial T}\right)_V \geq 0 \quad \text{or} \quad C_v \geq 0}$$

... Le Chatelier's principle.



ii) T fixed $(T = T_0)$ V fluctuates around $\tilde{V}$

$$\Rightarrow G(V) = G_0(\tilde{V}) + \left(\frac{\partial G}{\partial V}\right)_T \Delta V + \frac{1}{2}\left(\frac{\partial^2 G}{\partial V^2}\right)_T (\Delta V)^2 + \cdots$$

$$\Rightarrow \left(\frac{\partial G}{\partial V}\right)_T = 0 = \left(\frac{\partial E}{\partial V}\right)_T - T_0\left(\frac{\partial S}{\partial V}\right)_T + P_0 \qquad dE = TdS - PdV$$

$$= \cancelto{0}{(T-T_0)\left(\frac{\partial S}{\partial V}\right)_T} - (P - P_0) \qquad \boxed{\therefore P = P_0}$$

평형조건

$$\left(\frac{\partial^2 G}{\partial V^2}\right)_T \geq 0 . \Rightarrow \boxed{-\left(\frac{\partial P}{\partial V}\right)_T \geq 0. \quad \text{or} \quad \kappa \geq 0.} \qquad \left(\text{Remind: } \kappa \equiv \frac{-1}{V}\cdot\left(\frac{\partial V}{\partial P}\right)_T\right)$$

iii) Density fluctuations. (?)

$$N \cdot \frac{\tilde{V} - V}{V\tilde{V}}$$

Density $n = \frac{N}{V}$ ⇒ mean value $\tilde{n} = \frac{N}{\tilde{V}}$

$$\Delta n = n - \tilde{n} = N \cdot \left(\frac{1}{V} - \frac{1}{\tilde{V}}\right) = -\frac{\tilde{n}\,\Delta V}{\tilde{V}^{\cancel{2}}} \quad \left(= \frac{N}{\tilde{V}} \cdot \left(\frac{-\Delta V}{V}\right)\right)$$

$$\Rightarrow \langle(\Delta n)^2\rangle = \left(\frac{\tilde{n}}{\tilde{V}}\right)^2 \langle(\Delta V)^2\rangle$$

$$\Rightarrow P(V)\,dV \propto e^{-\beta G(V)}\,dV \quad \text{where} \quad G(V) = G_0(\tilde{V}) + \frac{1}{2}\left(\frac{\partial^2 G}{\partial V^2}\right)_T (\Delta V)^2$$

$$= \frac{1}{2}\,\frac{1}{\tilde{V}\kappa}(\Delta V)^2$$

$$\Rightarrow P(V)\,dV = B \cdot \exp\left[-\frac{1}{2}\cdot\frac{(\Delta V)^2}{k_B T_0 \tilde{V} \kappa}\right] dV$$

$$\langle(\Delta V)^2\rangle = k_B T_0 \tilde{V} \kappa .$$

For critical point : $\left(\frac{\partial P}{\partial V}\right)_T = 0.$

$\Rightarrow \kappa \to \infty, \ \langle(\Delta n)^2\rangle \to \infty.$

$\therefore \langle(\Delta n)^2\rangle \propto \kappa.$

5. Phase Transitions

5.1) Phase equilibrium

- a single component system of two phases; 1 & 2 at $\underbrace{\text{constant } T \,\&\, P}$

$\Rightarrow$ Gibbs Potential

$G = E - TS + pV$

$\Rightarrow$ Can exist together (coexist or mixed)

$\Rightarrow G = g_1 N_1 + g_2 N_2$ $\quad \left[\begin{array}{l} g_i : i \text{ phase의 Gibbs energy per particle.} \\ N_i : \text{numbers of particle in phase } i \end{array} \right.$

is minimized at equilibrium

$dG = \cancel{VdP - SdT}^{\,0} + \sum \underbrace{\mu_i}_{= g_i} dN_i$

(sec 22.5)

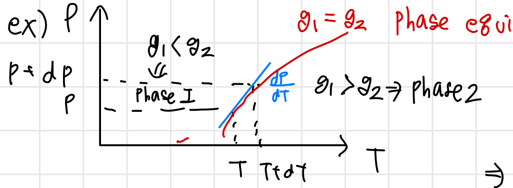
< At equilibrium > $dG = 0 \Rightarrow g_1 dN_1 + g_2 dN_2 = 0 \quad (N_1 + N_2 = N)$

$\Rightarrow (g_1 - g_2) dN_1 = 0$

$$\boxed{g_1(T,P) = g_2(T,P)}$$

... Def of coexistance of 2 phases (phase equilibrium)

ex)



$g_1 = g_2$ phase equilibrium line (Solution line, Phase boundary)

$\Rightarrow$ Coexist at phase boundary ($g_1 = g_2$ for (T,P))

$\Rightarrow g_1(T+dT, P+dP) = g_2(T+dT, P+dP)$

$$\Rightarrow \cancel{g_1(T,P)} + \underbrace{\left(\frac{\partial g_1}{\partial T}\right)}_{= -S_1} dT + \underbrace{\left(\frac{\partial g_1}{\partial P}\right)}_{= +v_1} dP$$

$$= \cancel{g_2(T,P)} + \underbrace{\left(\frac{\partial g_2}{\partial T}\right)}_{= -S_2} dT + \underbrace{\left(\frac{\partial g_2}{\partial P}\right)}_{= v_2} dP$$

$(S_1 - S_2)dT + (v_2 - v_1)dP = 0$

particle 1개에 해당하는 에너지

$\Rightarrow \underbrace{d\varepsilon} = Tds - pdv \leadsto dg(T,P) = -\underbrace{s}dT + \underbrace{v}dP$

s ↳ Entropy per particle

v → Volume per particle

$$\boxed{\therefore \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}}$$

small s

... Clausius – Clapeyron equation.

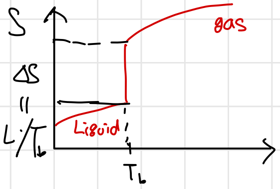
Remind) $C_x = T \cdot \left(\frac{\partial S}{\partial T}\right)_x$, $L \equiv \Delta Q_{rev} = T\Delta S$ (Latent heat) $\quad (x = P, V, H \cdots)$

Capital S

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta S / N}{\Delta v} = \frac{L/N}{T \Delta v} = \frac{l}{T \cdot \Delta v} = \frac{L}{T \cdot \Delta V}$$

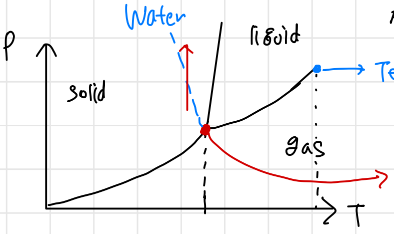
↳ C_x가 $T = T_c$에서 $\exists$ spike.

$$\left(l = T\Delta s = T \cdot \frac{\Delta S}{N} = \frac{L}{N} \right)$$



(ef) $dP = \frac{L \, dT}{T \Delta V}$. $\Rightarrow \Delta P = \frac{L}{\Delta V} \cdot \ln\left(\frac{T}{T_0}\right)$ ($\because L, \Delta V$ T independent 가정)

$\therefore P = P_0 + \underbrace{\frac{L}{\Delta V}}_{\text{Very small}} \ln\left(\frac{T}{T_0}\right) \uparrow \rightarrow \frac{dP}{dT}$ is steep for liquid-solid phase boundary



Not gas or liquid, fluid : Continuous change

Terminate : Critical point. $\Delta v = v_\ell - v_g = 0$ ($T > T_c$: No S-shaped)

$$\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta v}$$

Triple point (coexist 3 phases)

⟨Typical phase diagram⟩

ex) Vapor pressure : Determine phase boundary of liquid and gas ($\overset{N\ell}{L}$ = temperature independent 가정)

gas
Liquid

$$\frac{dP}{dT} = \frac{\ell}{T\Delta v} = \frac{\ell}{Tv_2}$$

($\Delta v = v_2 - v_1 \approxeq v_2$ where $v_2 \gg v_1$)

An ideal gas ⇒ $Pv_2 = k_B T$. (양변 N 나눔)

$$\int \frac{dP}{P} = \frac{\ell\, dT}{k_B T^2} \qquad \left(\frac{dP}{dT} = \frac{\ell P}{k_B T^2}\right)$$

$$\Rightarrow \ln P = -\frac{1}{k_B T}. \quad \therefore P = P_0 \exp\left(-\frac{\ell}{k_B T}\right)$$

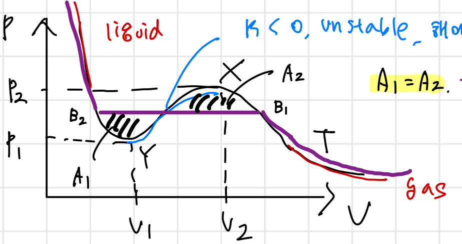
5.2. The van der Waals gas

이상기체 ⇒ 분자간 interaction X. 다른 model 필요.

- The equation of state for the vdW gas of one mole.

$$\left(P \oplus \underbrace{\frac{a}{V^2}}_{\text{intermolecular interaction}}\right)\left(V \ominus \underbrace{b}_{\text{excluded volume}}\right) = RT. \iff PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

(at $V \gg b$, $V \gg \sqrt{\frac{a}{P}}$ ⇒ $PV = RT$)

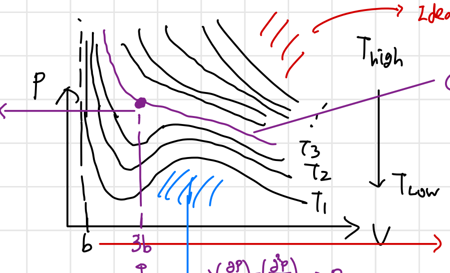


$K < 0$, unstable 해에서 제외

$A_1 = A_2$.

Maxwell construction

$P_c = \frac{a}{27b^2}$ Critical point



Ideal-like region

$T_c = 8a/27Rb$

Critical Isotherm

⇒ 이 온도 밑으로도 S-shape.

V → b 일때

P 가 shoots up.

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0..$$

S-shaped graph

For $P > P_2$, $P < P_1$, $\left(\frac{\partial P}{\partial V}\right)_T \le 0 \longrightarrow K = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T \ge 0$ ⇒ stable.

Where $\left|\frac{\partial P}{\partial V}\right|_T$ is small ⇒ K is large ⇒ gas

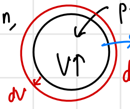
Where $\left|\frac{\partial P}{\partial V}\right|_T$ is large ⇒ K is small ⇒ liquid.

(Q) $K = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ 가 양/음수 둘다 보임.

⇒ K<0은 말이 안됨 (unstable)

P fluctuation에서, K<0이면 P↑ ⇒ V↑.

Then,



→ 외부에 대해 일 : P 다시 ↑.

$dW = -PdV < 0$.

⇓

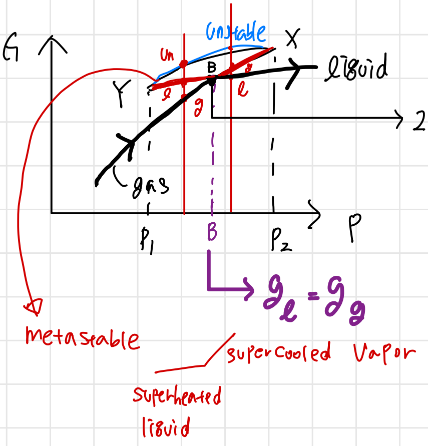
unstability

For $P_1 < P < P_2$ $\quad dG = -S\cancel{dT} + VdP$ $\Rightarrow G(P_1,T) - G(P_0,T_0) = \int_0^{P_1} V\,dP$

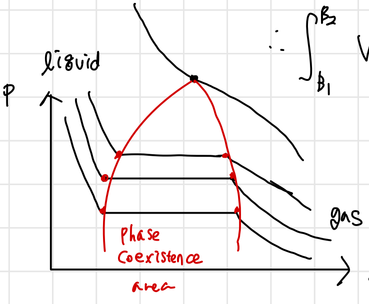
$= 0$

=(Area between V(P) and P axis)

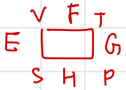
($\because V = \left(\frac{\partial G}{\partial P}\right)_T$)



$\therefore \int_{B_1}^{B_2} V\,dP = 0$



5.3. Nucleation

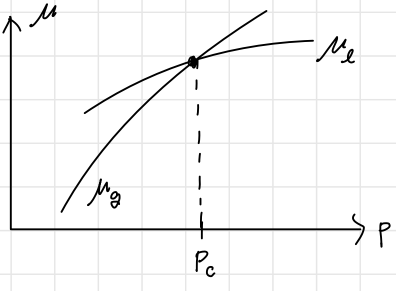


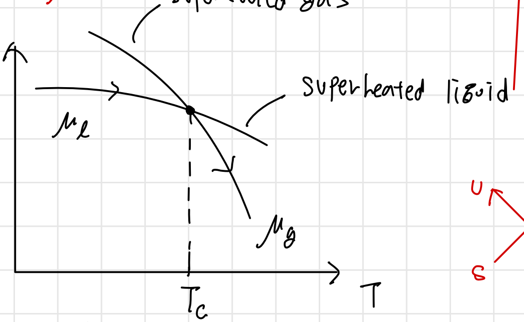
• At constant T, P, $G = E - TS + PV$ ($dE = TdS - PdV + \sum_i \mu_i N_i$)

$\Rightarrow dG = \cancel{-SdT + VdP} + \sum_i \mu_i dN_i = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_1 - \mu_2)dN_1 = 0$.

$= 0$

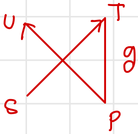
$\boxed{\therefore \mu_1 = \mu_2}$ … Rewriting g into μ





metastable

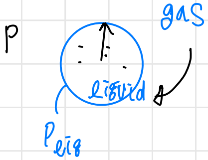
(순간적으로 도달 가능)



$\Rightarrow \left(\frac{\partial \mu}{\partial P}\right)_T = v > 0$ $\qquad \Rightarrow \left(\frac{d\mu}{dT}\right)_P = -s < 0$

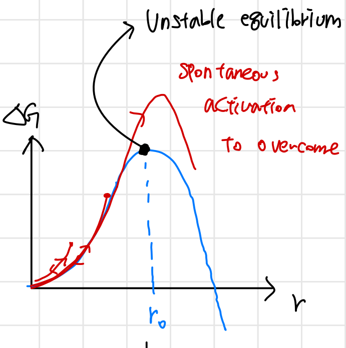
Q. Why the thermodynamically most stable state sometime doesn't form

⇒ Suppose a liquid droplet in equilibrium with vapor



$\Delta G = \sigma \cdot A + (\mu_l - \mu_g)\cdot V \cdot \frac{\rho_{liq}}{m}$

$= 4\pi\sigma r^2 - (\Delta\mu)\cdot\frac{\rho_{liq}}{m}\cdot\frac{4\pi r^3}{3}$ $\quad (\Delta\mu = \mu_g - \mu_l > 0)$



↳ $dG = \mu_\ell dN_\ell + \mu_g dN_g + \sigma dA.$ ↳ $\left.\frac{dG}{dr}\right|_{r_0} = 0.$

5.4. Gibbs phase rule.

Consider a multi component, multi phase system. $\left(\begin{array}{ll} j = 1, 2, \cdots, J & \text{Component} \\ k = 1, 2, \cdots, K & \text{Phases} \end{array} \right)$ (solid, liquid, gas, ferro/paramagnetic, superconducting ···)

↳ different substances

(T, P) is fixed (controlled)

$$\sum_{j=1}^{J} C_j = C \ (\text{Total concentration},\ \theta_j = \frac{C_j}{C_J})$$

[(J−1) 자유도] × (K phase 자유도), ⟨T, P

$$\Rightarrow D = [2 + (J-1)K] - (K-1)J$$

$$= \boxed{2 + J - K} \ \text{... Gibbs phase rule}$$

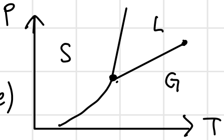
For j, Gibbs equilibrium $\mu_j^1 = \mu_j^2 = \cdots \mu_j^K$ (K−1) equations

↳ For J substances

ex) J = 1, K = 1 (water) ⇒ D = 2.

J = 1, K = 2 (S & ℓ, S & g, ℓ & g) ⇒ D = 1 (line)

J = 1, K = 3 ⇒ D = 0

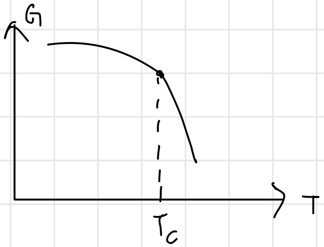


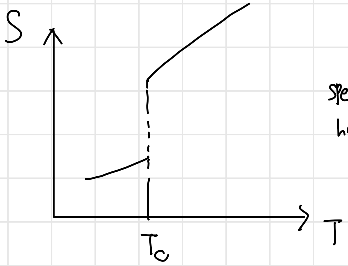
5.5. Classifications of phase Transitions

Ehrenfest 가 제시.

i) 1st-order

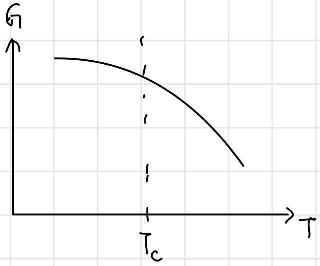
L = TΔS

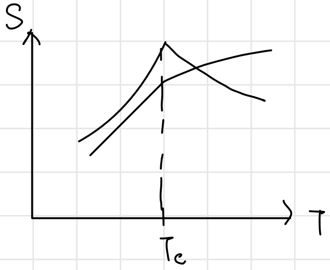


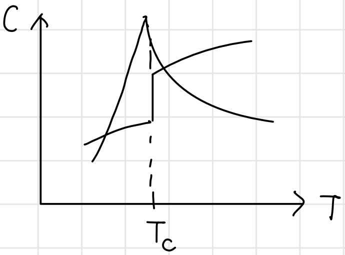


⇒ Discontinuous phase

ii) 2nd-order (최근에는 Higher-order도 구분) ⇒ Continuous phase transition







CH 5 & 6.

$$g(v_x) \sim e^{-\beta E} = e^{-\frac{\frac{1}{2}mv_x^2}{kT}} \quad (v_x, v_x + dv_x)$$

$$g(v_x) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mv_x^2}{2k_BT}}$$

v_x : $-\infty$ to ∞

Same to v_y, v_z

$$\Rightarrow g(\vec{v}) = g(v_x)g(v_y)g(v_z)\, dv_x dv_y dv_z$$

$$\sim \exp\left(\frac{1}{2}mv^2/k_BT\right) dv_x dv_y dv_z$$

$V = 4\pi v^2 dv$. $\quad f(v)\,dv \propto V \cdot g(\vec{v})$

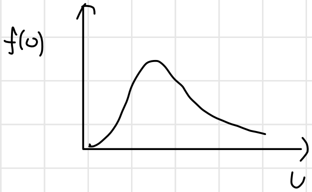
$$= v^2 \cdot \exp\left(-\frac{mv^2}{2kT}\right)$$

$$\xrightarrow[\text{Normalize}]{} f(v)\,dv = \frac{4}{\sqrt{\pi}} \cdot \left(\frac{m}{2k_BT}\right)^{\frac{3}{2}} \cdot v^2 \cdot \exp\left(-\frac{mv^2}{2kT}\right) dv.$$

... M.B speed distribution

$v_{max} < \langle v \rangle < v_{rms}$

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} \qquad \langle v^2 \rangle = \frac{3k_BT}{m}$$



Ⅲ. Kinetic Theory.

0. Brief Introduction

Classical Mechanics : Newtonian, Hamiltonian. (결정론적)

$(\vec{p}, \vec{q}) = (p_1, \cdots, p_{3N}, q_1, \cdots, q_{3N}) \in \mathbb{R}^{6N}$ where $\dot{q}_i = \frac{\partial H}{\partial p_i}$ $\dot{p}_i = -\frac{\partial H}{\partial q_i}$

($t \to -t$, same. symmetry)

⇒ Impossible

19th, kinetic Theory

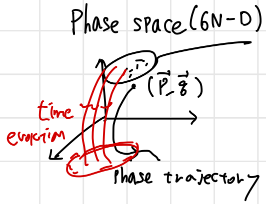
Boltzmann

Thermodynamics : Carnot, Clausius, Maxwell, Gibbs ···

E, N, T, V, P ··· ⇒ Equation of states : Phenomenological Laws (Empirical)

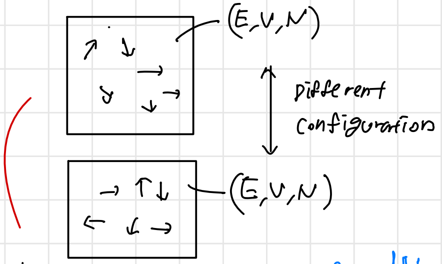
⟶ S, W, Q

- Statistical Mechanics : ?



collection of μ-state point.

⇒ same ($\bar{E}$, V, N) macro state



⇒ Density function $\rho(\vec{p}, \vec{q}, t)$: Ω에 해당하는 weight function (?)   macrostate 복사본의 집합 (but different microstate)

$\rho \cdot d\Gamma = \lim_{N\to\infty} \frac{dN}{N}$

1. Liouville Theorem

- Consider a closed system of N classical particles
- A set of representative points $(\vec{p}, \vec{q})$ ⇒ Gibbs (Statistical) Ensemble

- Phase space probability density

⇒ $\int \frac{d\vec{p} \cdot d\vec{q}}{N!\, h^{3N}} \rho(\vec{p}, \vec{q}, t)$: Probability that your system is in the volume element around $(\vec{p}, \vec{q})$

= 1 (Normalized)

(*) Time evolution of $\rho(\vec{p}, \vec{q}, t)$

V 내에서 n의 변화량   (들어오는 양) = (나가는 양) × −1

$$\frac{dn}{dt} = \frac{d}{dt}\int_V N\rho(\vec{p}, \vec{q}, t)\, d\vec{p}\, d\vec{q} = N \int_V \frac{\partial \rho}{\partial t}\, d\vec{p}\, d\vec{q} = -N \cdot \int_{\partial V} (\rho \vec{u}) \cdot \hat{n}\, dS \quad (\vec{u} = (\dot{\vec{p}}, \dot{\vec{q}}))$$

↳ phase velocity

$$= -N \cdot \int_V \nabla \cdot (\rho \vec{u})\, d\vec{p}\, d\vec{q}$$

$$\boxed{\therefore \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0}$$

$\left(\nabla \equiv \sum_i \left(\frac{\partial}{\partial p_i} \hat{p}_i + \frac{\partial}{\partial q_i} \hat{q}_i\right)\right)$ (?)

$$\Rightarrow \frac{\partial \rho}{\partial t} + \rho\cdot(\nabla\cdot\vec{u}) + \vec{u}\cdot(\nabla\rho) = 0$$

$$\left[\begin{array}{l} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{array}\right.$$

3N ?

$$\Rightarrow \frac{\partial \rho}{\partial t} + \sum_{i=1} \rho\cdot\underbrace{\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right)}_{=\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0} + \sum_i \underbrace{\left(\frac{\partial \rho}{\partial q_i}\cdot\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right)}_{=\frac{\partial \rho}{\partial q_i}\cdot\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\cdot\frac{\partial H}{\partial q_i}} = 0$$

→ 푸아송 Bracket.

$$\boxed{\therefore \frac{\partial \rho}{\partial t} + \underline{\{\rho, H\}} = 0}$$

... Liouville theorem $\left(\Leftrightarrow \frac{d\rho}{dt} = 0\right)$

$$\equiv i\hat{L}\rho \quad (L \equiv \text{Liouville Operator})$$

- Consider $A(\vec{p}, \vec{q}, t)$

$$\Rightarrow \frac{dA}{dt} = \frac{\partial A}{\partial t} + \sum_i\left(\frac{\partial A}{\partial q_i}\dot{q}_i + \frac{\partial A}{\partial p_i}\dot{p}_i\right) = \frac{\partial A}{\partial t} + \{A, H\} = \frac{\partial A}{\partial t} + \underline{iL}A$$

Liouile operator

(?)

$$\therefore \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + iL\rho = 0.$$

ρ가 시간이 지남에 따라 움직이는 총 밀도는 변하지 않는다. (액체같이)

∴ Phase space density ρ 는 t에 대해 invariant. (Incompressible)

$$\Rightarrow \frac{\partial \rho}{\partial t} + iL\rho = 0 \Leftrightarrow \rho(\vec{p}, \vec{q}, t) = e^{-iLt}\cdot\rho(\vec{p}, \vec{q}, 0) \quad \text{where } \underline{L}\rho_\alpha = \underline{\lambda_\alpha}\rho_\alpha$$

Hermitian   E/B.

$$= \sum_\alpha C_\alpha \cdot \underline{e^{-i\lambda_\alpha t}}\rho_\alpha$$

Poincare recurrence theorem

⇒ Time − Reversal symmetry : Not consistent with daily life observation

(*) Average of $\langle A\rangle$ $A(\vec{p}, \vec{q})$

$$\langle A\rangle = \frac{1}{N!\,h^{3N}}\int A(\vec{p}, \vec{q})\,\underbrace{\rho(\vec{p}, \vec{q}, t)}_{=e^{-iLt}\rho(\vec{p}, \vec{q})}\,d\vec{p}\,d\vec{q} \Rightarrow \frac{d\langle A\rangle}{dt} = \frac{1}{N!\,h^{3N}}\cdot\underline{(-i)}\cdot\int A\,\underbrace{L\rho}_{=\{H,\rho\}}\,d\vec{p}\,d\vec{q} \cdots ①$$

$$A(\vec{p}(t), \vec{q}(t)) \Rightarrow \langle A\rangle = \frac{1}{N!\,h^{3N}}\cdot\int \vec{A}(\vec{p}(t), \vec{q}(t))\,\rho(\vec{p}, \vec{q})\,d\vec{p}\,d\vec{q}$$

$$\Rightarrow \frac{dA(\vec{p}(t), \vec{q}(t))}{dt} = \underbrace{\frac{\partial A}{\partial t}}_{=0} + \sum\left(\frac{\partial A}{\partial p_i}\dot{p}_i + \frac{\partial A}{\partial q_i}\dot{q}_i\right) = \sum_i\left(\frac{\partial A}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial H}{\partial q_i}\right) = iLA$$

(A의 시간 의존은 P, q로 포함)

$$\therefore A = e^{iLt}A(\vec{p}, \vec{q})$$

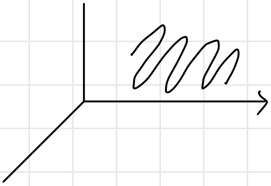
$$\Rightarrow \frac{d\langle A\rangle}{dt} = \frac{1}{N!\,h^{3N}}\, i \int d\vec{p}\, d\vec{q}\; 2A\rho \cdots ②$$

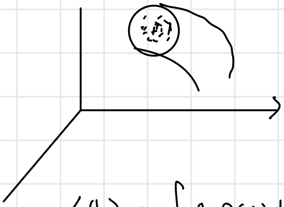
From ①, ① $\Rightarrow -\sum_i \int A\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right) d\vec{p}\, d\vec{q}$

$$= \cancel{A\rho\frac{\partial H}{\partial p_i}}\Big|_S - \int d\vec{p}\,d\vec{q}\;\rho\cdot\{H, A\} = \langle\{A, H\}\rangle$$

$$\boxed{\frac{d\langle A\rangle}{dt} = \langle\{A, H\}\rangle}$$

⇒ 슈뢰딩거 / 하이젠베르크 2 Approach identical result.





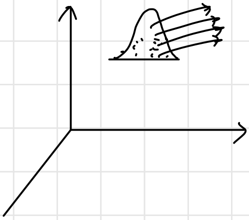
Ensemble Average

$\langle A\rangle = \int A\rho(t)\, d\vec{p}\, d\vec{q}$ (Theory)

Time average

$\bar{A} = \frac{1}{T}\int_0^T A(\vec{p}(t), \vec{q}(t))\, d\vec{p}\, d\vec{q}$ $\overset{?}{=}$ (Ergodic hypothesis, not been proved (?))

(Experiment)



$f_N(\vec{q}_1, \vec{q}_2, \cdots, \vec{q}_N, \vec{p}_1, \vec{p}_2 \cdots, \vec{p}_N; t)$

$\Rightarrow$ (Number of particle) $\sim \int \frac{\partial f_N}{\partial t}\, d\vec{p}\cdot d\vec{q} = -\oint_{\partial V} (f_N\vec{u})\cdot\hat{n}\, dS$

$= -\int \nabla\cdot(\vec{u} f_N)\, d\vec{p}\, d\vec{q}$

Hamiltonian, Poisson bracket, Liouville operator

$$\Rightarrow \frac{df}{dt} = \frac{\partial f}{\partial t} + iLf = 0.$$

⇝ Precise, but cannot explain time-irreversibility, too many equations, difficulty to solve.

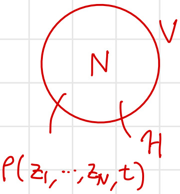
Non-interacting 일 때는 풀이 가능 (?)

⇝ Exact, but useless

2. BBGKY Hierarchy

- Consider a classical system of identical N particles. $z_i = (\vec{p}_i, \vec{q}_i)$

f_N: Probability finding N particles having specified p, q



① $\langle A_1(t)\rangle = \int \underbrace{\left[\sum_{i=1}^{N} A_1(z_i)\right]}_{} f_N(z_1, z_2, \cdots, z_N, t)\, dz_1 \cdots dz_N$

$= A_1(z_1) + A_1(z_2) + \cdots + A_1(z_N)$

↳ dummy index 취급 가능 N배.

$= \int dz_1 A_1(z_1) \cdot \underbrace{N \int dz_2 \cdots dz_N f_N}_{\equiv \boxed{f_1(z_1,t)}} = \int dz_1 A_1(z_1) f_1(z_1, t)$

$\equiv \boxed{f_1(z_1,t)}$ → N개 中 1개가 t에 $\vec{p}_1, \vec{q}_1$ 존재 할 확률밀도.

② $\langle A_2(t)\rangle = \int \left[\sum_{i\neq j} A_2(z_i, z_j)\right] f_N(z_1, \cdots, z_N, t)\, dz_1 \cdots dz_N$ (Interaction)

$= \int dz_1 dz_2\, A_2(z_1, z_2)\, \underbrace{N(N-1) \int dz_3 \cdots dz_N f_N}_{} = \int dz_1 dz_2\, A_2(z_1, z_2) f_2(z_1, z_2, t)$

$\equiv \boxed{f_2(z_1, z_2, t)}$ … S particle reduced distribution function

$$\boxed{\therefore f_S(z_1, z_2, \cdots, z_S, t) = \frac{N!}{(N-S)!} \int dz_{S+1} \cdots dz_N f_N(z_1, \cdots, z_N, t)}$$

(Ex) For kinetic energy, $A_i = \frac{p_i^2}{2m}$; $\langle K\rangle = \int dz_1 \frac{p_1^2}{2m} f_1(z_1, t)$

For potential energy, $U_{ij} \Rightarrow \langle U\rangle = \frac{1}{2}\int dz_1 dz_2\, U(q_1, q_2) f_2(z_1, z_2, t)$

($\because U(q_i, q_j) = U(q_j, q_i)$ = 중복, 따라서 $\frac{1}{2}$배 해줘야 한다)

⇒ Single or 2-particle distribution 으로 average value 계산 가능.

(*) Some Properties

- $\int dz_1 f_1(z_1, t) = N$
- $\int dP_1 f_1(z_1, t) = n(q_1, t)$ ⟶ Particle number density, function of position
- $\int dP_1 \left(\frac{\vec{p}^2}{2m}\right) f_1(z_1, t) \equiv \frac{3}{2} n(\vec{q}, t) \cdot \underline{T(\vec{q}, t)}$

$\int dP_1 \cdot \vec{p} f_1(z_1, t) \equiv \underline{m} \cdot n(\vec{q}, t) \underline{u(\vec{q}, t)}$ Continuum Temperature

Momentum

(*) BBGKY 유도.

- Suppose $H = \left[\sum_{i=1} \frac{p_i^2}{2m} + \sum U_i(q_i)\right] + \sum_{i<j} U_{ij}(q_i - q_j)$ for N particles

$\Rightarrow iL_N = \sum_{\ell=1}\left(\underline{\frac{\partial H}{\partial p_\ell}} \frac{\partial}{\partial q_\ell} - \underline{\frac{\partial H}{\partial q_\ell}} \frac{\partial}{\partial p_\ell}\right)$ (편의상 $p_\ell = \vec{p}_\ell$, $q_\ell = \vec{q}_\ell$ 이다)

$= \sum_i \frac{p_i}{m} \delta_{i\ell}$ $= \sum_i \frac{\partial U_i}{\partial q_i} \delta_{i\ell} + \sum_{i<j}\left(\frac{\partial U_{ij}}{\partial q_i} \delta_{i\ell} + \frac{\partial U_{ij}}{\partial q_j} \delta_{j\ell}\right)$

$$= \sum_i \frac{p_i}{m}\frac{\partial}{\partial q_i} - \sum_i \frac{\partial U_i}{\partial q_i}\frac{\partial}{\partial p_i} - \underline{\sum_{i<j}\left(\frac{\partial U_{ij}}{\partial q_i}\frac{\partial}{\partial p_i} + \frac{\partial U_{ij}}{\partial q_j}\frac{\partial}{\partial p_j}\right)} \quad \Leftarrow U_{ij}(q_i - q_j)$$

$$= \sum_{i<j} -\left(\frac{\partial U_{ij}}{\partial q_i}\right)\left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j}\right) \qquad F_{ij} \equiv -\frac{\partial U_{ij}}{\partial q_i}$$

$$= \sum_{i=1}^{N}\underbrace{\left(\frac{p_i}{m}\frac{\partial}{\partial q_i} + F_i^{ext}\frac{\partial}{\partial p_i}\right)}_{\equiv S_i} + \sum_{i<j}\underbrace{F_{ij}\left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j}\right)}_{\equiv P_{ij}}$$

(지금까지는 constraint X. 그냥 둔거)

(이제 decompose 하자)

(s particle 로)

(1 ⋯ s) (s+1 ⋯ N) (Interaction)

$$\Rightarrow i\mathcal{L}_N = \underbrace{\sum_{i=1}^{s} S_i + \sum_{\substack{i<j \\ i=j=1}}^{s} P_{ij}}_{i\mathcal{L}_s \ ①} + \underbrace{\sum_{i=s+1}^{N} S_i + \sum_{\substack{i,j=s+1 \\ (i<j)}}^{N} P_{ij}}_{i\mathcal{L}_{N-s} \ ②} + \underbrace{\sum_{i=1}^{s}\sum_{j=s+1}^{N} P_{ij}}_{③}$$

$$\begin{array}{cc} & \overset{s}{} \\ N & \left(\begin{array}{c|c} ① & ③ \\ \hline ③ & ② \end{array}\right) \\ & N \end{array}$$

From Liouville, $\frac{\partial f_N}{\partial t} + i\mathcal{L}_N f_N = 0$. and we defined f_s before.

(LHS) $\Rightarrow i\mathcal{L}_N f_N = -\frac{\partial f_N}{\partial t}$ 양변을 $\frac{N!}{(N-s)!}\int dz_{s+1}dz_{s+2}\cdots dz_N$. 적분하면, $f_N \to f_s$ 이다.

(LHS) $= -\frac{\partial}{\partial t}f_s$. similarly ① $= i\mathcal{L}_s f_s$. (No integration by part, 그대로 적분항밖으로) $f_N|_s = 0$.

피적분은 s+1 ~ N까지 이니

$$② = \frac{N!}{(N-S)!}\int dz_{s+1}\cdots dz_N\, i\mathcal{L}_{N-s}\, f_N = \frac{N!}{(N-S)!}\int dz_{s+1}\cdots dz_N\left[\sum_{i=s+1}^{N}\left(\frac{p_i}{m}\frac{\partial f_N}{\partial q_i} + F_i^{ext}\frac{\partial f_N}{\partial p_i}\right)\right.$$

$= 0$. ($\because$ $i = s+1 \sim N$ 범위 일치, $\int \frac{\partial f_N}{\partial q_i}dq_i = f_N|_s = 0$ for surface S) $\left.+ \sum_{i,j=s+1}^{N}\left(\frac{\partial f_N}{\partial p_i} - \frac{\partial f_N}{\partial p_j}\right)\right]$

$\Rightarrow$ ② term vanishes. (Other 's+1~N'의 evolution은 신경쓰지 않아도 되게 된다)

$$③ = \frac{N!}{(N-S)!}\int dz_{s+1}\cdots dz_N \sum_{i=1}^{s}\sum_{j=s+1}^{N} F_{ij}\left(\frac{\partial f_N}{\partial p_i} - \cancel{\frac{\partial f_N}{\partial p_j}}\right)$$

→ $j = s+1 \sim N$, ② 에서같이, $f_N|_s = 0$

$$= \sum_{i=1}^{S}\frac{N!}{(N-S)!}\int dz_{s+1}\cdots dz_N \sum_{j=s+1}^{N} F_{ij}\frac{\partial f_N}{\partial p_i} = \sum_{i=1}^{s}\frac{N!\,(N-S-1+1)}{(N-S)!}\int dz_{s+1}\cdots dz_N\, F_{i,s+1}\frac{\partial f_N}{\partial p_i}$$

(임의로 $j = s+1$ 지정)

$$= \left[\sum_{i=1}^{S}\int dz_{s+1}\, F_{i,s+1}\frac{\partial}{\partial p_i}\right]\left[\underbrace{\frac{N!}{(N-S-1)!}\int dz_{s+2}\cdots dz_N\, f_N}_{= f_{s+1}}\right]$$

Now, 위 결과를 합하면, $-\frac{\partial}{\partial t}f_s = i\mathcal{L}_s f_s + ③$, $\left[i\mathcal{L}_s + \frac{\partial}{\partial t}\right]f_s = -③$.

$$\boxed{\Rightarrow \left[\frac{\partial}{\partial t} + i\mathcal{L}_s\right] f_s(z_1, z_2, \cdots, z_s, t) = -\sum_{i=1}^{S}\int dz_{s+1}\, F_{i,s+1}\frac{\partial}{\partial p_i} f_{s+1}(z_1, \cdots, z_{s+1}, t)}$$

$\frac{df_s}{dt} \neq 0$.

⋯ Bogoliubov – Born – Green – Kirkwood – Yvon hierarchy (BBGKY)

S=1 ; $\left(\frac{\partial}{\partial t}+\frac{p_1}{m}\frac{\partial}{\partial x_1}+F_1\frac{\partial}{\partial p_1}\right)f_1(x_1,p_1,t) = -\int dz_2\, F_{1,2}\frac{\partial}{\partial p_1}f_2(x_1,p_1,x_2,p_2,t)$

S=2 ; $\left(\frac{\partial}{\partial t}+\frac{p_1}{m}\frac{\partial}{\partial x_1}+\frac{p_2}{m}\frac{\partial}{\partial x_2}+F_1\frac{\partial}{\partial p_1}+F_2\frac{\partial}{\partial p_2}+F_{12}\left(\frac{\partial}{\partial p_1}-\frac{\partial}{\partial p_2}\right)\right)f_2$

$$= -\int dz_3\left(F_{13}\frac{\partial}{\partial p_1}+F_{23}\frac{\partial}{\partial p_2}\right)f_3(x_1,p_1,x_2,p_2,x_3,p_3,t)$$

S=3 · · · ⤳ 계속해서 반복되는 '계층 구조'. How to terminate?

⇒ 물리적 직관을 동원한 approximation,

3. Vlasov Equation.

$$\cdot\left(\frac{\partial}{\partial t}+\frac{\vec p}{m}\frac{\partial}{\partial \vec x}+\vec F\frac{\partial}{\partial \vec p}\right)f_1(\vec x,\vec p,t)=\int d\vec x' d\vec p' \cdot\frac{\partial u(\vec x,\vec x')}{\partial \vec x}\cdot\frac{\partial}{\partial \vec p}\underline{f_2(\vec x,\vec p,\vec x',\vec p',t)}$$

$$= f_1(\vec x,\vec p,t)\cdot f_1(\vec x',\vec p',t)$$

... Vlasov Equation

(Vector notation 생략, Drop off 1 subscript)

$$(\text{RHS}) = \underline{\int dx'dp' \frac{\partial u}{\partial x}\cdot f(x',p',t)}\cdot\frac{\partial f}{\partial p} = -\bar F(x,t)\,\underline{\frac{\partial f(x,p,t)}{\partial p}}$$

$$= \int dx'\cdot\frac{\partial u}{\partial x}\cdot n(x',t) = \frac{\partial}{\partial x}\int dx'\, u(x,x')\, n(x',t)$$ → Interaction with others in system

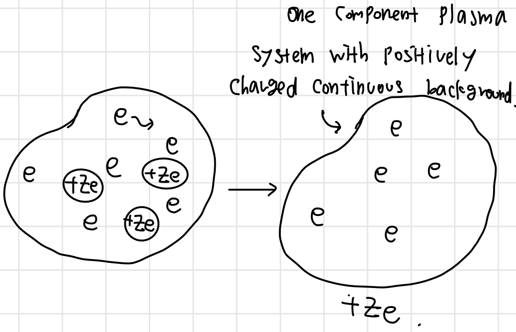
$\frac{Df}{Dt}$,, $= -\bar F(x,t)$ ⤳ Mean field force

$$\Rightarrow \left[\frac{\partial}{\partial t}+\frac{p}{m}\frac{\partial}{\partial x}+\left(\cancel{F^{ext}}+\bar F\right)\frac{\partial}{\partial p}\right]f(x,p,t)=0.$$

Let 0

→ Time - reversible Invariant (Symmetry)

(*) Let's see what happening in the plasma,



One component plasma system with positively charged continuous background

· Plasma parameter $\rho_p = \frac{e^2/d}{k_B T}$ ($d \equiv$ average distance)

$$\simeq \frac{e^2 n^{-\frac{1}{3}}}{k_B T} = \frac{1}{4\pi}\cdot\frac{d^2}{\lambda_D^2} \ll 1$$

$\nabla^2 u = -4\pi e^2\delta(r)$

$\frac{1}{\lambda_D^2}\sim\frac{4\pi e^2 n}{k_B T}$ (λ_D : Debye length)

⟶ Electric potential을 parameter로 / perturbation 간주 가능. : weakly coupled plasma.

now, by Vlasov Eq,

$$\frac{\partial f}{\partial t}+\frac{\vec p}{m}\cdot\frac{\partial f}{\partial \vec r}+e\left(\vec E+\cancel{\frac{1}{c}\vec v\times\vec H}\right)\frac{\partial f}{\partial \vec p}=0.$$ ⟶ nonlinear equation

where $\bar F = e\vec E_{(r,t)} = -\frac{\partial}{\partial r}\int dr'\, u(r-r')\, n(r',t)$ ⟶ $\int f dp = n$. ⇒ Perturbative approach

Let $f(\vec{r},\vec{p},t) = \overset{\text{E 없을 때 f라고 생각}}{f_0(\vec{p})} + \underbrace{\delta f(\vec{r},\vec{p},t)}_{\text{weak Coulomb interaction에 의한 term}}$ $\left(f_0(p) = n\cdot\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}}\cdot e^{-\frac{\beta p^2}{2m}} \right)$

Vlasov equation 대입.

$$\Rightarrow \frac{\partial}{\partial t}(f_0+\delta f) + \frac{p}{m}\frac{\partial}{\partial r}(f_0+\delta f) = -e\vec{E}\cdot\frac{\partial}{\partial p}(f_0+\delta f)$$

$$n(r',t) = \overset{0}{\cancel{n_0}} + \delta n(r',t)$$

$$\left(= \int (f+\delta f)\,dp'\right)$$

ρ', r'; p'

Then, (BHS): $\frac{\partial f_0}{\partial t} + \frac{p}{m}\frac{\partial f_0}{\partial r} = 0$, (trivial)

$$\boxed{\frac{\partial}{\partial t}\delta f + \frac{p}{m}\cdot\frac{\partial}{\partial r}\delta f = -e\vec{E}\cdot\frac{\partial f_0}{\partial p}}$$

... Linearized Vlasov equation.

이제, wave-like solution idea를 이용하자. P는 vel 비례하는 물리량이니, 수학적으로 다음과 같이 푸리에 변환이 가능하다.

$$\begin{cases} \delta f(\vec{v},\vec{r},t) = \delta f(\vec{v},\vec{k},\omega)\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)} \\ \delta n(\vec{r},t) = \delta n(\vec{k},\omega)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \end{cases}$$

이를 위식에 대입하여 정리하면,

$$\Rightarrow -i\omega\,\delta f(\vec{v},\vec{k},\omega) + i\vec{k}\cdot\vec{v}\,\delta f(\vec{v},\vec{k},\omega) = -e\vec{E}(\vec{k},\omega)\frac{\partial f_0}{\partial p}.$$

$$e\vec{E} = -\mathcal{F}^{-1}[\quad]$$

where $e\vec{E} = -\frac{\partial}{\partial r}\int dr'\,u(r-r')\,\delta n(r',t) = \underline{-i\vec{k}\cdot u(\vec{k})\,\delta n(\vec{k},\omega)}.$

$$\Rightarrow (\text{BHS}) = +i\,u(\vec{k})\,\delta n(\vec{k},\omega)\cdot\vec{k}\frac{\partial f_0}{\partial p} = i(\vec{k}\cdot\vec{v}-\omega)\,\delta f(\vec{v},\vec{k},\omega)$$

$$\boxed{\therefore \delta f = -\frac{u(\vec{k})\,\delta n(\vec{k},\omega)}{\omega-\vec{k}\cdot\vec{v}}\cdot\vec{k}\cdot\frac{\partial f_0}{\partial p}}$$

이제, δf를 구했으니, 다음 식을 이용하자. $\int d\vec{p}\,\delta f(v,k,\omega) = \delta n(\vec{k},\omega).$

$$\Rightarrow \cancel{\delta n} = -\int \frac{u(\vec{k})\,\cancel{\delta n(\vec{k},\omega)}}{\omega-\vec{k}\cdot\vec{v}}\cdot\vec{k}\cdot\frac{\partial f_0}{\partial p}\cdot dp$$

$\Rightarrow$ Dispersion relation을 구할 수 있다.

이 때, $u(\vec{k})$는 electric potential이고, $\nabla^2 u(\vec{r}) = -4\pi e^2\delta(\vec{r})$ 푸리에 $-k^2 u(\vec{k}) = -4\pi e^2$.

$$\Rightarrow -\frac{4\pi e^2}{k^2}\int d\vec{p}\,\frac{1}{\omega-\vec{k}\cdot\vec{v}}\left(\vec{k}\cdot\frac{\partial f_0}{\partial\vec{p}}\right) = 1.$$

$$\therefore u(k) = \frac{4\pi e^2}{k^2}.$$

이 때, f_0가 Gaussian 꼴인 공식을 이용하면, $\frac{\partial f_0}{\partial\vec{p}} = -\frac{2\beta\vec{p}}{2m}f_0 = -\beta\cdot\vec{v}f_0.$

$$\therefore 1 = \frac{4\pi e^2}{k^2}\int d\vec{p}\cdot\underline{\frac{\vec{k}\cdot\vec{v}}{\omega-\vec{k}\cdot\vec{v}}}\,\beta f_0.$$

$$\left(\frac{\partial f_0}{\partial E}\cdot\frac{\partial E}{\partial p},\ f_0\sim\alpha\cdot e^{-\beta E}\right)$$

$$= \frac{\vec{k}\cdot\vec{v}}{\omega}\cdot\left(\frac{1}{1-\frac{\vec{k}\cdot\vec{v}}{\omega}}\right) = \frac{\vec{k}\cdot\vec{v}}{\omega}\left(1+\frac{\vec{k}\cdot\vec{v}}{\omega}+\left(\frac{\vec{k}\cdot\vec{v}}{\omega}\right)^2+\cdots\right)$$

$$\Rightarrow 1 \simeq \frac{4\pi e^2}{k^2}\int d\vec{p}\cdot\left[\underset{\text{0, odd function}}{\cancel{\frac{\vec{k}\cdot\vec{v}}{\omega}}} + \left(\frac{\vec{k}\cdot\vec{v}}{\omega}\right)^2 + \underset{0}{\cancel{\left(\frac{\vec{k}\cdot\vec{v}}{\omega}\right)^3}} + \cdots\right]\beta f_0.$$

(Small region의 k에서 첫항만 고려)

non zero

$$= \frac{4\pi e^2}{k^2}\cdot 2\pi\int d(\cos\theta)\cdot\int_0^\infty dp\cdot p^2\cdot\frac{k^2p^2\cos^2\theta}{m^2\omega^2}\,\rho\cdot n\cdot\left[\frac{\rho}{2\pi m}\right]^{\frac{3}{2}} e^{-\frac{\rho p^2}{2m}}.$$

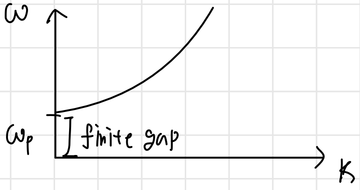
$$= \frac{4\pi e^2 n}{m^2\omega^2} = \frac{\omega_p^2}{\omega^2} \qquad \boxed{\omega_p^2 \equiv \frac{4\pi e^2 n}{m^2}}$$ plasma frequency.

So, $\omega_p = \omega$ 이고, plasma frequency가 e, n, m 의 함수인 상수이며,
system의 wave frequency가 잘 정의된 ω_p로 진행한다.
$\omega > 0$. no imaginary, no damping] oscillation

Equilibrium behavior

$\Rightarrow$ 근사항을 고려하면, 위 적분식이 $1 = \frac{\omega_p^2}{\omega^2}\cdot\left[1+\frac{k^2}{\omega^2}\langle v^2\rangle\right] \longleftarrow E = \frac{m\langle v^2\rangle}{2} = \frac{3k_BT}{2}$

$\Rightarrow \omega^2 \cong \omega_p^2 + k^2\langle v^2\rangle$



$$\delta f = -\frac{\underbrace{\vec k\cdot u(\vec k)\,\delta n(\vec k,\vec\omega)}_{=\,-ie\vec E}}{\omega-\vec k\cdot\vec v}\cdot\left(\frac{\partial f_0}{\partial p}\right)$$

$$\Downarrow$$

$$\underline{-i\cdot e\cdot\vec E\cdot\int d\vec p\cdot\frac{1}{\omega-\vec k\cdot\vec v}\left(\frac{\partial f_0}{\partial \vec p}\right)}$$
$$= \delta n(\vec k,\vec\omega)$$

(*) Response function.

$$\delta n(\vec k,\omega) = \int \delta f(\vec k,\vec p,\omega)\,d\vec p$$

and, we know
$$\begin{cases}\nabla\cdot\vec P = -4\pi\rho_b = -4\pi e\cdot\delta n(\vec r,t)\\ i\vec k\cdot\vec P = -4\pi e\,\delta n(\vec k,\omega)\end{cases}$$

$$\therefore \vec P(\vec k,\omega) = \underline{\frac{4\pi e^2}{k^2}\int d\vec p\cdot\frac{1}{\omega-\vec k\cdot\vec v}\left(\frac{\partial f_0}{\partial \vec p}\cdot\vec k\right)}\,\vec E$$
$= \chi_e$ $\longrightarrow$ 위 식과 같은 형태, 해의 형태 동일.

we know $\vec P(r,t) = \int dr'\,dt'\,\underline{\chi(r-r',t-t')}\,\vec E(r',t')$

Green function, susceptibility

$$\vec P(\vec k,\omega) = \chi(\vec k,\omega)\,\vec E(\vec k,\omega)$$ Let $\vec P, \vec E$ 가 특정 방향 (평행)

$$\Rightarrow P(k,\omega) = \chi_e(k,\omega)\,E(k,\omega)$$ (cf) $\overleftrightarrow{\varepsilon} = \overleftrightarrow{I} + \overleftrightarrow{\chi}$

$$\therefore \chi_e = -\frac{\omega_p^2}{\omega^2}\cdot\left[1+\frac{k^2}{\omega^2}\langle v^2\rangle+\cdots\right]$$

$$\Rightarrow \varepsilon_e = 1+\chi_e = 1 - V(k)\cdot\int \frac{d\vec{p}\ \ \vec{k}}{\vec{k}\cdot\vec{v}-\omega}\cdot\left(\frac{\partial f_0}{\partial \vec{p}}\right) = 1-\frac{4\pi e^2}{k^2}\int \frac{dp_x\cdot k\ \frac{\partial f_x}{\partial p_x}}{kv_x-\omega-i\eta}$$

Perturbation → (S) → response.

$$= \varepsilon_e' + i\cdot\varepsilon_e''.$$

$\omega \rightarrow \omega + i\eta$

$\hat{k} \,//\, \hat{x}$

where $\lim\limits_{\eta\to 0} \frac{f(z)}{z-i\eta}\,dz = \underbrace{P.}_{\text{Cauchy principle value}}\int_{-\infty}^{\infty}\frac{f(z)}{z}\,dz + i\pi f(0)$

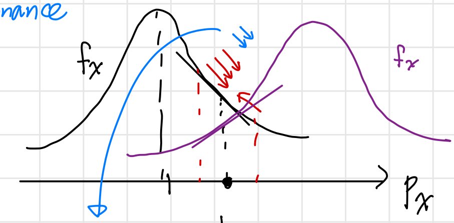
… Sokhotski – Plemelj theorem

$$\Rightarrow \varepsilon_e'' = -\frac{4\pi e^2}{k^2}\cdot\int \underbrace{dp_x}_{m\,dv_x}\cdot k\cdot\frac{\partial f_x}{\partial p_x}\cdot\underbrace{\delta(kv_x-\omega)}_{v_x=\frac{\omega}{k}\ \text{resonance}} = -\frac{4\pi e^2 m}{k^2}\,k\cdot\left(\frac{\partial f_x}{\partial p_x}\right)_{v_x=\frac{\omega}{k}}$$

System 의 에너지 Loss/Absorption 에 대한 지표

(∵ wave 와 particle 간에 에너지 전달)

ε_e'' 에 기여.



$\Delta v_x > 0$.

$m v_x = m\frac{\omega}{k}$

Particle gain energy ⇔ wave losing energy

$$\varepsilon_e'' = \begin{cases} + : & \text{Damping (wave lost energy)} \\ - : & \text{Growing (wave gain energy)} \end{cases}$$

$$\varepsilon_e'' = (-) \times \left(\frac{\partial f_x}{\partial p_x}\right)$$

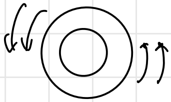
$\boxed{\text{입자 간 충돌이 없음에도 (초기 조건) 에너지 잃음.}}$

… Landau damping

$\leftarrow$ − − +

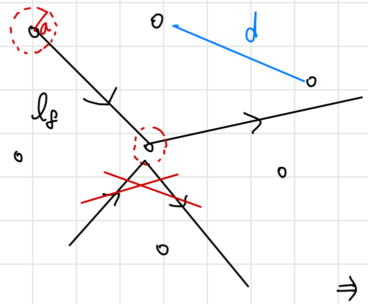
System gaining energy. $\leftarrow$ − + −

(∵ f_x 가 우편향, 전체 입자계 가속, 토카막)



4. Boltzmann Equation : Time irreversibility

- Consider a dilute classical gas undergoing binary collisions.



d = Average distance, a = Interaction range.
l_f = Mean free path.

(*) 가정 i) $l_f > d$, collision event rare
ii) No three particle collision event.

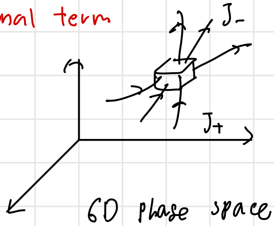
⇒ Using Vlasov equation, one notices

$$\frac{Df_1}{Dt} = J[f_2]$$

$$\frac{Df_2}{Dt} = \underset{0}{\cancel{J[f_3]}}$$

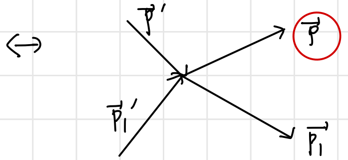
$$\frac{Df_1}{Dt} = \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial}{\partial \vec{p}}\right)f = \underbrace{J[f_2]}_{\text{Collisional term}} = \overset{\text{Influx}}{J_+} - \overset{\text{Out flux}}{J_-}$$

⇒ $J_\pm(\vec{r},\vec{p},t)$ = (outgoing flux) influx of f into the volume element $d\vec{r}\,d\vec{p}$ around $(\vec{r},\vec{p})$ during dt.



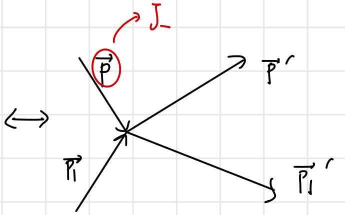
- One notices that;

$$J_+ = \int d\vec{p}_1\cdot d\vec{p}\,'\,d\vec{p}_1{}'\cdot \underbrace{W(\vec{p},\vec{p}_1\,|\,\vec{p}\,',\vec{p}_1{}')}_{\text{transmission probability}}\ \overbrace{f_2(\vec{r},\vec{p}\,',\vec{r},\vec{p}_1{}',t)}^{\text{Initial Condition}}$$



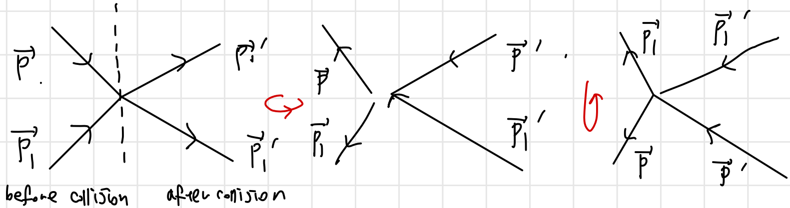
$(\vec{r},\vec{p})$ phase space Σ, 대한 influx → J_+

$$J_- = \int d\vec{p}_1\,d\vec{p}\,'\,d\vec{p}_1{}'\ W(\vec{p}\,'\vec{p}_1{}'\,|\,\vec{p}\,\vec{p}_1)\ f_2(\vec{r},\vec{p},\vec{r},\vec{p}_1,t)$$



(*) Symmetric Property of Probability.

$$W(\vec{p}\,',\vec{p}_1{}'\,|\,\vec{p}\,\vec{p}_1) = W(\vec{p}\,\vec{p}_1\,|\,\vec{p}\,',\vec{p}_1{}')$$



And, Boltzmann assumed Stosszahlansatz

= Collision number hypothesis

$\Rightarrow f(v_1, v_2) = f(v_1) f(v_2)$

$\Rightarrow$ uncorrelated before the collision.] $f_2(\vec{r}, \vec{p}, \vec{r}, \vec{p}_1, t) = f(\vec{r}, \vec{p}, t) \cdot f(\vec{r}, \vec{p}_1, t)$

Therefore, we can make above equation as; → Not Time-Reversal Invariant.

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \left[\frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{r}} + \vec{F} \cdot \frac{\partial}{\partial \vec{p}}\right] f = J_+ - J_- = \int d\vec{p}\,' d\vec{p}_1\,' d\vec{p}_1 \cdot W(\vec{p}\,', \vec{p}_1\,' | \vec{p}, \vec{p}_1)\left[f' f_1' - f f_1\right]$$

$t \to -t$: $\vec{p} \to -\vec{p}$

$(f' = f(\vec{r}, \vec{p}\,', t),\ f_1' = f(\vec{r}, \vec{p}_1\,', t))$

(*) H-Theorem

Let's define

$$H = \int d\vec{r}\, d\vec{p}\ f(\vec{r}, \vec{p}, t) \cdot \ln f(\vec{r}, \vec{p}, t)$$

$$S(\vec{r}, t) = -k_B \cdot \int d\vec{p} \cdot f \ln f.$$ → Localized entropy density

$$\Rightarrow \frac{\partial S}{\partial t} = -k_B \int d\vec{p} \frac{\partial}{\partial t}[f \ln f] = -k_B \int d\vec{p} \cdot [1 + \ln f]\left(\frac{\partial f}{\partial t}\right)$$

$$= -k_B \cdot \int d\vec{p} \cdot (1 + \ln f)\left[\underbrace{-\frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{r}}}_{①} \underbrace{- \vec{F} \cdot \frac{\partial f}{\partial \vec{p}}}_{②} + \underbrace{J[f_2]}_{③}\right]$$

← BBGKY hierarchy

$$① = +k_B \int d\vec{p}\ \frac{\vec{p}}{m} \cdot (1 + \ln f) \frac{\partial f}{\partial \vec{r}} = k_B \int d\vec{p} \cdot \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{r}}(f \cdot \ln f) = \frac{\partial}{\partial r} \underbrace{k_B \int d\vec{p} \cdot \frac{\vec{p}}{m} f \ln f}_{= -\vec{J}_s}$$

entropy current

$$② = k_B \cdot \int d\vec{p}\ (1 + \ln f)\, \vec{F} \frac{\partial f}{\partial \vec{p}} = k_B \cdot \vec{F} \int d\vec{p} \frac{\partial}{\partial \vec{p}}(f \ln f) \propto (f \cdot \ln f)\Big|_S = 0.$$

$$③ = -k_B \cdot \int d\vec{p} \cdot (1 + \ln f)\, J[f_2]$$

$\Rightarrow$ 대입하고 이항하여 정리하면, $J = J_+ - J_-$ 이므로

$$\frac{\partial S}{\partial t} + \vec{\nabla}_r \cdot \vec{J}_s = -k_B \cdot \int d\vec{p} \cdot d\vec{p}_1\, d\vec{p}\,' d\vec{p}_1\,' \cdot W(p' p_1' | p\, p_1)(f' f_1' - f f_1)(1 + \ln f) \quad \cdots (i)$$

+ By $p \leftrightarrow p_1$ Symmetry,

$$(\qquad\qquad) = -k_B \int d\vec{p}\, d\vec{p}_1\, d\vec{p}\,' d\vec{p}_1\,' W \cdot (p' p_1' | p\, p_1)(f' f_1' - f f_1)(1 + \ln f_1) \quad \cdots (i)'$$

+ Half Sum (i) and (i)', we get

$$\left(\frac{\partial S}{\partial t} + \vec{\nabla}_{\vec r}\cdot \vec{\partial s}\right) = -\frac{k_B}{2}\int d\vec p\, d\vec p_1\, d\vec p\,'\, d\vec p_1\,'\; W\,(f'f_1' - ff_1)(2+\ln ff_1) \quad \cdots \text{(ii)}$$

→ Same way, (ii) 에서 $(P, P_1) \leftrightarrow (P', P_1')$ symmetry 이용.

$$\left(\qquad\qquad\right) = -\frac{k_B}{2}\int d\vec p\, d\vec p_1\, d\vec p\,'\, d\vec p_1\,'\; W\,(ff_1 - f'f_1')(2+\ln f'f_1') \quad \cdots \text{(ii)}'$$

→ Again, half sum

$$\underline{\left(\frac{\partial S}{\partial t} + \vec{\nabla}_{\vec r}\cdot \vec{\partial s}\right)} = +\frac{k_B}{4}\int d\vec p\, d\vec p_1\, d\vec p\,'\, d\vec p_1\,'\; W\,\underline{(f'f_1' - ff_1)\ln\frac{f'f_1'}{ff_1}} \geq 0.$$

$$= \frac{ds(\vec r, t)}{dt}$$

$$(x-y)\ln\left(\frac{x}{y}\right) \geq 0. \longleftarrow \begin{cases} x > y \\ y > x \\ x = y \end{cases}$$

→ Total entropy of the system

$$S(t) \equiv \int d\vec r\, s(\vec r, t) = -k_B\int d\vec r \int d\vec p\, f\ln f = -k_B H(t).$$

즉, $\frac{dS}{dt} \geq 0 \iff \frac{dH}{dt} \leq 0$ 이다.

(*) Equilibrium Distribution.

- At equilibrium, as required property, $ff_1 = f'f_1'$ $(dH = 0)$
- $\lim_{t\to\infty} f(\vec r, \vec p, t) = f_0(\vec p)$ $(\because \vec r$ symmetry$)$ $(\delta f_0(\vec r, \vec p, t) \to 0)$

$$\Rightarrow f_0(\vec p) f_0(\vec p_1) = f_0(\vec p\,') f_0(\vec p_1\,')$$

$$\Rightarrow \underline{\ln f_0(\vec p) + \ln f_0(\vec p_1)} = \ln f_0(\vec p\,') + \ln f_0(\vec p_1\,')$$

= Conserved quantity 처럼 보인다. (충돌 전 후에)

$$\longrightarrow \chi(\vec p\,') + \chi(\vec p_1\,') = \chi(\vec p) + \chi(\vec p_1) \qquad (\chi = \text{collision invariant})$$

$$\Rightarrow \ln f_0(\vec p) = a + \vec b\cdot\vec p + c\cdot\frac{p^2}{2m} \qquad (\text{conserved quantity})$$

- $\int d\vec p\, f(\vec r, \vec p, t) = \underline{n(\vec r, t)}$ local density
- $\int d\vec p\, \vec v f(\vec r, \vec p, t) = n(\vec r, t)\cdot\underline{\vec u(\vec r, t)}$ local field velocity
- $\int d\vec p\, \frac{(\vec p - mu)^2}{2m}\cdot f = \frac{3}{2}k_B \underline{T(\vec r, t)}\, n(\vec r, t)$ Local temperature

#5 equations ⟶ $a, \vec b, c$

Generalized Boltzmann distribution

... Spacial Variance of T, n exist.

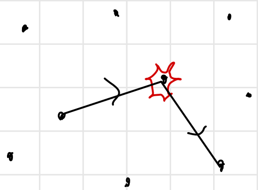
$$\boxed{f_0(\vec r, \vec p, t) = \frac{n(\vec r, t)}{[2\pi m k_B T(\vec r, t)]^{\frac{3}{2}}}\cdot \exp\left(-\frac{[\vec p - m\vec u(\vec r, t)]^2}{2mk_B T(\vec r, t)}\right)}$$

(f = 1 particle distribution function = prob of finding 1 particle in $\vec{r}, \vec{p}$ at t)

6/13(목) 시험일정
1.p.m ~ 4.p.m.
중간 이후 ~
하지만 전체 이해해야

5. Hydrodynamic equations

→ a dilute classical gas undergoing binary collisions



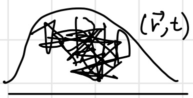
┌ duration of collisions

$\tau_0 \ll \Delta t$

$f(\vec{r}, \vec{p}, t) \longleftarrow$ Boltzmann equation

⇒ kinetic stage

$\tau_r \ll \Delta t$ — relaxation time



$n(\vec{r},t)$: Local density

$u(\vec{r},t)$: Local average velocity

$T(\vec{r},t)$: Local temperature

→ Hydrodynamic equation

(Hydrodynamic stage)

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\frac{\partial f}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

(*) Conservation Laws

Let χ be a collisional invariant quantity. $\chi = \chi(\vec{r}, \vec{p}, t)$

$$\boxed{\int d\vec{p}\cdot\chi(\vec{r},\vec{p},t)\left(\frac{\partial f}{\partial t}\right)_{coll} = 0}$$ 임을 보이자. By Boltzmann equation, (LHS) become :

$$\Rightarrow \int d\vec{p}\int d\vec{p}_1\, d\vec{p}\,'\, d\vec{p}_1{}' \, W(\vec{p}\,', \vec{p}_1{}' | \vec{p}, \vec{p}_1)\left[f'f_1' - f f_1\right]\chi$$

$\chi_1 = \chi(\vec{r}, \vec{p}_1, t)$ 일 때, by symmetry, (half sum)

$$= \frac{1}{2}\int d\vec{p}\int d\vec{p}_1\, d\vec{p}\,'\, d\vec{p}_1{}'\, W(\vec{p}\,', \vec{p}_1{}' | \vec{p}, \vec{p}_1)\left[f'f_1' - f f_1\right](\chi_1 + \chi)$$

⇒ By $(p, p_1) \leftrightarrow (p', p_1')$ symmetry and half sum,

$$= \frac{1}{4}\int d\vec{p}\, d\vec{p}_1\, d\vec{p}\,'\, d\vec{p}_1{}'\, W(\vec{p}\,', \vec{p}_1{}' | \vec{p}, \vec{p}_1)\left[f'f_1' - f f_1\right]\cancelto{0}{(\chi + \chi_1 - \chi' - \chi_1')}$$

(∵ Collisional invariant, $\chi = \chi_1 = \chi' = \chi_1'$)

▨

⇒ By Boltzmann equation, Let's rewrite this : $\int d\vec{p}\ \chi(\vec{r},\vec{p},t)\cdot\left(\frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\frac{\partial f}{\partial \vec{r}} + \vec{F}\frac{\partial f}{\partial \vec{p}}\right) = 0.$

⇒ By expanding this equation;

$$\left[\frac{\partial}{\partial t}\int d\vec{p}\cdot(\chi f) - \int d\vec{p}\cdot f\left(\frac{\partial \chi}{\partial t}\right)\right] + \left[\frac{\partial}{\partial \vec{r}}\cdot\int d\vec{p}\cdot(\chi\cdot\vec{v}\cdot f) - \int d\vec{p}\cdot\left(\frac{\partial \chi}{\partial \vec{r}}\right)\cdot\vec{v}\, f\right] + \left[\cancelto{0}{\int d\vec{p}\cdot\frac{\partial}{\partial \vec{p}}(\chi\vec{F}f)} - \int d\vec{p}\left(\frac{\partial \chi}{\partial \vec{p}}\right)\vec{F}f\right] = 0.$$

(∵ Surface integral 이니 0으로 취급 가능)

Now, Let's define kinetic average of $A \Rightarrow \langle A \rangle = \dfrac{\int d\vec{p}\cdot(Af)}{\int d\vec{p}\cdot f} = \dfrac{\int d\vec{p}\,(Af)}{n(\vec{r},t)}$

$\Rightarrow$ Then, we can get the final equation :

$$\boxed{\frac{\partial}{\partial t} n\langle \chi \rangle - n\cdot\left\langle \frac{\partial \chi}{\partial t}\right\rangle + \vec{\nabla}\cdot n\langle \chi\vec{v}\rangle - n\cdot\langle(\nabla\chi)\cdot\vec{v}\rangle - n\langle(\nabla_{\vec{p}}\,\chi)\cdot\vec{F}\rangle = 0}$$

... Conservation Laws

$\Rightarrow$ Now, Let's see what happen if we substitute χ in invariant quantity.

i) Let $\chi = m$. and, we know by definition, $\langle\vec{v}\rangle = \vec{u}(\vec{r},t)$

$\Rightarrow \dfrac{\partial}{\partial t}(nm) - n\cdot 0 + \vec{\nabla}\cdot nm\vec{u} = 0 \quad (\nabla m = \nabla_p m = 0)$ Let $\rho(\vec{r},t) = mn(\vec{r},t)$

$$\Rightarrow \boxed{\frac{\partial \rho(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot(\rho\vec{u}) = 0}.$$

ii) Let $\chi = mv_i \quad (i = x, y, z)$ similarly,

$$\frac{\partial}{\partial t} mn\langle v_i\rangle + \vec{\nabla}\cdot mn\langle v_i\vec{v}\rangle - n\left\langle\left(\frac{\partial}{\partial p_i}\cdot p_i\cdot\hat{i}\right)\cdot\vec{F}\right\rangle = 0$$

$$\Rightarrow \frac{\partial}{\partial t}\cdot mn\,u_i(\vec{r},t) + \vec{\nabla}\cdot(mn\cdot\langle v_iv_j\rangle) - \frac{\rho}{m}F_i = 0 \quad (j = 1,2,3)$$

$$\Rightarrow \langle v_iv_j\rangle = \langle(v_i-u_i)(v_j-u_j)\rangle + \Big(\underbrace{\underset{=u_i}{\underline{\langle v_i\rangle}}u_j + u_i\underset{u_j}{\underline{\langle v_j\rangle}} - u_iu_j}_{=\,u_iu_j}\Big)$$

$$\vec{\nabla}\cdot(\rho\langle v_iv_j\rangle) = \vec{\nabla}\cdot\Big\{\underbrace{\rho\langle(v_i-u_i)(v_j-u_j)\rangle}_{\equiv\,P_{ij}\ (\text{Pressure tensor})} + u_iu_j\rho\Big\}$$

이를 대입하면 정리 가능.

now, for $\forall i = x, y, z$, 이 식을 Vector form으로 정리하면

$$\underline{\frac{\partial}{\partial t}(\rho\vec{u})} + \vec{\nabla}\cdot\overleftrightarrow{P_{ij}} + \underline{\vec{\nabla}\cdot\rho(\vec{u}\,\vec{u})} = \frac{\rho}{m}\vec{F}$$

$$\underline{\vec{u}\frac{\partial\rho}{\partial t}} + \rho\cdot\frac{\partial\vec{u}}{\partial t} \qquad = \underline{\vec{u}\,(\nabla\rho)\cdot\vec{u} + \rho\cdot(\nabla\cdot\vec{u})\vec{u}} + \rho\cdot(\vec{u}\cdot\nabla)\vec{u}$$

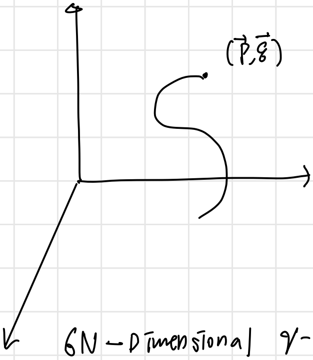
$$\vec{u}\cdot\left(\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{u}) = 0\right)$$

$$\boxed{\therefore\ \frac{\partial\vec{u}}{\partial t} + (\vec{u}\cdot\nabla)\vec{u} = \frac{\vec{F}}{m} - \frac{\vec{\nabla}\cdot\overleftrightarrow{P_{ij}}}{\rho}}$$

... Euler equation

$\Rightarrow$ 아직도 특별한 결과X. 결국 f를 알아야한다... (Perterbative method, hard to deal)

(*) Summary. N particle system



6N-Dimensional γ-space.

$$\Rightarrow \dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\Big\updownarrow$$

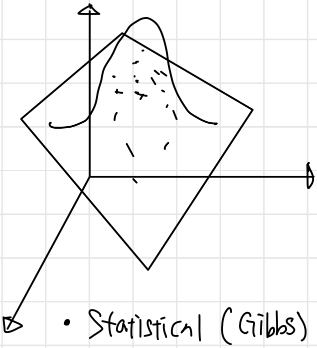
Relation: "Kinetic Theory" in 19th.

A Few thermodynamic variables (E, T, N, V, P ...)

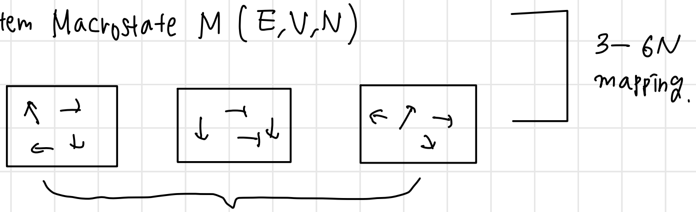
via S, W, Q.

IV. Foundation of Equilibrium Statistic Mechanics

1. Statistical Ensemble.



- System Macrostate $M(E,V,N)$



Different microstate configuration, same M-state.

- Statistical (Gibbs) Ensemble

⇒ A collection of a large number of copies of identical systems
(Each constructed to have the given M-State)

- $\rho(\vec{p},\vec{q},t)$: phase space density.

⇒ $d\vec{p}\,d\vec{q}\,\rho$ = number of representive points in the volume elements
(μ-states)

Remind)

$$\begin{cases} \dfrac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{v}) = 0. \quad (\nabla = \text{phase space operator}) \\ \dfrac{\partial\rho}{\partial t} + \sum_i \left(\dfrac{\partial\rho}{\partial q_i}\dfrac{\partial H}{\partial p_i} - \dfrac{\partial\rho}{\partial p_i}\dfrac{\partial H}{\partial q_i}\right) = \underbrace{\dfrac{\partial\rho}{\partial t} + \{\rho, H\}}_{=\frac{d\rho}{dt}} = 0. \end{cases}$$

... Liouville thm.

$$\left(\because\ \dot{p}_i = -\frac{\partial H}{\partial q_i},\quad \dot{q}_i = +\frac{\partial H}{\partial p_i}\right)$$

2. Statistical Postulate

- Consider a physical quantity $\Theta(\vec{p},\vec{q})$ → physical meaningful : average.

$$\langle\Theta\rangle = \int d\vec{p}\,d\vec{q}\;\rho(\vec{p},\vec{q},t)\,\Theta(\vec{p},\vec{q}),\qquad \frac{d\langle\Theta\rangle}{dt} = \int d\vec{p}\,d\vec{q}\,\underbrace{\left(\frac{\partial\rho}{\partial t}\right)}_{=-\{\rho,H\}}\Theta(\vec{p},\vec{q})$$

$$\frac{d\langle\Theta\rangle}{dt} = -\int d\vec{p}\,d\vec{q}\cdot\Theta\cdot\sum_{i=1}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right)$$

$$\xrightarrow[\text{omit } \Sigma.]{\text{부분적분}} \cancel{-\Theta\cdot\rho\cdot\frac{\partial H}{\partial p_i}\Big|_S} + \int d\vec{p}\,d\vec{q}\cdot\rho\cdot\frac{\partial\Theta}{\partial q_i}\frac{\partial H}{\partial p_i} + \cancel{\int d\vec{p}\,d\vec{q}\;\rho\cdot\Theta\cdot\frac{\partial^2 H}{\partial q_i\partial p_i}}$$

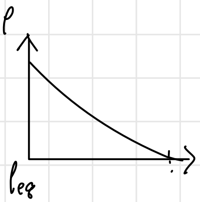
$$+ \cancel{\Theta\cdot\rho\cdot\frac{\partial H}{\partial q_i}\Big|_S} - \int d\vec{p}\,d\vec{q}\cdot\rho\cdot\frac{\partial\Theta}{\partial p_i}\cdot\frac{\partial H}{\partial q_i} - \cancel{\int d\vec{p}\,d\vec{q}\cdot\rho\cdot\Theta\cdot\frac{\partial^2 H}{\partial p_i\partial q_i}}$$

$S\to\infty$, 0.

$$\boxed{\therefore\ \frac{d\langle\Theta\rangle}{dt} = \langle\{\Theta, H\}\rangle}$$

... time dependence of $\langle\Theta\rangle$ $= \int d\vec{p}\,d\vec{q}\cdot\rho\cdot\{\Theta, H\}$

- Now, for equilibrium condition. $\Leftrightarrow \dfrac{d\langle\theta\rangle}{dt} = 0.$



(*) Equilibrium (Stationary) Ensemble.

$$\frac{d\langle\theta\rangle}{dt} = 0. \longrightarrow \left(\frac{\partial\rho}{\partial t}\right) = 0 \quad \left(\text{not } \frac{d\rho}{dt},\ \text{this is always } 0 \text{ for incompressible } \rho\right)$$

$$\xrightarrow[\text{Liouville}]{} \{\rho, \mathcal{H}\} = 0$$

→ these are not rigorous, but physically acceptable.

→ one possible way of satisfying this : To assume $\rho = \rho_{eq}(\mathcal{H}(\vec{p}, \vec{q}))$

The fundamental assumption of statistical mechanics

(Postulate of a equal priori probability)

In thermodynamic equilibrium, an isolated system is equally likely to be any state satisfying the given macroscopic conditions

↳ 외부 영향 X, E (or $\mathcal{H}$) invariant

$\Rightarrow \rho_{eq}$ is fixed

$\Rightarrow \rho_{eq}$ is constant on constant energy (M state) surface

3. Ergodic Hypothesis (Not yet proved rigorously still now)

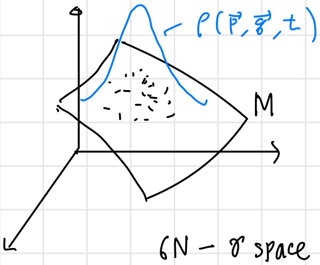
- In Statistic, average value (for physical quantity) is meaningful, important.

⇒ 이 값은, 정의대로라면 수 많은 sample 준비, 측정해야 얻을 수 있다. (Ensemble average)

⇒ but, 실제 실험에서는 Temporal average를 측정. 이를 사용. 왜일까?

- Two different averages

① Ensemble average



$$\langle\theta\rangle = \int d\vec{p}\, d\vec{q}\ \theta \cdot \rho(\vec{p}, \vec{q}, t)$$

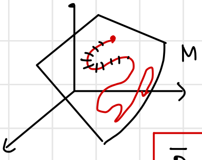
$$\Big\downarrow t \to \infty$$

$$\frac{d\langle\theta\rangle}{dt} = 0, \quad \rho_{eq} = \rho_{eq}(\mathcal{H}(\vec{p}, \vec{q})) \to \text{constant}$$

$$\Rightarrow \boxed{\langle\theta\rangle_{eq} = \int d\vec{p}\, d\vec{q} \cdot \theta\,(\text{const.})}$$

$\neq$?

② Temporal average



$$\bar{\theta} = \frac{1}{T}\int_0^T dt \cdot \theta(\vec{p}, \vec{q}, t)$$

$$\Big\downarrow T \to \infty$$

$$\boxed{\bar{\theta} = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt \cdot \theta(\vec{p}, \vec{q}, t)}$$

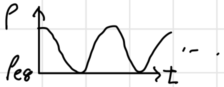
• Ergodic hypothesis

after a sufficiently long time, Γ- trajectory passes through every point in the allowed Γ-space with equal number of time.

cf)

quasi-ergodic

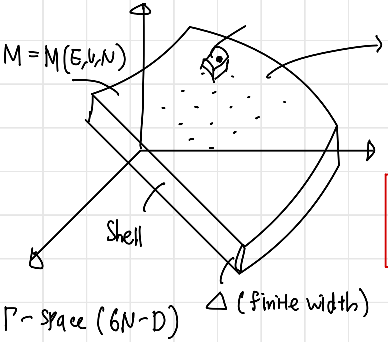
Spanning time << relaxation time scale, is it ok?



4. Microcanonical Ensemble. $M=(E,V,N)$

- Consider an isolated system (No exchange of Q, W, ···) Based on fundamental assumption

→ Energy Conservation: $\rho=\rho_{eq}=\text{const.}$ → equally 분포된 representative points on M. (equally likely)



$$\boxed{\rho(\vec{p},\vec{q})=\frac{1}{\sigma(E)}\delta[\mathcal{H}(\vec{p},\vec{q})-E]}$$

($\sigma(E)$ = Surface area of hypersurface)

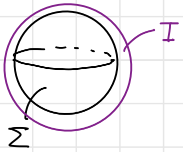
→ hard to evaluate σ?

⇒ Allow uncertainty Δ in energy.

$$\boxed{\rho=\begin{cases}\frac{1}{\Gamma(E)}\cdot & (E\le\mathcal{H}\le E+\Delta)\\ 0 & \text{otherwise.}\end{cases}}$$

• Let's define $\Gamma\equiv$ Volume of the shell $=\int_{E\le\mathcal{H}\le E+\Delta}d\vec{p}\,d\vec{q}$

$\Sigma\equiv$ Volume of the enclosed volume $=\int_{E<\mathcal{H}}d\vec{p}\,d\vec{q}$



then, $\Gamma=\Sigma(E+\Delta)-\Sigma(E)\simeq\underline{\frac{\partial\Sigma}{\partial E}}\cdot\Delta$

$=\sigma(E)$.

(Quantum mechanical) $\Delta p\,\Delta q\gtrsim\hbar$. $(\Delta p\,\Delta q)^{3N}\gtrsim\hbar^{3N}$

$$\boxed{\therefore\ \Omega(E,V,N)\equiv\frac{\Gamma(E,V,N)}{\Gamma_0}}$$

Γ_0 → unit volume

⇒ number of different microscopic states

(that we can distinguish)

$$\Rightarrow P(\vec{\mu})=\begin{cases}\frac{1}{\Omega(E)} & \text{if } E\le\mathcal{H}\le E+\Delta\\ 0 & \text{otherwise}\end{cases}$$

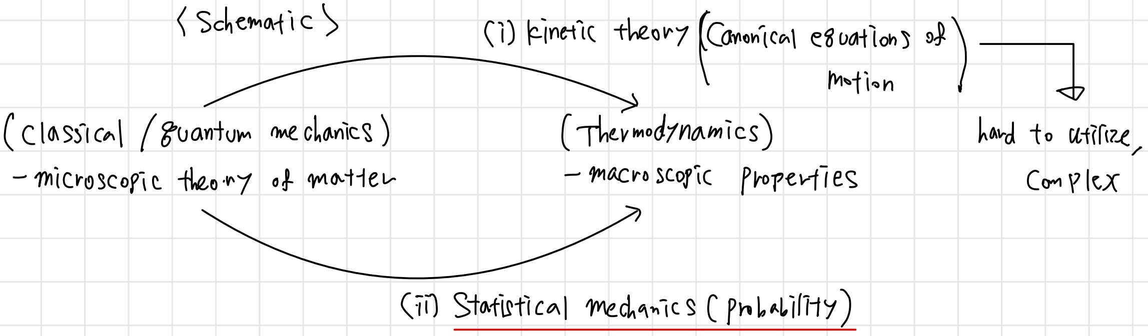
$(\rho(\vec{p},\vec{q})=P(\vec{\mu}))$

$\left(\int d\vec{p}\,d\vec{q}\,\rho(\vec{p},\vec{q})=1\right)$

5. Entropy

- Statistical Mechanics : A probablistic Approach to equilibrium

⟨Schematic⟩



(*) Entropy

$$S(E,V,N) = -k_B \cdot \langle \ln P(\vec{\mu}) \rangle = -k_B \cdot \sum_{\vec{\mu}} P(\vec{\mu}) \cdot \ln P(\vec{\mu}) \qquad \left(P(\vec{\mu}) = \frac{1}{\Omega(E)} \right)$$

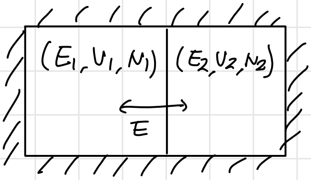
$$= +k_B \sum \frac{1}{\Omega} \cdot \ln \Omega$$

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

$$\boxed{\therefore S(E,V,N) = k_B \cdot \ln \Omega(E,V,N)}$$

(*) Zeroth Law (Power of Entropy)

- When two systems are in thermal equilibrium, the temperatures of the two systems are the same .



(V, N) → fixed. only allowed to exchange E.

$$\begin{cases} \vec{\mu} = \vec{\mu}_1 \otimes \vec{\mu}_2 \\ E = E_1 + E_2 . \end{cases} \qquad P(E) = \begin{cases} \dfrac{1}{\Omega(E)} & \mathcal{H}_1 + \mathcal{H}_2 = E \ldots \\ 0 & \text{otherwise} \end{cases}$$

$$\Rightarrow \Omega(E) = \int dE_1 dE_2 . \Omega_1(E_1) \Omega_2(E_2) \delta(E - E_1 - E_2)$$

$$= \int dE_1 \cdot \Omega_1(E_1) \Omega_2(E - E_1) = \int dE_1 \cdot \exp\left[\frac{1}{k_B} \cdot \left(S_1(E_1) + S_2(E - E_1) \right) \right]$$

(Approx) $F = \sum_{i=1}^{M} F_i$, $F_i \sim O(e^{N\phi_i})$, $M \sim N^p$. $F_{max} = max(F_i)$

$$F_{max} \le F \le M \cdot F_{max}$$

$$\lim_{N \to \infty} \left(\frac{1}{N} \ln F_{max} \le \frac{1}{N} \ln F \le \frac{1}{N} \ln F_{max} + \cancelto{0}{\frac{1}{N} \ln M} \right) \longrightarrow F \to F_{max}$$

$$\Omega(E) \simeq e^{\frac{1}{k_B}\cdot\left(S_1(E_1^*)+S_2(E_2^*)\right)} \qquad S(E) = k_B \ln\Omega = S_1(E_1^*) + S_2(E_2^*)$$

$$\boxed{\delta\left(\Omega_1(E_1)\Omega_2(E_2)\right) = 0.} \qquad \Omega_2\cdot\frac{\partial\Omega_1}{\partial E_1} + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = 0. \qquad \frac{1}{\Omega_1}\frac{\partial\Omega_1}{\partial E_1} + \frac{1}{\Omega_2}\cdot\frac{\partial\Omega_2}{\partial E_1} = 0.$$

$$\boxed{\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1^*} + \left.\frac{\partial S_2}{\partial E_1}\right|_{E_1^*} = 0.}$$

$$\Rightarrow \left.\frac{\partial}{\partial E_1}\ln\Omega_1\right|_{E_1^*} = \left.\frac{\partial}{\partial E_2}\ln\Omega_2\right|_{E_2^*}$$

$$\boxed{\therefore \left.\frac{\partial S_1}{\partial E_1}\right|_{E_1^*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2^*} \xrightarrow[\substack{\uparrow \\ \left(\frac{\partial S}{\partial E}\right)=\frac{1}{T}}]{\qquad\qquad} \frac{1}{T_1} = \frac{1}{T_2}.}$$