Course Notes for Statistical Mechanics

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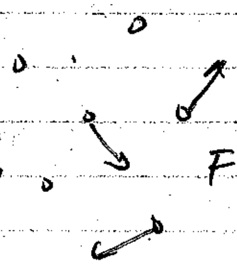
Stat Mech 1/6/2025

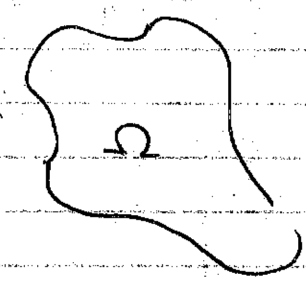
Provides answers to questions concerning connection between microscopic & macroscopic view of the world.

$\{\underline{r}_i, \underline{P}_i\}$



time-reversible

$F = ma$



$\underline{u}, T, p, \ldots$

→ why there is an arrow of time t?

→ what is entropy S?

↳ deriving thermodynamics from classical mechanics

→ provides theoretical basis for molecular simulations.

emerging properties, S, T, p.

"only makes sense when you have a large number of particles"

- ensemble.

* promises to derive thermodynamics

Probability

random variables. $\underline{X}$ $\longrightarrow \sum_{X} P(X = x) = 1$.

$$p(X = x)$$

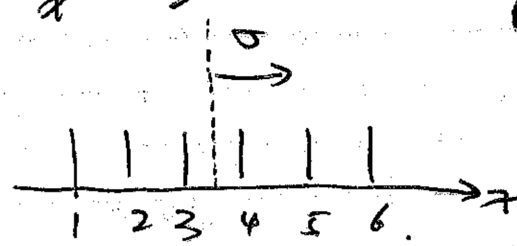
- expected value. $\mu \equiv \langle X \rangle = \sum_x x\, p(X = x)$.

- variance. $\langle X - \mu \rangle = 0$ (not variance).

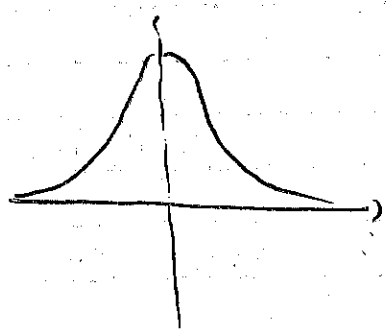
$$V \equiv \langle (X - \mu)^2 \rangle = \sum_x (x - \mu)^2 p(X = x)$$

- standard deviation.

$$\sigma(x) = \sqrt{V(x)}$$



continuous R.V. $f_X(x)$



$$\int_{-\infty}^{+\infty} f_X(x)\, dx = 1.$$

$$\mu = \int_{-\infty}^{+\infty} x f_X(x)\, dx$$

Gaussian. $f(x) = \frac{1}{\ \ } \exp\left[- \frac{(x-\mu)^2}{2\sigma^2} \right]$

two random variables. $\underline{X}, Y$

$$\langle \underline{X} + Y \rangle = \langle \underline{X} \rangle + \langle Y \rangle.$$

$$\langle a\underline{X} + bY \rangle = a\langle \underline{X} \rangle + b\langle Y \rangle.$$

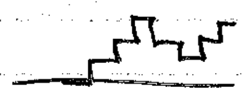
"additive"

$$\langle \underline{X} \cdot Y \rangle = \underbrace{\langle \underline{X} \rangle \cdot \langle Y \rangle}_{= \mu_X \mu_Y} \quad \text{iff } \underline{X}, Y \text{ are independent.}$$

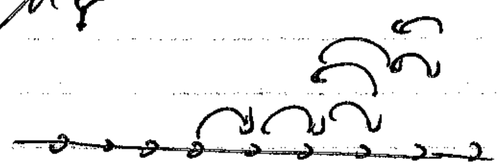
$$\langle \underline{X} \cdot \underline{X} \rangle \neq \langle \underline{X} \rangle \cdot \langle \underline{X} \rangle.$$

$$\mathrm{Cov}\langle \underline{X}, Y \rangle = \langle (\underline{X} - \mu_X)(Y - \mu_Y) \rangle$$

"positions"

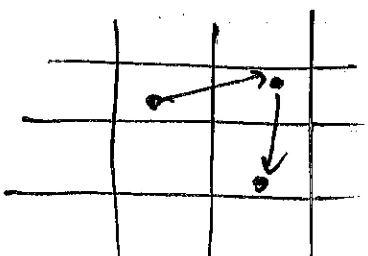


$$= \langle \underline{X} Y \rangle - \mu_X \mu_Y$$



Diffusion.

... microscopic view. ~ random walk



.... macroscopic view

~ diffusion equation.

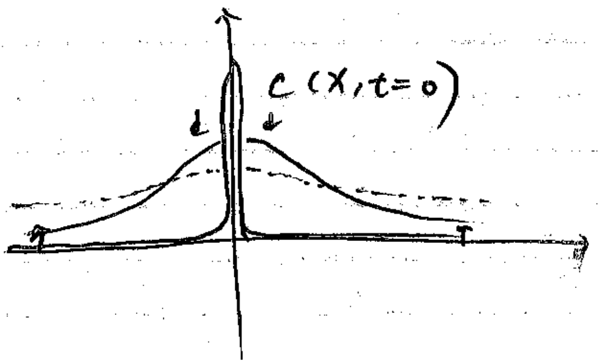
(density)

$c(x,t)dx$

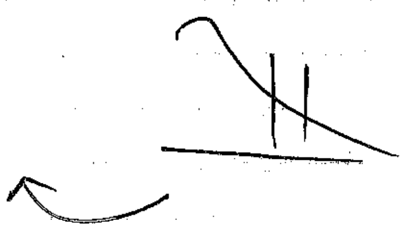
$$= \frac{\#(x, x+dx)}{dx}$$

diffusion equation.

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$



diffusion of flux



▷ observed from concentration gradients.

Additional Notes. 1/7/2025

▷ Sample space Ω

▷ Event. $p(E)$

▷ Probability.

↳ Frequency interpretation

$$\lim_{n \to \infty} \frac{\text{num. occurrence } E}{n} = p(E)$$

Probability Rules

① - <u>Additive Rule</u>. $p(A \cup B) = p(A) + p(B) - p(A \cap B)$

$A \cup B$: A or B

$A \cap B$: A and B

② A & B disconnected.

$p(A \cup B) = p(A) + p(B)$

$A \cap B = \emptyset$ i.e., mutually exclusive

③ <u>Conditional Probability</u>

$$p(B|A) = \frac{P(A \cap B)}{P(A)} \quad \text{provided } p(A) > 0.$$

④ Events A & B independent if $P(B|A) = p(B)$

⑤ Multiplicative rule: $p(A \cap B) = p(B|A)\,p(A)$

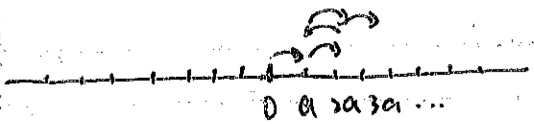
⑥ if A & B independent, $p(A \cap B) = p(A)\,p(B)$

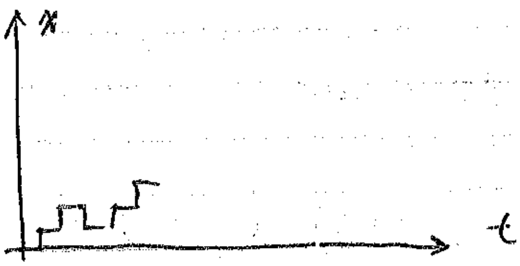
Week 1 - Lec 2. 1/8/2025

diffusion

Microscopic → macroscopic

random walk.



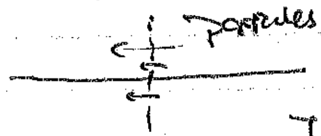


$$C(x) = \frac{\#\text{ of particles}}{\Delta V}.$$

$$\frac{\partial C(x,t)}{\partial t} = D\,\frac{\partial^2 C(x,t)}{\partial x^2}$$

1. Conservation of mass.

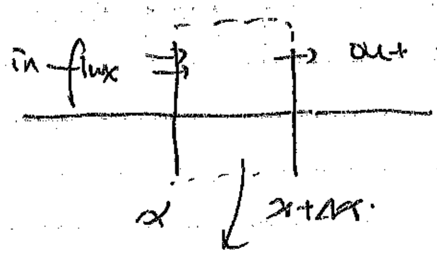
flux.



$J(x)$

$$\frac{\text{number of particles crossing the plane (to the right)}}{\Delta A \cdot \Delta t}$$

per unit time

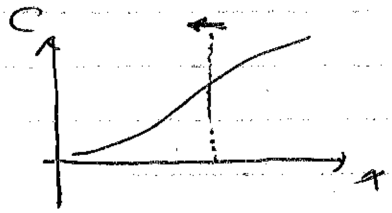


change of concentration of particles

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} J(x,t) \cancel{- \frac{\partial}{\partial y} J_y} \cancel{- \frac{\partial}{\partial z} J_z}.$$

2. Fick's law.

$$J(x,t) = -D \frac{\partial}{\partial x} C(x,t)$$



Combine $$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(-D\frac{\partial}{\partial x} C\right).$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x} C\right).$$

If D is a const., then you can take out D.

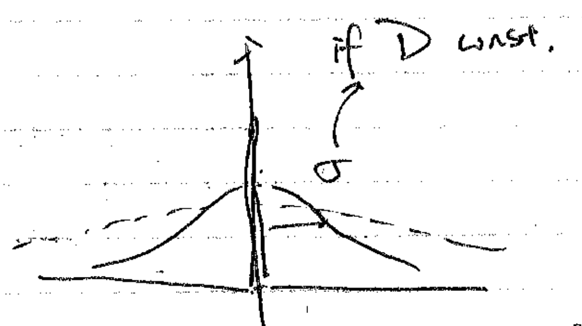
... Important assumption

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

if D(c).

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\frac{\partial C}{\partial x}\right).$$

$$\frac{\partial C}{\partial t} \neq D(c)\frac{\partial^2}{\partial x^2} C$$



Related problem. heat conduction

$$C(x,t) = \frac{N}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

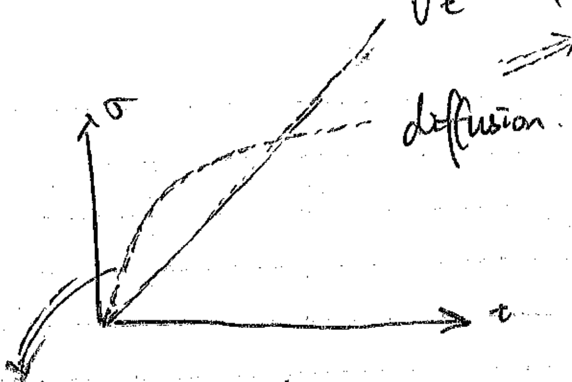
Gaussian distribution.

$$f_X(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

implying.

$$\sigma^2 = 2Dt$$
$$\hookrightarrow \sigma = \sqrt{2Dt}$$

(long-time scale. diffusion can be slow)



short time-scale. diffusion is effective.

Probability. $\langle X + Y \rangle = \langle X \rangle + \langle Y \rangle$

$\langle aX + bY \rangle = a\langle X \rangle + b\langle Y \rangle$

↳ always hold true for the 2 vars.

$\langle XY \rangle = \langle X \rangle \langle Y \rangle$ if they are independent.

↳ only means covariances are zero. not necessarily independent.

$$x(t+\tau) = \begin{cases} x(t) + a, & \text{prob} = \frac{1}{2} \\ x(t) - a, & \text{prob} = \frac{1}{2} \end{cases}$$

$x(0) = 0$

$$x(\tau) = \begin{cases} a & \text{prob} = \frac{1}{2} \\ -a & \text{prob} = \frac{1}{2} \end{cases}$$

$$x(2\tau) = \begin{cases} 2a & \text{prob} = \frac{1}{4} \\ 0 & \text{prob} = \frac{1}{2} \\ -2a & \text{prob} = \frac{1}{4} \end{cases}$$

$$x(3\tau) = \begin{cases} 3a & \text{prob} = \frac{1}{8} \\ a & \text{prob} = \frac{3}{8} \\ -a & \text{prob} = \frac{3}{8} \\ -3a & \text{prob} = \frac{1}{8}. \end{cases}$$

$$x(n\tau) = l_1 + l_2 + \cdots + l_n.$$

$$l_i = \begin{cases} a & \text{prob} = \frac{1}{2} \\ -a & \text{prob} = \frac{1}{2} \end{cases}$$

$l_i,\ l_j$ are independent $\quad i \neq j$.

$$\mu = \langle l_i \rangle = a \cdot \tfrac{1}{2} + (-a) \cdot \tfrac{1}{2} = 0$$

$$\boxed{\mu = 0}$$

$$\langle l_i^2 \rangle = (a)^2 \tfrac{1}{2} + (-a)^2 \cdot \tfrac{1}{2} = a^2$$

$$\langle l_i^3 \rangle = 0$$

$$\langle l_i^4 \rangle = a^4.$$

$$V = \sigma^2 = \langle l_i^2 \rangle - \langle l_i \rangle^2 = a^2$$

$$\langle l_i^n \rangle = \begin{cases} 0 & n \text{ odd} \\ a^n & n \text{ even}. \end{cases}$$

$$\boxed{\sigma = a}$$

$$\langle l_i + l_j \rangle = \langle l_i \rangle + \langle l_j \rangle = 0$$

$$\left.\begin{array}{ll} \langle l_i \cdot l_j \rangle = \langle l_i \rangle \cdot \langle l_j \rangle = 0 & i \neq j \\ \langle l_i \cdot l_i \rangle = \langle l_i^2 \rangle = a^2 & i = j \end{array}\right\}$$ discuss & simplify

$$\langle l_i \cdot l_j \rangle = \delta_{ij}\, a^2$$

"correct statement".

$$\langle x(n\tau) \rangle = \langle l_1 + l_2 + \cdots + l_n \rangle = 0$$

$$\langle (x(n\tau))^2 \rangle = \langle (l_1 + l_2 + \cdots + l_n)^2 \rangle$$

$$= \langle l_1^2 + l_1 l_2 + \cdots l_1 l_n + l_2 l_1 + l_2^2 + \cdots + l_n^2 \rangle$$

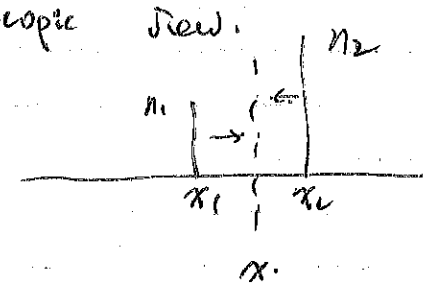
$$= \langle \underbrace{\sum_i l_i^2}_{n \text{ terms.}} + \underbrace{\sum_{i \neq j} l_i l_j}_{n(n-1) \text{ terms.}} \rangle$$

$$= \sum_i \langle l_i^2 \rangle + \sum_{i \neq j} \langle l_i l_j \rangle = na^2$$

$$\sigma_{x(n\tau)} = \sqrt{na^2} = \sqrt{n}\, a$$

... see pg. #10 & #11.

microscopic view.



$$J(x) = \frac{\frac{1}{2}\langle N_1 \rangle - \frac{1}{2}\langle N_2 \rangle}{\tau}$$

(per unit time)

$$c(x_1) = \frac{\langle N_1 \rangle}{a}$$

$$c(x_2) = \frac{\langle N_2 \rangle}{a}.$$

we then have

$$= a\, \frac{c(x_1) - c(x_2)}{2\tau}$$

$$= -\frac{a^2}{2\tau}\, \frac{c(x_1) - c(x_2)}{a}$$

$$= -\frac{a^2}{2\tau}\, c'(x).$$

implying.

$$D = \frac{a^2}{2\tau} \longleftarrow = -D\, c'(x).$$

1/10/25 Problem Session.

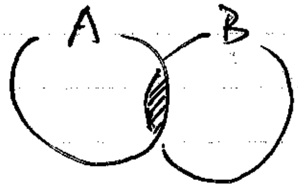
1. Definition
2. Rules
3. Central limit thm.
4.
5.

Discrete vs. Continuous.

example 1- none of $\quad 1 - \dfrac{P^{20}_{365}}{365^{20}} = 0.4$

$P^{20}_{365} \rightarrow \overbrace{365 \cdot 364 \cdots 346}^{20}$

~ Rules



- $P(A+B) = P(A) + P(B) - P(A \cap B)$

Conditional probability

- $P(B|A) =$

$$P(A) \cdot P(B|A) = P(A \cap B)$$

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

- Independent events.

$$P(B|A) = P(B) \rightarrow P(A \cap B) = P(A)P(B)$$

Example. X, Y, D.R.V.

$$\langle XY \rangle = \langle X \rangle \langle Y \rangle \quad \text{if } X, Y \text{ i.i.d.}$$

$$\sum_x x P(X=x) \cdot \sum_y y P(Y=y)$$

$$\left[P(x_1) + P(x_2) + \dots P(x_n)\right]\left[P(y_1) + P(y_2) + \dots + P(y_n)\right]$$

$$P(x_1)P(y_1) + P(x_1)P(y_2) + \cdots P(x_1)\cdot P(y_n)$$

$$+ P(x_2)P(y_1) + \cdots \qquad + P(x_n)P(y_1) + \dots + P(x_n)P(y_n)$$

$$\sum_i P(x_i)P(y_i) + P(x_i)P(y_j).$$

$$\therefore P(X=x, Y=y) = P(X=x)\cdot P(Y=y)$$

for discrete case

Central limit theorem.

$X_i \quad \langle X_i \rangle = \mu. \qquad i = 1, 2, 3, \dots, N.$

$Var(X_i) = \sigma^2$

$$\bar{X} = \frac{1}{N}\sum_i^N X_i \qquad \langle \bar{X} \rangle = \frac{1}{N}\sum_{i=1}^N \langle X_i \rangle = \mu$$

assume X_i s are independent of each other

$$\langle X_i, X_j \rangle = \mu^2 \quad (i \neq j).$$

$$Var(X) = E(X^2) - E(X)^2$$

Example

$$\langle X_i^2 \rangle = Var(X_i) + \langle X_i \rangle^2$$

$$= \sigma^2 + \mu^2$$

$$Var(\bar{X}) = \langle (\bar{X} - \langle \bar{X} \rangle)^2 \rangle$$

$$= \langle \bar{X}^2 + \langle \bar{X} \rangle^2 - 2\bar{X}\langle \bar{X} \rangle \rangle$$

$$= \langle \bar{X}^2 \rangle + \langle \bar{X} \rangle^2 - \underbrace{2\langle \bar{X} \rangle \langle \bar{X} \rangle}_{2\langle \bar{X} \rangle^2}$$

$$= \langle \bar{X}^2 \rangle - \underbrace{\langle \bar{X} \rangle^2}_{\mu^2}$$

Q: $\langle \bar{X}^2 \rangle = ?$

$$= \left\langle \left(\frac{1}{N} \sum_i^N X_i \right)^2 \right\rangle = \frac{1}{N^2} \left\langle \left(\sum_{i=1}^N X_i \right) \left(\sum_{i=1}^N X_i \right) \right\rangle$$

$$= \sum_i X_i^2 + 2 \sum_{i \neq j} X_i X_j$$

$$= \underbrace{\sigma^2 + \mu^2}_{\text{as derived previously}} + 2\mu^2$$

1/13/2025

Diffusion w/ Drift.

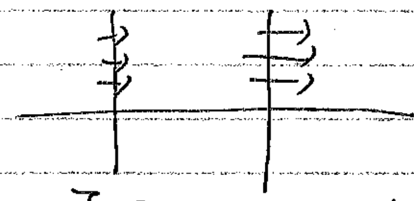
Einstein notation.

Classical Mechanics.

- Statistical (Microcanonical ensemble)

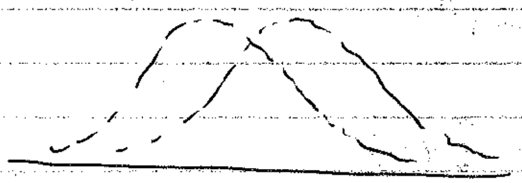
Diffusion Equation.

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$



$J(x)$ $\quad$ $J(x+dx)$

$$J(x,t) = -D\frac{\partial}{\partial x} c(x,t)$$

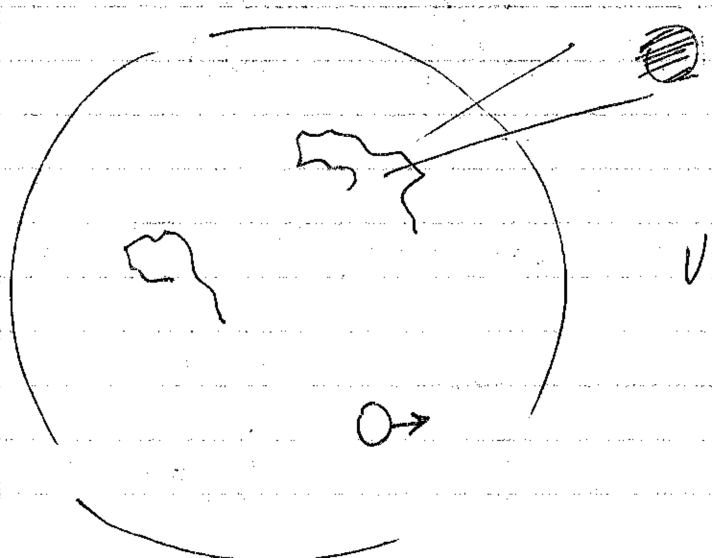


+ $\quad$ Fick's law

$v \cdot c(x,t)$ $\quad$ w/ drift term

$\mu F(x,t)$

Brownian motion



$v = \mu F$

$$\left[\frac{\#^2}{m^2 s}\right] \quad \left[\frac{\#}{m^3}\right]$$

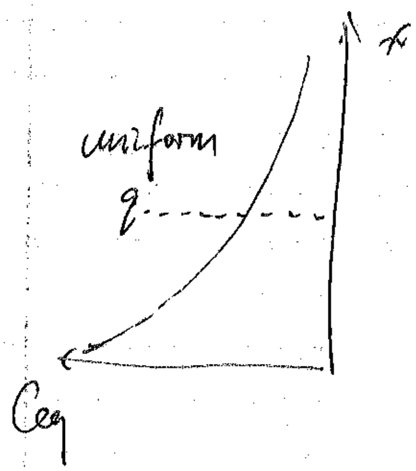
$$\left[\frac{m^2}{s}\right]\cdot\left[\frac{1}{m}\right].$$

$$\left[\frac{m}{s}\right]\left[\frac{\#}{m^2}\right]$$

$$\left[\frac{m}{s}\right] = \left[\frac{m}{N s}\right]\cdot N$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \mu\frac{\partial}{\partial x}\left[F(x)\, c(x)\right]$$

C_{eq}: $J(x) = 0 = -D\frac{\partial}{\partial x} C_{eq} + \mu F(x)\, C_{eq}(x)$



$$F(x) = \frac{\partial \phi(x)}{\partial x}$$

e.g. $\phi(x) = mgx$

$F(x) = -mg$

$V(x) = -mg\mu$

$$D\frac{\partial}{\partial x} C_{eq}(x) = \mu \frac{\partial \phi(x)}{\partial x} \cdot C_{eq}(x)$$

$$C_{eq}(x) = A\, e^{-\frac{\mu}{D}\phi(x)}$$

$$\frac{\mu}{D} = \frac{1}{k_B T} \qquad \boxed{\mu = \frac{D}{k_B T}}$$ Einstein Relation

Fluctuation-Dissipation Theorem

Equilibrium: flux cancels out $\frac{\partial c}{\partial t} = 0$

Steady-State: const. flux $\frac{\partial c}{\partial t} = 0$

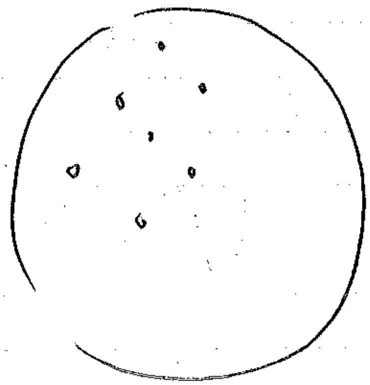
Microscopic → Macroscopic

Classical mechanics   thermodynamics

($F = ma$)

Lagrangian

Hamiltonian



N- particles

$\underline{r}_1, \underline{r}_2, \ldots \underline{r}_N$

$= (q_1, q_2, q_3, \ldots, q_{3N})$

$\underline{v}_1, \underline{v}_2, \ldots, \underline{v}_N$

$= (\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_{3N})$

$$\ddot{q}_i = -\frac{1}{m}\frac{\partial U(\{q_i\})}{\partial q_i} \qquad i = 1, 2, \ldots 3N$$

$$L(\{q_i\}, \{\dot{q}_i\}) = K - U$$

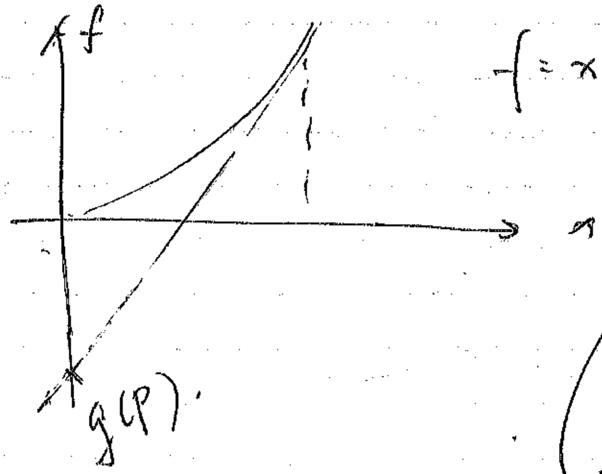
$$= \sum_i \frac{1}{2} m \dot{q}_i^2 - U(\{q_i\})$$

Lagrange's E.o.M. $\quad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \left(\frac{\partial L}{\partial q_i}\right) = 0 \quad i = 1, 2, \ldots, 3N$

Legendre transform

Define var. $P_i = \frac{\partial L}{\partial \dot{q}_i}$ $\qquad$ $P_i = m\dot{q}$

$$H(\{q_i\},\{p_i\}) = \sum_{i=1}^{3N} P_i \dot{q}_i - L$$



$f = x^3$ $\qquad$ $p = 3x^2$

$$g(p) = xp - f$$

$$\begin{cases} x = \left(\frac{p}{3}\right)^{1/2} \\ g = \left(\frac{p}{3}\right)^{1/2} p - \left(\frac{p}{3}\right)^{3/2} \end{cases}$$

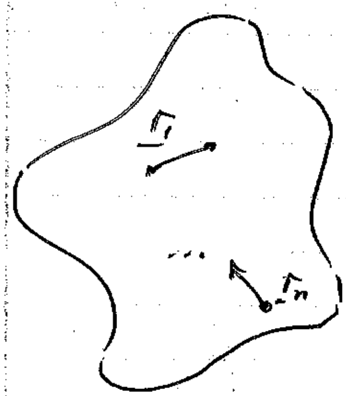
$$H = \sum_i \frac{p_i^2}{2m} + U(\{q_i\})$$

Hamilton's EoM

$$\begin{cases} \dot{P}_i = \frac{\partial H}{\partial q_i} \\ \dot{q}_i = \frac{\partial H}{\partial P_i} \end{cases}$$

1/15/2023 Lecture 4.

- classical mechanics.
- microcanonical ensemble



Coordinates: $(q_1, q_2, \cdots q_{3N}) \rightarrow \{q_i\}$.

Momenta: $(p_1, p_2, \cdots p_{3N}) \rightarrow \{p_i = m\dot{q}_i\}$.

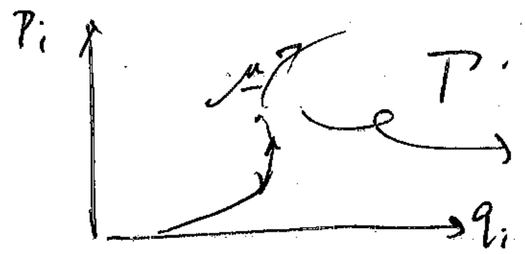
$H(\{q_i\}, \{p_i\})$ — Hamilton's eqs of motion.

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad \hookrightarrow \sum_i \frac{p_i^2}{2m} + U(\{q_i\})$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

Phase Space

$\underline{\mu} = (q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N})$.



Γ contains full information for your system.

$$\dot{\underline{u}} = \underbrace{\left[\begin{array}{c:c} 0 & I \\ \hdashline -I & 0 \end{array}\right]}_{3N\times 3N} \frac{\partial H}{\partial \underline{u}}$$

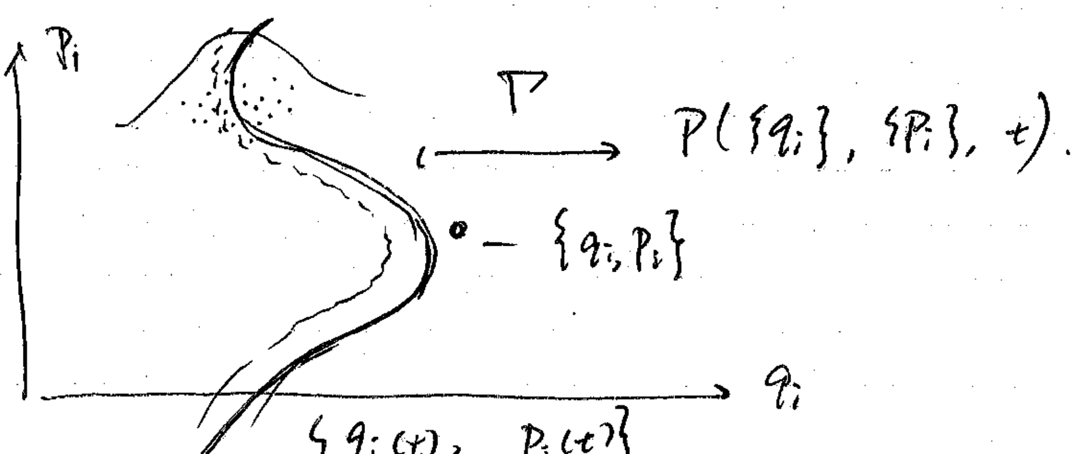
enclose the Hamiltonian relation

simplifies to $\dot{\underline{u}} = \omega \cdot \dfrac{\partial H}{\partial \underline{u}}$

$$\begin{bmatrix} \dot q_1 \\ \dot q_2 \\ \vdots \\ \dot q_{3N} \\ \dot p_1 \\ \dot p_2 \\ \vdots \\ \dot p_{3N} \end{bmatrix} = \begin{bmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \end{bmatrix} \begin{bmatrix} \frac{\partial H}{\partial q_1} \\ \frac{\partial H}{\partial q_2} \\ \vdots \\ \frac{\partial H}{\partial q_{3N}} \\ \hline \frac{\partial H}{\partial p_1} \\ \vdots \\ \frac{\partial H}{\partial p_{3N}} \end{bmatrix}$$

Ensemble

collection of points in the phase space



$$\frac{\partial c}{\partial t} = \underbrace{-D\frac{\partial^2 c}{\partial x^2}}_{\text{diffusion}} + \underbrace{\mu\left(F(x)\frac{\partial c}{\partial x}\right)}_{\text{drift}}$$

Equilibrium ensemble

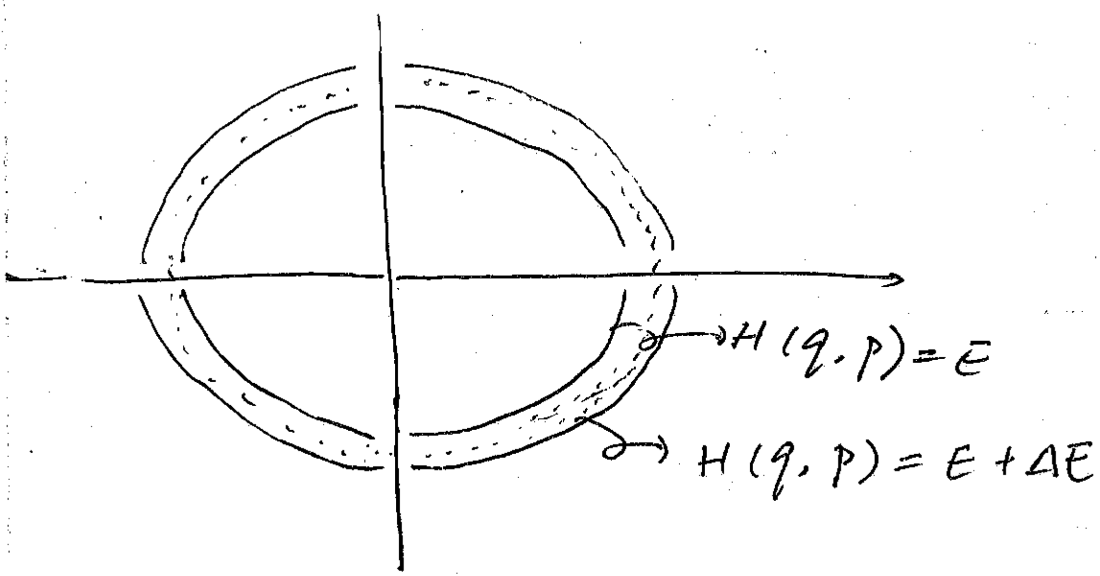
$$\rho_{eq}(\{q_i\}, \{p_i\})$$

it is implied that

$$\dot{H} = 0$$

Microcanonical ensemble

$$\rho_{mc}(\{q_i\}, \{p_i\}, t) = \begin{cases} \text{const} & \text{if } E \le H(\{q_i\}, \{p_i\}) < E+\Delta E \\ 0 & \text{otherwise} \end{cases}$$



ergodicity

1/17/2025

if $\langle XY \rangle = \langle X \rangle \langle Y \rangle \rightarrow$ independent. F

$\&$

only means cov are zero

$J = \frac{N}{At}$ ✓

$P(Y = y | X = x) = P(Y = y)$

for all y

Newtonian - Lagrangian - Hamiltonian

Recall Newton $F_i = m\ddot{q}_i$

(1687)

$$\frac{dP_i}{dt} = F_i$$

Lagrange : $\mathcal{L} = K - U = \sum_i \frac{1}{2} m \dot{q}_i^2 - U(\{q_i\})$

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial q_i} = 0 \quad \forall_i \quad (1860)$$

$m\dot{q}$ $\quad \left(-\frac{\partial}{\partial q_i} U(q_i)\right)$

$$\frac{d}{dt}(m\dot{q}) - \left(- \frac{\partial}{\partial q_i} U(q_i)\right) = 0$$

$$\ddot{q} = -\frac{1}{m}\nabla U(q_i)$$

$$\ddot{q}_i = -\frac{1}{m}\frac{\partial U}{\partial q_i}$$

Hamilton: $$dL = \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

$$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial L}{\partial \dot{q}_i}\frac{d\dot{q}_i}{dt}$$

$$\frac{\partial L}{\partial \dot{q}_i} \cdot \frac{d}{dt}(\dot{q}_i)$$

$$\frac{\partial L}{\partial q_i}\frac{dq_i}{dt} = \frac{\partial \dot{q}_i}{\partial q_i} \cdot \frac{\partial L}{\partial \dot{q}_i}\left(\frac{dq_i}{dt}\right) \rightarrow \dot{q}_i$$

$$= \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right)\dot{q}_i$$

$$= \frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}_i}\dot{q}_i\right] + \frac{dL}{d\dot{q}_i}\frac{d}{dt}(\dot{q}_i)$$

$$\frac{dL}{dt} = \frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}_i}\dot{q}_i\right]$$

$$\Rightarrow \frac{d}{dt}\Big[\underbrace{L + \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i}_{H_i}\Big] = 0$$

$$H = -L + \frac{\partial L}{\partial \dot{q}_i}\dot{q}_i$$

$$= -L + p_i \dot{q}_i$$

Example

$$H = \frac{p^2}{2m} + U(x). \qquad H = H(x,p)$$

$$L = -H + \left(\frac{\partial H}{\partial p}\right)p = -H + vp.$$

① $dH = \frac{\partial H}{\partial p}dp + \frac{\partial H}{\partial x}dx$

$$= v\,dp + v'dx$$

② $dL = -dH + v\,dp + p\,dv$ $\quad H = -L + \left(\frac{\partial L}{\partial v}\right)v$

$\hookrightarrow L(x, v)$

$$\frac{\partial L}{\partial \dot q_i} = p_i \qquad \frac{\partial L}{\partial q_i} = \frac{\partial \dot q_i}{\partial q_i}\cdot\frac{\partial L}{\partial \dot q_i} = \frac{d}{dt} p_i = \dot p_i$$

EOM L

$$H = -L + \sum_i p_i \dot q_i$$ ~~xxx~~ Legendre transform

$$dH = \sum_i dp_i\, \dot q_i + d\dot q_i\, p_i - \underbrace{\frac{\partial L}{\partial q_i} dq_i}_{p_i dq_i} - \underbrace{\frac{dL}{d\dot q_i} dq_i}_{\dot p_i dq_i}$$

$$= \underbrace{\dot q_i\, dp_i}_{\frac{\partial H}{\partial p_i}} - \underbrace{\dot p_i\, dq_i}_{\frac{\partial H}{\partial \dot q_i}}$$

$$\begin{cases} \dfrac{\partial H}{\partial p_i} = \dot p_i \\[2ex] \dfrac{\partial H}{\partial \dot q_i} = -\dot p_i \end{cases}$$

EOM H

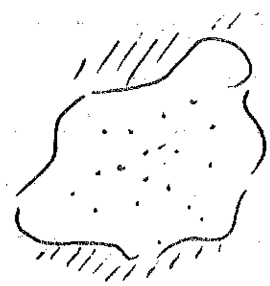
1/22/2025

Today

- microcanonical ensemble
- example : ideal gas.
- Legendre transform. in thermodynamics.

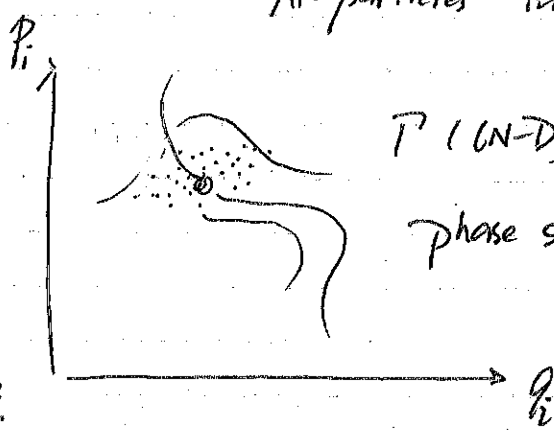
$H(\{q_i\}, \{p_i\})$

$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases} \quad \forall i = 1, \cdots, 3N$$



Recall p.16

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



Define: Poisson's bracket.

$$\{A, B\} = \sum_{i=1}^{3N} \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i}$$

$\rho(\{q_i\}, \{p_i\}, t)$

this term can thus be rewritten as

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}$$

One may derive that $\{A, B\} = -\{B, A\}$. $\{A, A\} = 0$

$\{A, f(A)\} = 0$, $\quad C = f(A)$. $\frac{\partial C}{\partial p_i} = f'(A) \cdot \frac{\partial A}{\partial p_i}$

$\frac{\partial}{\partial t} \rho_{eq}(\{q_i\}, \{p_i\}) = 0 \quad \cdots (*)$

sufficient condition. $\boxed{f(H(q_i, p_i)) = \rho_{eq}}$

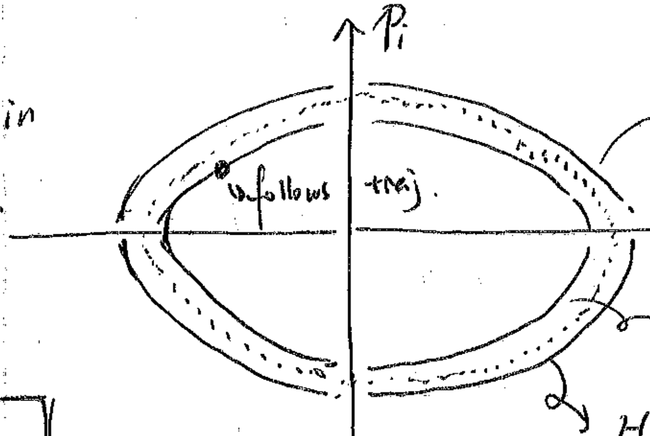
Hamiltonian is given

i.e. as long as this is satisfied.

$\rightsquigarrow$ Eqn. $(*)$ can be satisfied.

Micro-canonical Ensemble

uniform in 6N-D



trajectory preserves because energy is conserved in a closed system.

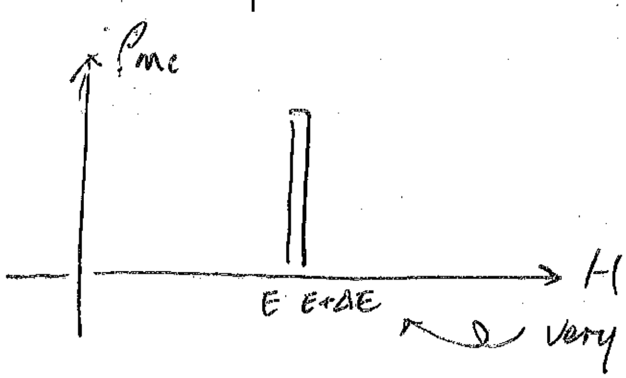
$H(q_i, p_i) = E$

$H(q_i, p_i) = E + \Delta E$.

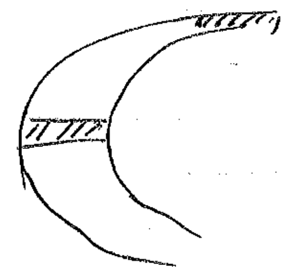
Erogodicity assumption

$\hookrightarrow \rho_{MC} = \begin{cases} \text{const} & \text{if } E \le H \le H + \infty \\ 0 & \text{otherwise}. \end{cases}$

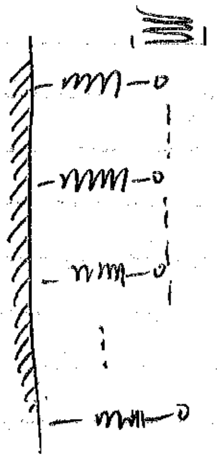
energy surface



very small interval



An counter example of ergodicity



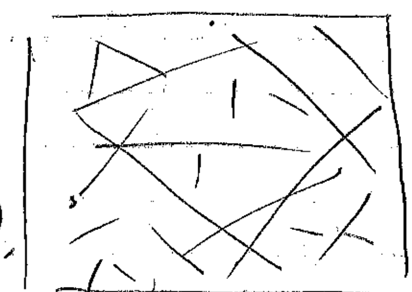
$$\left.\begin{aligned} \ddot{x}_1 &= -kx_1 \\ \ddot{x}_2 &= -kx_2 \\ &\vdots \end{aligned}\right\} \quad \begin{aligned} U &= \tfrac{1}{2}kx_1^2 + \tfrac{1}{2}kx_2^2 + \cdots \\ &\text{from potential energy} \end{aligned}$$

↳ no ergodic system
when they are not coupled

Ideal Gas

$$H(\{q_i\}, \{p_i\}) = \sum_i \frac{p_i^2}{2m} + \sum_i \phi(x_i)$$

"By itself is not ergodic".



↳ nonergodic.

in reality, some interactions between the particles (when gas not ideal).

$$\ldots + \sum_i \mathcal{U}(\{q_i\})$$

$$\Downarrow \quad \cdots \to 0$$

large enough to be ergodic

small enough that we can ignore it in the calculation

$$\rho_{mc}(\{q_i\}, \{p_i\}) = \begin{cases} C' & E \le H(\underline{\mu}) < E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

$$\underbrace{\{q_i\}, \{p_i\}}_{\underline{\mu}}$$

$$1 = \int d^{6N}\underline{\mu}\, \rho_{mc}(\underline{\mu}) = C' \int_{E \le \sum_i \frac{P_i}{2m} < E + \Delta E} dP_1 \cdots dP_{3N} \;\; \left(\int dq_1\, dq_2\, dq_3\right)(\cdots)$$

$$= C' \left(\int_{2m E \le \sum_i P_i^2 \le (E+\Delta E)2m} dp_1 \cdots dp_{3N} \right) V^N$$

Assuming a closed system

"3N- dimensional sphere".

$$V_{sp}(R, d) = \frac{\pi^{d/2} R^d}{(d/2)!}$$

(by definition)

$$C' \tilde{\Omega}(E + \Delta E) - \tilde{\Omega}(E) \qquad \text{So} \quad C' = \left[\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)\right]^{-1}$$

$$\tilde{\Omega}(E) = V^N \frac{\pi^{3N/2} R^{3N}}{(3N/2)!} \quad \rightarrow \text{6N-dimensional volume}$$

$$R = \sqrt{2mE}$$

3N-D volume.

unit $\hat{\Omega}(E)$

$R = \sqrt{2mE}$

$[m]^{3N}$ $\qquad [kg \frac{m}{s}]^{3N}$ $\qquad (kg \cdot J)^{\frac{1}{2}}$

$[m^3]^N$ $\qquad [kg \cdot \frac{m^2}{s}]^{3N}$ $\qquad [kg \cdot kg \cdot \frac{m^2}{s^2}]^{\frac{1}{2}}$

$\qquad\qquad ||$ $\qquad\qquad kg \frac{m}{s}$

... same w/ Planck const.

$\sim h^{3N}$

$$f(p_1) = \int dq_1 \dots dq_{3N} \underbrace{dp_2 \dots dp_{3N}}_{3N-1} \rho_{mc}(q_i, p_i)$$

$$= [V_{sp}(\dots, 3N-1) \dots] V^N$$

as $N \to$ large,

$$= \frac{1}{\sqrt{\dots}} e^{-\frac{p^2}{2m}\frac{3N}{2E}}$$

key takeaway $\qquad \dots \sim e^{-\frac{p^2}{2mk_BT}}$

→ single particle: Gaussian; → many particles: uniform.

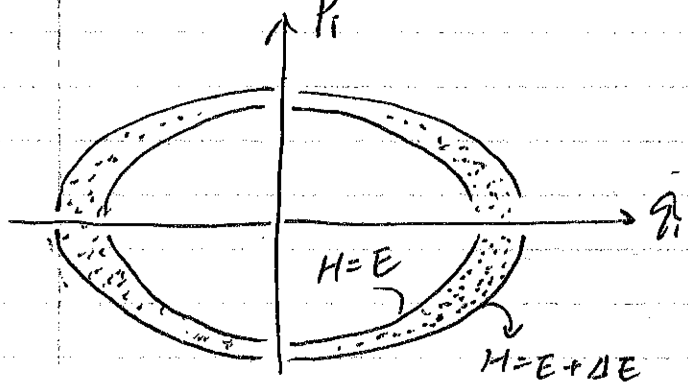
1/24/2025

- microcanonical ensemble ~ ideal gas
- Thermodynamics review.
  - fundamental eq. of state.
  - Legendre transform.

microcanonical ensemble.

$$d\underline{\mu} = dq_1 dq_2 \cdots dq_{3N} dp_1 dp_2 \cdots dp_{3N}$$

$$\rho_{mc}(\underline{\mu}) = \begin{cases} C' & E \le H(\underline{\mu}) \le E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$



$$\int d\underline{\mu}\, \rho_{mc}(\underline{\mu}) = 1.$$

$$\tilde{\Omega}(E) = \int_{H(\underline{\mu}) \le E} d\underline{\mu}$$

$$C' = \frac{1}{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)} \cdots \simeq \tilde{\Omega}'(E)\cdot\Delta E$$

↳ normalization constant

⇓

partition function

$\underbrace{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)}_{E, V, N.} = \tilde{\Omega}'(E)\,\Delta E$ provides the connection between thermodynamics & entropy no randomness in partition func.

entropy $S(E, V, N) = k_B \ln \dfrac{\tilde{\Omega}(E+\Delta E) - \tilde{\Omega}(E)}{h^{3N}}$

Macroscopic state

$\underbrace{\text{Macroscopic state}}_{\text{depends on EoS}}$

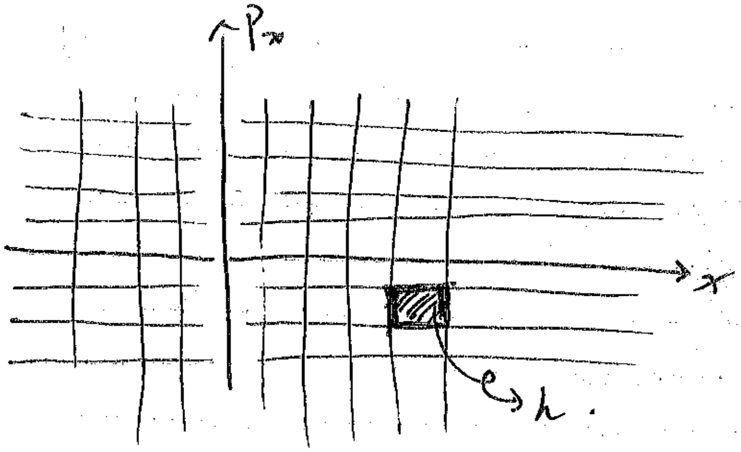
$N!$

↳ "all atoms are the same".

Boltzmann: $S = k \log W$

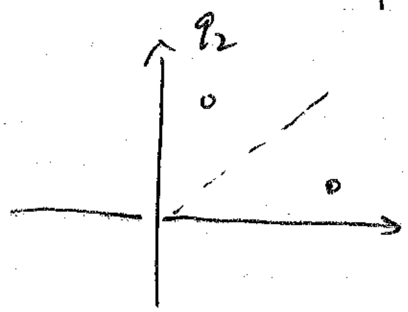
number of macroscopic states. (infinite in continuum)

Planck Const.: $\Delta x \cdot \Delta p_x \geq h$



h^{3N} $\quad \left[m \cdot kg \cdot \frac{m}{s} \right]^{3N}$

* Swap particle's positions → different microscopic state



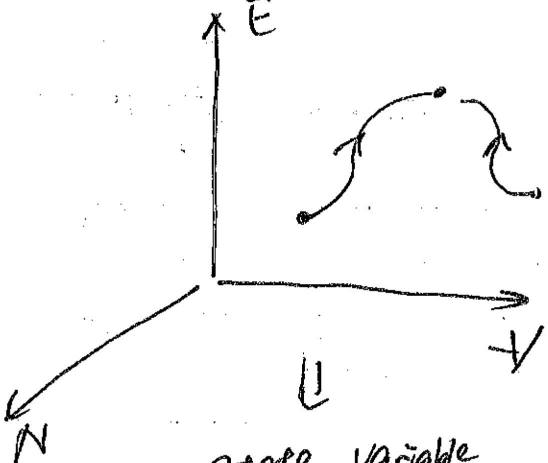
double-count in classical mechanics

Thermodynamics

(equilibrium)

~ We can describe the macroscopic state in three variables, i.e., N, V, E

rewriting entropy: $S = Nk_B\left[\log \frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2} + \frac{5}{2}\right]$



State vars.: N, V, E

exist another state variable: entropy $\underline{\underline{S}}$.

$\Downarrow$

$S(N, V, E)$

$\Downarrow$

state variable

does not depend on path.

$S(N, V, E) \rightarrow E(S, V, N) \Leftrightarrow$ fundamental equation of state

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

$$dE = TdS - pdV + \mu dN$$

$$dE = đQ + đW$$

$\Vert$

not a state variable.

$\rightsquigarrow dS = đQ/T$

$$p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}$$

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

$$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$\int_{A\to B} đQ = \text{total energy change from heat}$$

$$\int_{A\to B} \frac{đQ}{T} = S_B - S_A$$

does not depend on path, indicating this a fundamental thermodynamic variable

▷ Maxwell relation

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

Legendre transform

$E(S, V, N)$

$\downarrow$

$A(T, V, N) = E - TS$

$dE = TdS - pdV + \mu dN$

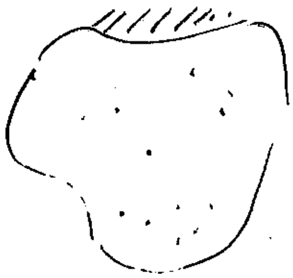
Helmholtz free energy

$$\begin{cases} S \equiv -\left(\frac{\partial A}{\partial T}\right)_{V,N} \\ P \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N} \\ \mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V} \end{cases}$$

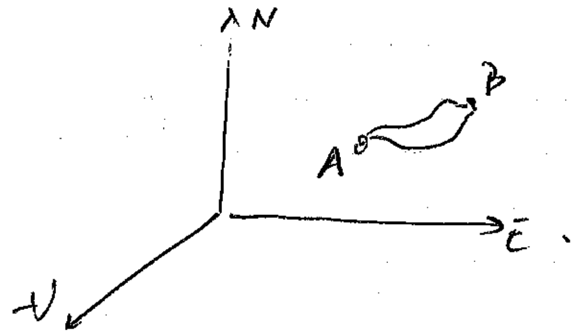
$$\begin{aligned} dA &= dE - d(TS) \\ &= TdS - pdV + \mu dN - TdS - SdT \\ &= -SdT - pdV + \mu dN \end{aligned}$$

1/29/2005 #7

Thermodynamics.



N, V, E.



thermodynamic state
(Equilibrium). 3-D.o.F.

entropy S is (4th) thermodynamic variable.

Fundamental. E.O.S. (N.V.E.)

$$dS = \frac{dQ}{T} \qquad S(N, V, E)$$

$$\downarrow$$

$$E(S, V, N).$$

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

$$\boxed{dE = T\,dS - p\,dV + \mu\,dN}$$

Extensive	Intensive quantities
N, V, E, S	$v \equiv V/N$. E/N. S/N. $\underbrace{T, p, \mu}$

"does not grow w/ N".

partial derivatives from ext. quant.

Homogeneous function (of order 1).

$$f(x_1, x_2, \dots, x_n)$$

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda f(x_1, x_2, \dots, x_n)$$

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

theorem. — virial.

$$f(x_1, x_2, \dots, x_n) = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} x_i$$

applies to all homogeneous equations of order 1 !!!

$$\boxed{E = TS - pV + \mu N}$$

full derivative

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

$$\boxed{SdT - Vdp + Nd\mu = 0}$$ (Equation of state for intensive quantities)

also true, ← Gibbs-Duhem relation

$A \xrightarrow{dT, dp}$

$$d\mu = \frac{V}{N}dp - \frac{S}{N}dT$$

$\mu = \mu(p, T)$.

Legendre transform.

$E(S, V, N)$

$\downarrow$ (writing in terms of ...)

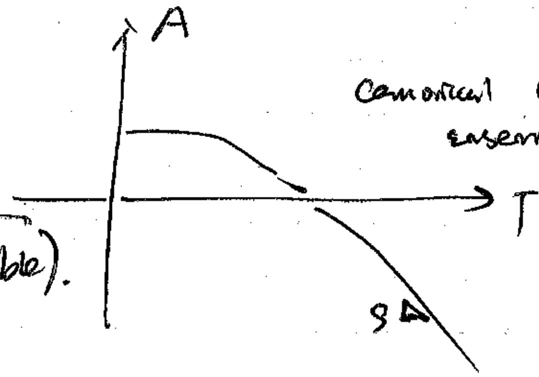
$A(T, V, N)$

$= E - TS \qquad (N, V, T)$

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

$$p \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N} \qquad \mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

$$S \equiv -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$



canonical (NVT) ensemble.

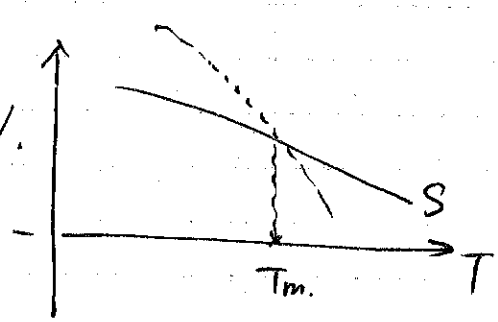
$A(T, V, N)$. (NPT ensemble).

$\downarrow$

$G(T, p, N) = A + pV$.

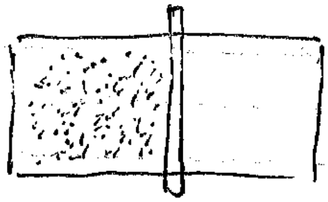
$$dG = -pdV + \mu dN - SdT + pdV + Vdp.$$

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



$$S \equiv \left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad \mu \equiv \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

Gibbs free energy



$E(S, V, N)$

$\downarrow$

$H(S, p, N) = E + pV$ ... enthalpy

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

$\downarrow$

Helmh: $A = -pV + \mu N$

$\downarrow$

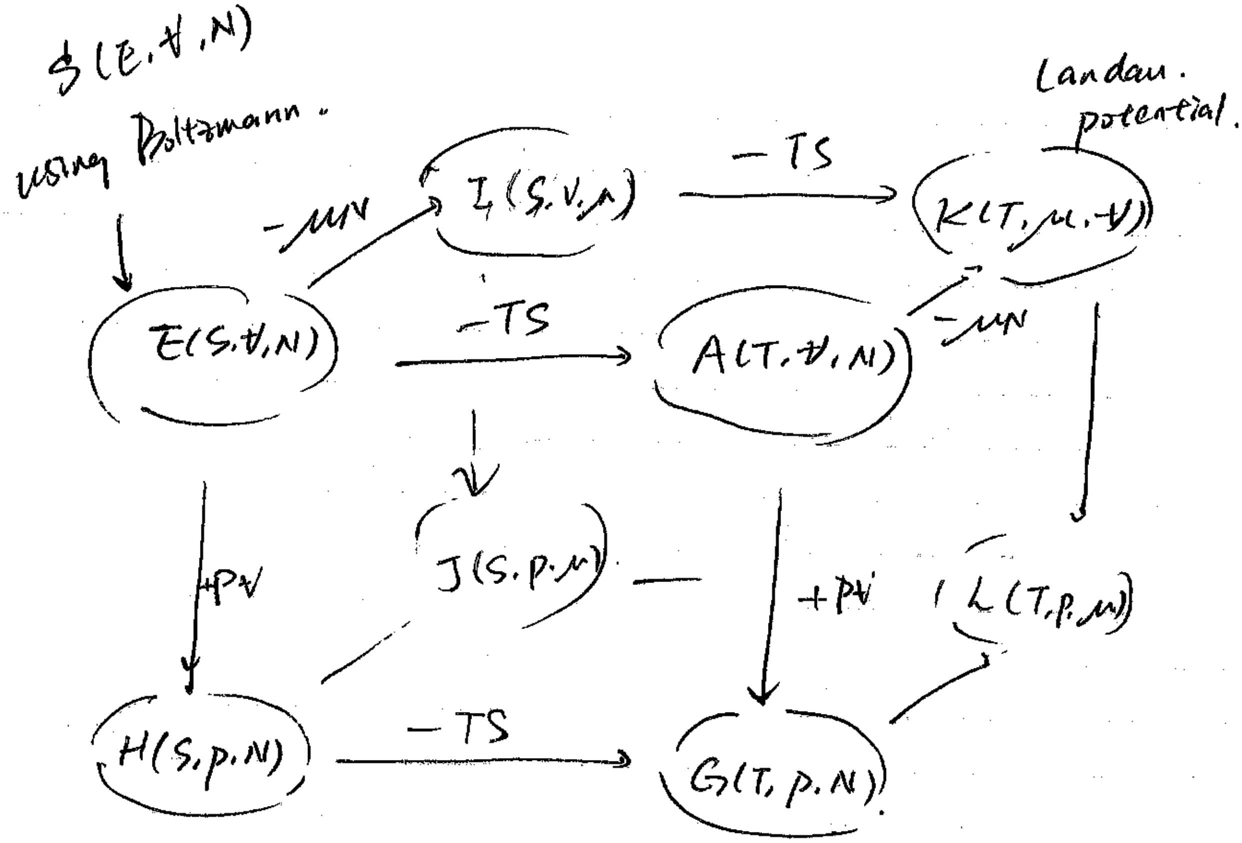
Gibbs: $G = A + pV$

$\downarrow$

$G = \mu N \rightarrow \mu = \frac{G}{N}$

$$
\begin{tikzcd}
\begin{matrix} E(S, V, N) \\ = TS - pV + \mu N \end{matrix} \arrow[r, "-TS"] \arrow[d, "+pV"] & \begin{matrix} A(T, V, N) \\ = -pV + \mu N \end{matrix} \arrow[d, "+pV"] \\
\begin{matrix} H(S, p, N) \\ = TS + \mu N \end{matrix} \arrow[r, "-TS"] & \begin{matrix} G(T, p, N) \\ = \mu N \end{matrix}
\end{tikzcd}
$$

$\mu = \frac{G}{N}$



$$\mu = \frac{G}{N}$$

$$T = \frac{J}{S}$$

1/29/2025. #8

Today
- Entropy
- Canonical ensemble

$E(S, V, N)$.

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

"Room of thermodynamics

$S(E, V, N) = k_B \ln \Omega(E)$ ..... Key Q.: why this form.

$A = -k_B T \ln Z$ — canonical ensemble

microcanonical ensemble

$$\begin{tikzcd} E \arrow[r] \arrow[d] & A \arrow[d] \\ H \arrow[r] & G \end{tikzcd}$$

Entropy

1. Information entropy

2. Irreversibility (heat conduction)

3. Irreversibility

Shanon's Information entropy.

experient : n outcomes

w/ probability P_i ... $\sum_i^n P_i = 1$.

$\hookrightarrow i = 1, \dots, n$.

formula: $S = -K \sum_{i=1}^{n} P_i \ln P_i$

if $P = 1$ or 0, $\rightarrow S = 0$ (no uncertainty).

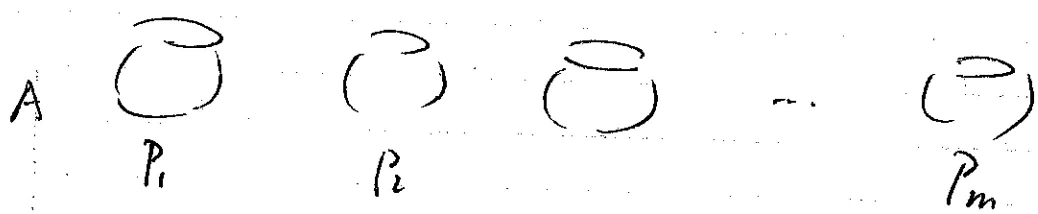
$P_i = \frac{1}{n}$, for all i, $S = -k \sum_{i=1}^{n} \frac{1}{n} \ln \frac{1}{n} = k \ln n$

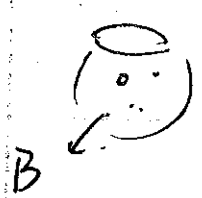
$\hookrightarrow$ just for unit matching

$S(P_1, P_2, \dots, P_n)$ ... 3 conditions

$$\boxed{S(AB) = S(A) + \sum_{k=1}^{m} P_k S(B|A)}$$

.. "picking from the same jar as in the first step".

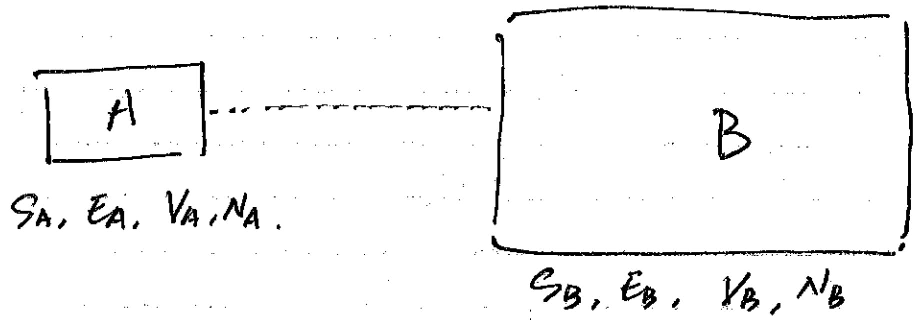




$\begin{cases} A: \text{ step } 1 \\ B: \text{ step } 2 \end{cases}$

.. "uncertainty involved in picking two from 2 steps"

" A thought experiment "

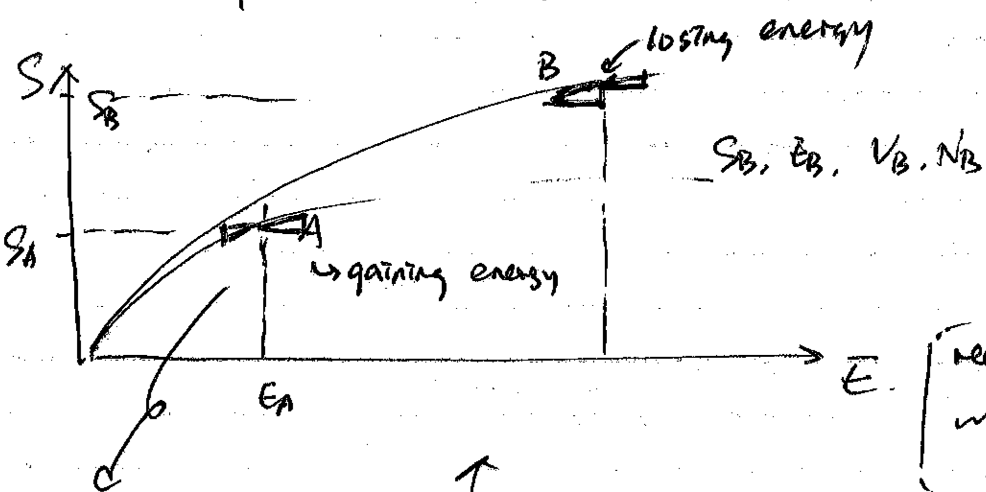


$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

$$\downarrow$$

$$T = \frac{\partial E}{\partial S}.$$

flows according to temperature.



reaches equilibrium when the slopes are the same. (same T)

"B has a higher slope than A"

total energy is conserved

"if A is gaining energy (meanwhile B losing energy), the system's entropy is increasing, which does not make sense."

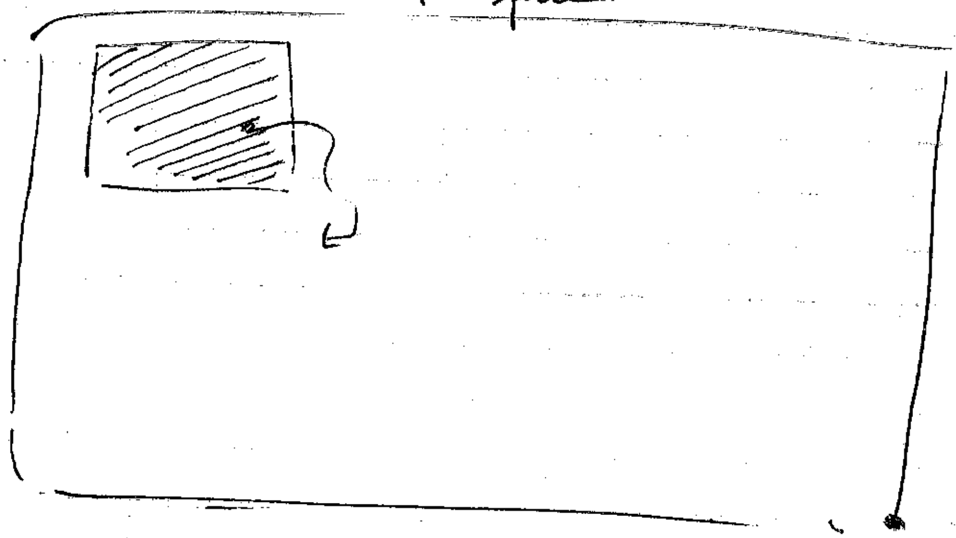
considering A has a higher slope than B.

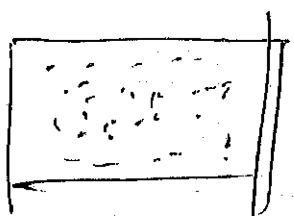
Hence, B must be gaining energy, & A losing, which agrees with the entropy argument.

$S_A < S_A'$

$V_A < V_A'$

P- space





0.99 | 0.1

one particle back 0.99

two particles $(0.99)^2$

$\vdots$

N particles $(0.99)^N$

↳ N is huge ... probability is extremely small.

1/31/2025. Problem Session.

$$S = k_B N \left[\log\left(\frac{V}{N} \left(\frac{4\pi m E}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

S.T. eq.

Sackur-Tetrode

$S(N, V, E)$

↳ micro canonical

(a). $$E = \frac{3Nh^2}{4\pi m} \left(\frac{N}{V} \right)^{2/3} \exp\left[\frac{2S}{3Nk_B} - \frac{5}{3} \right]$$

(ideal gas)

$$S = -\frac{\partial A}{\partial T}$$

$$dE = TdS - pdV + \mu dN.$$

$$A = E - TS.$$

$\downarrow$

$$\frac{dA}{dT} = -S - TdS + TdS.$$

$$T = \left(\frac{\partial E}{\partial S} \right)_{N,V} \Rightarrow T = \frac{2}{3Nk_B} E. \Rightarrow E = \frac{3}{2} N k_B T$$

$$p = -\left(\frac{\partial E}{\partial V} \right)_{S,N}. \Rightarrow p = \frac{2}{3} \frac{1}{V}. E \Rightarrow pV = Nk_B T$$

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

(b). $A = E - TS$

$$= \frac{3}{2}Nk_BT - \left[\log\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\cdot\frac{V}{N}\right] + \frac{5}{2}\right]\overbrace{Nk_BT}^{\text{unit of energy}}$$

(N, V, T)

(c). $G = E - TS + \underbrace{pV}_{Nk_BT}$

$$= -Nk_BT\left[\log\left(\frac{k_BT}{p}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\right)\right] \quad (N, P, T)$$

......

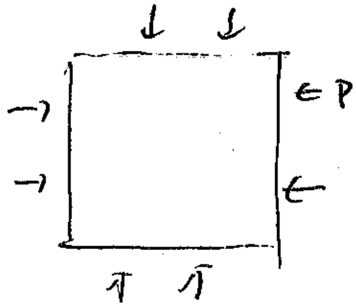
(d) C_v $\frac{dQ}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{3}{2}Nk_B \quad (N, V, T).$

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

$$C_p = \frac{dQ}{dT} = T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \frac{5}{2}Nk_B \quad (N, P, T)$$

(e) $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{1}{V}\cdot\frac{\partial}{\partial T}\cdot\frac{Nk_BT}{p}$

$= \frac{1}{V}\cdot\frac{Nk_B}{p} = \frac{1}{T}$



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

$C_p - C_v = Nk_B$

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

Laplace.

Some derivations.

$$\frac{S}{k_B N} - \frac{5}{2} = \ln\left(\frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}\right)$$

$$\exp\left[\frac{S}{k_B N} - \frac{5}{2}\right] = \frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}$$

$$\left(\frac{N}{V}\exp\left[\frac{S}{k_B N} - \frac{5}{2}\right]\right)^{2/3} = \frac{4\pi m E}{3Nh^2}$$

$$E = \frac{3Nh^2}{4\pi m}\left[\frac{N}{V}\exp\left[\frac{S}{k_B N} - \frac{5}{2}\right]\right]^{2/3}$$

II Midterm Review

Probability

$P(A \cap B) \rightarrow A$ and B ; $P(A \cup B) \rightarrow A$ or B.

Additive : $P(A \cup B) = P(A) + P(B) - P(A \cap B)$.

Conditional Probability : $P(B|A) = \dfrac{P(A \cap B)}{P(A)}$.

$\Downarrow$

independent : $P(B|A) = P(B)$

$P(A \cap B) = P(A)\,P(B)$

↳ if independent

$\langle XY \rangle = \langle X \rangle \langle Y \rangle$ independent

$\langle X + Y \rangle = \langle X \rangle + \langle Y \rangle$ universal.

$\langle X \rangle = \sum_x x\, P(X = x) = \sum_x x f_X(x)$.

↓

event $V(X) = \langle X^2 \rangle - \langle X \rangle^2 = \mu_2 - (\mu_1)^2$

$\mu_k = \langle X^k \rangle$. $\sigma(X) = \sqrt{V(X)}$

Mathematical tools

$$\int_{-\infty}^{+\infty} \exp(-ax^2)\,dx = \sqrt{\frac{\pi}{a}}.$$

$$\int_{-\infty}^{+\infty} \exp(-x^2)\,dx = \sqrt{\pi}$$

$$\ln(N!) \cong N\ln(N) - N.$$

$$\ln\left(\frac{1}{N!}\right) = -\ln(N!)$$

$$\exp(A+B) = \exp(A)\exp(B)$$

$$\ln(ab) = \ln(a) + \ln(b)$$

Statistics.

$$C_A^B = \frac{B!}{A!(B-A)!}$$

$$P_A^B = \frac{B!}{(B-A)!}$$

geometric sum

$$\sum_n ar^n = \frac{a}{1-r}$$

$$(e^a)^n = \exp(a\cdot n)$$

Taylor expansion

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

$$\exp(-x) = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \cdots$$

...istics

...ouville's theorem.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

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

$$\rightarrow \frac{d\rho}{dt} = 0$$

1/3/2025 Week 5 #1.

~ Canonical ensemble

- justification
- partition function
- energy fluctuation
- examples.

$E(S, V, N)$.

$dE = TdS - pdV + \mu dN$.

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

$\xrightarrow{-TS}$

$A(T, V, N)$

$A = -pV + \mu N$.

$\downarrow +pV$

$H(S, p, N)$.

$H = TS + \mu N$

$\downarrow +pV$.

$\xrightarrow{-TS}$.

$G(T, p, N)$.

$G = \mu N$

enter

micro canonical

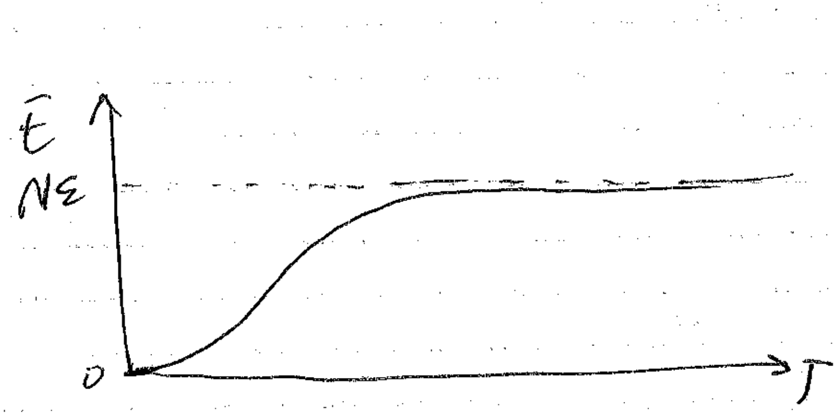
ensemble

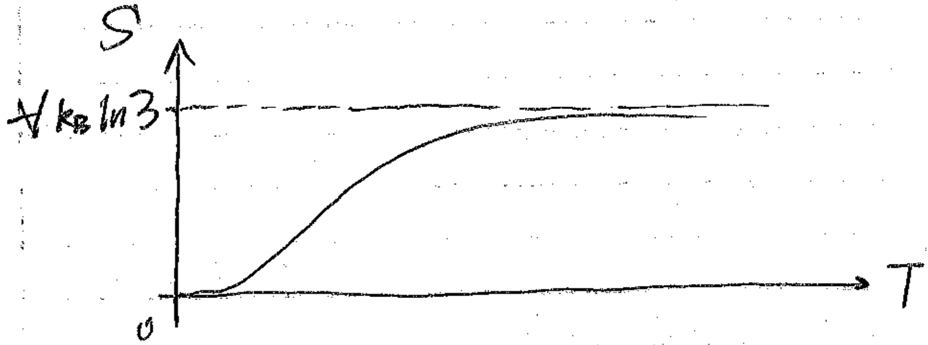
(N, V, E).

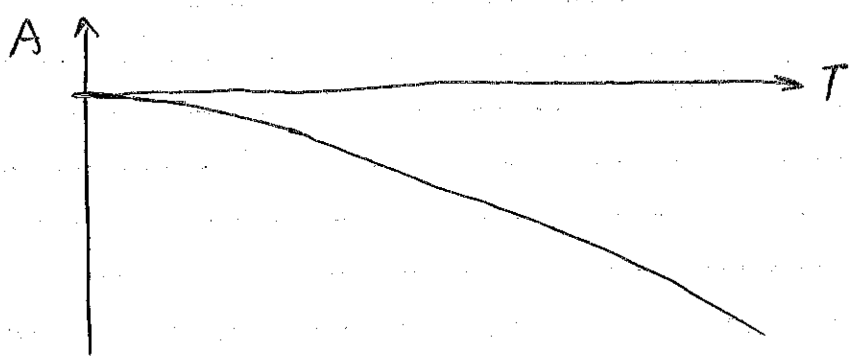
$S(E, V, N) = k_B \ln \Omega(E, V, N)$.

$$\Omega = \int \cdots \int dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}$$

$$E - \Delta E \le H(\{q_i\}, \{p_i\}) \le E$$







$$e^{-\beta H} = \exp\left(-\beta\varepsilon\sum_{i=1}^{N} n_i\right) = \prod_{i=1}^{N} e^{-\beta\varepsilon n_i}$$

artition function

$$Z = \sum_{\{n_i\}} \prod_{i=1}^{N} e^{-\beta\varepsilon n_i} = \prod_{i=1}^{N}\left(\sum_{n_i=0,1,2} e^{-\beta\varepsilon n_i}\right)$$

$$= \left(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right)^{N}$$

Helmholtz free energy: $A = -k_B T \ln Z$,

$$A = -N k_B T \ln(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon})$$

$$S = -\frac{\partial A}{\partial T} = N k_B T \ln(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon})$$

$$+ N k_B T \frac{e^{-\beta\varepsilon}\frac{\varepsilon}{k_B T^2} + e^{-2\beta\varepsilon}\frac{2\varepsilon}{k_B T^2}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

$$\bar{E} = A + TS = N\varepsilon \frac{e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}.$$

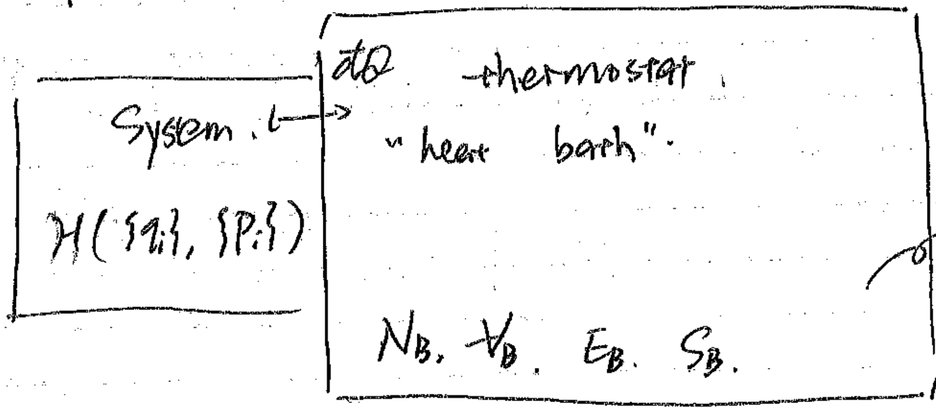
E can be obtained differently:

$$\bar{E} = -\frac{\partial}{\partial\beta}(\ln Z) = -\frac{\partial}{\partial\beta}\left[N \ln(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon})\right]$$

$$= N\varepsilon \frac{e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

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

Define temperature.



$$\frac{1}{T} \equiv \left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B}$$

"macroscopic"

Equilibrium $\xrightarrow[\text{by}]{\text{defined}}$ distribution ρ thermodynamic limit. $N_B \to \infty$

"the distribution is the ensemble".

$$\rho_c(\{q_i\},\{p_i\}) = \frac{1}{\tilde{Z}} e^{-\frac{H(\{q_i\},\{p_i\})}{k_B T}} \qquad N_B \to \infty$$

$\tilde{Z}$ → normalization function

$$\tilde{Z} = \int dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}$$

$$= \frac{1}{\tilde{Z}} e^{-\beta H(\{q_i\},\{p_i\})} \qquad \beta = \frac{1}{k_B T}$$

$$Z = \frac{1}{N! h^{3N}} \tilde{Z}$$

"partition function". $Z = \frac{1}{N! h^{3N}} \int dq_1 \cdots dq_{3N}\, dp_1 \cdots dp_{3N}$.

$$A(N, V, T) = -k_B T \ln Z(N, V, T).$$

ensemble → some density distribution in the phase space

justification ("proof")

(system + thermostat) → isolated system.

$$\rho_{mc}(\{q_i\},\{p_i\},\{q_i^B\},\{p_i^B\}) = \begin{cases} \text{const} & \hat{E} \le H(q_i,p_i) + H_B(q_i^B,p_i^B) \le \hat{E}+\Delta E \\ 0 & \end{cases}$$

Q: how to find $\rho(\{q_i\},\{p_i\})$.

"integrated out"

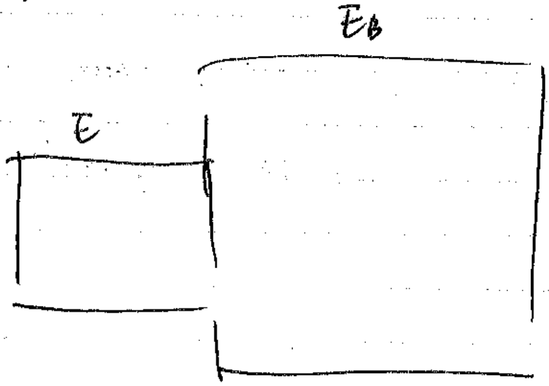
$$\rho(\{q_i\},\{p_i\}) = \int \prod_{i=1}^{3N^B} dq_i^B dp_i^B \, \rho_{mc}(q_i, p_i, q_i^B, p_i^B)$$

$$\left(f_X(x) = \int f_{XY}(x,y)\, dy \right)$$

$$= \text{const} \int \prod_{i=1}^{3N^B} dq_i^B dp_i^B \, 1$$

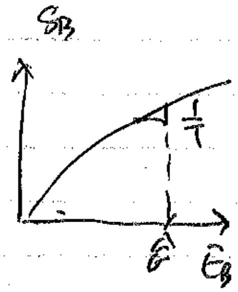
$\hat{E} - H(q_i, p_i) \le H_B \le \hat{E} - H(q_i,p_i) + \Delta E$

$$= \text{const} \cdot \Omega_B(\underbrace{\hat{E} - H(q_i;p_i)}_{E_B}, V_B, N_B)$$



$$E + E_B = \hat{E} \qquad E_B = \hat{E} - H(q_i, p_i).$$

$$\to \text{const.}\ e^{-\frac{H(q_i,p_i)}{k_B T}}$$



$$\boxed{S_B = k_B \ln \Omega_B}$$

$$\Downarrow$$

$$\Omega_B = e^{\frac{S_B}{k_B}}$$

$$S_B(\hat{E} - H(q_i, p_i))$$

$$= S_B(\hat{E}) - \frac{\partial S_B}{\partial E_B} \cdot H(q_i, p_i)$$

const

$$= S_B(\hat{E}) - \frac{1}{T} H(q_i, p_i)$$

"when you reach the thermodynamic limit, the ensemble you employ does not really matter"

... to be proved.

$$S = -k_B \int dq_i\, dp_i\, \rho_c(q_i, p_i) \ln \rho_c(q_i\, p_i)$$

Shannon's formula

$$S = \frac{E}{T} + k_B \ln \tilde{Z}$$

$$-k_B \ln \tilde{Z} = \frac{E}{T} - S$$

$$A = -k_B T \ln \tilde{Z} = E - TS$$

↳ one can hence define the partition function.

minimize A: canonical ensemble.

$$\tilde{Z} = \frac{1}{N! h^{3N}} \int dq_i\, dp_i\, e^{-\beta H(q_i, p_i)}$$

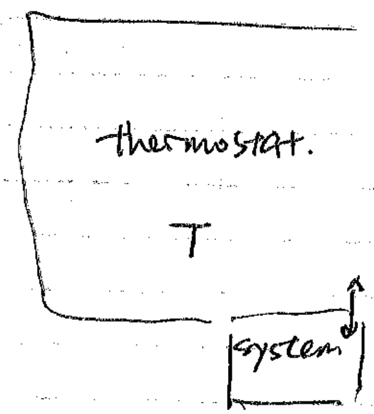
Hence, $A = A(N, V, T)$ (N, V, T)

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

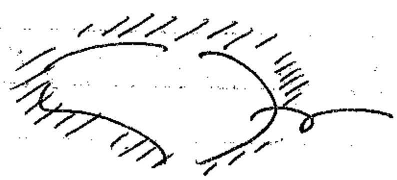
2/5/2025 Week 5 Lec. 2.

Canonical Ensemble

- energy fluctuations.
- Examples



microcanonical ensemble



isolated system

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

$\Omega(E, V, N) = \#$ microscopic states

$= \sum_{\mu_i} 1$

$E \le H(\mu_i) \le E + \Delta E$

$E(S, V, N)$

$E = TS - pV + \mu N$

$\xrightarrow{-TS}$

$A(T, V, N)$

$A(T, V, N) = -k_B T \ln Z$

partition func.

Canonical ensemble.

usually partition function is just referring to the canonical ensemble

$Z(T, V, N) = \frac{1}{N! h^{3N}} \int d\mu \, e^{-\beta H(\mu)}$

$= \sum_{\mu_i} e^{-\beta H(\mu_i)}$

$\mu = dq_1 \, dq_2 \cdots dq_{3N} \, dp_1 \cdots dp_{3N}$

key thing in stat mech:

finding the partition function corresponding to different ensemble

Canonical ensemble

$$B(\{q_i\}, \{p_i\}).$$

$$\langle B \rangle = \int \prod_{i=1}^{3N} dq_i\, dp_i\; B(\{q_i\}, \{p_i\})\, \rho_c(\{q_i\}, \{p_i\})$$

$$= \frac{1}{\tilde{Z}} \int \prod dq_i\, dp_i\; B(\{q_i\}, \{p_i\})\, e^{-\beta H(\{q_i\}, \{p_i\})}.$$

Calculate energy. $E = \langle \mathcal{H} \rangle$

$$= \frac{1}{\tilde{Z}} \int \prod_i dq_i\, dp_i\; \mathcal{H}(\{q_i\}, \{p_i\})\, e^{-\beta \mathcal{H}(\{q_i\}, \{p_i\})}$$

$$(\Delta E)^2 = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$$

$$\langle \mathcal{H}^2 \rangle = \frac{1}{\tilde{Z}} \int \prod_i dq_i\, dp_i\; \mathcal{H}^2(\{q_i\}, \{p_i\})\, e^{-\beta H(\{q_i\}, \{p_i\})}$$

$$\boxed{\tilde{Z} = \int \prod_i dq_i\, dp_i\; e^{-\beta \mathcal{H}(\{q_i\}, \{p_i\})}}$$

$$\frac{\partial \tilde{Z}}{\partial \beta} = -\int \prod_i dq_i\, dp_i\; \mathcal{H}(\{q_i\}, \{p_i\})\, e^{-\beta \mathcal{H}(\{q_i\}, \{p_i\})}$$

$$E = \frac{-\frac{\partial \tilde{Z}}{\partial \beta}}{\tilde{Z}} = -\frac{\partial}{\partial \beta} \ln \tilde{Z}$$

algebra: $A = -k_BT\ln Z$.

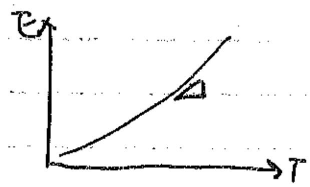
$$-\ln Z = \frac{A}{k_BT} = \beta A$$

$$E = \frac{\partial}{\partial\beta}(\beta A) = A + \beta\frac{\partial}{\partial\beta}A.$$

$$\langle \mathcal{H}^2\rangle = \frac{\partial^2\tilde{Z}}{\partial\beta^2} \Big/ \tilde{Z}$$

take the 2nd derivative of $\tilde{Z}$ w.r.t. β.

Intuition.



$$(\Delta E)^2 = k_BT^2\frac{\partial E}{\partial T}$$

"fluctuation"

In essence, $(\Delta E)^2 = \langle\mathcal{H}^2\rangle - \langle\mathcal{H}\rangle^2$

$$= \frac{1}{\tilde{Z}}\frac{\partial^2\tilde{Z}}{\partial\beta^2} - \left(\frac{1}{\tilde{Z}}\frac{\partial\tilde{Z}}{\partial\beta}\right)^2$$

$(E \pm \Delta E)$

$\Delta E = \sqrt{k_BT N C_v}\cdot \propto \sqrt{N}$

$$= \frac{1}{\tilde{Z}}\frac{\partial}{\partial\beta}\left(\frac{\partial\tilde{Z}}{\partial\beta}\right) + \left(\frac{\partial}{\partial\beta}\frac{1}{\tilde{Z}}\right)\left(\frac{\partial\tilde{Z}}{\partial\beta}\right)$$

$E \propto N$

$$= \frac{\partial}{\partial\beta}\left(\frac{1}{\tilde{Z}}\frac{\partial\tilde{Z}}{\partial\beta}\right)$$

$(\Delta E)^2 = k_BT^2 N\cdot C_v$.

specific

$$= -\frac{\partial}{\partial\beta}\langle\mathcal{H}\rangle \rightarrow E$$

no work to the system

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

$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}$

$$= k_BT^2\frac{\partial E}{\partial T} \rightarrow C_V = N C_V$$

recall diffusion $D = k_B T \frac{\partial v}{\partial f}$ mobility.

"Similar form"

Example ideal gas ... (P.S.)

Molecule with 2 energy levels

$E = \varepsilon$ - - - - - - - - - - - - - - - -

$E = 0$ - - - - - - - - - - - - - - - - - - - N
$1 \; 2 \; \cdots$

$\{n_i\}$, $\quad n_i \begin{cases} 0 \\ 1 \end{cases} \quad i = 1, 2, \ldots, N$

$$\mathcal{H}(\{n_i\}) = \sum_i n_i \varepsilon$$

microcanonical ensemble (don't do it in exam).

$S = k_B \ln \Omega(E, N)$. needs to find number of states their energy is E.

$\Downarrow$

$S(E, N)$

$\{n_i\}$

subject to the condition

$$\mathcal{H}(\{n_i\}) = E = m\varepsilon$$

$$\Omega(E, N) = \binom{N}{m}$$

canonical ensemble

$$Z(T, N) = \sum_{\{n_i\}} e^{-\beta \mathcal{H}(\{n_i\})} = \ldots$$

$\downarrow$

2^N terms

analytical expression

$$e^{-\beta \mathcal{H}(\{n_i\})} = e^{-\beta \sum_i n_i \varepsilon}$$

$$= \prod_i e^{-\beta \varepsilon n_i}$$

$\downarrow$

$$Z(T,N) = \sum_{\{n_i\}} \prod_i e^{-\beta \varepsilon n_i}$$

for 1 particle :

$$Z_1 = 1 + e^{-\beta\varepsilon}$$

$$A(T, N) = -k_B T \ln Z(T,N)$$

$$Z_1 = 1 + e^{-\beta\varepsilon}$$

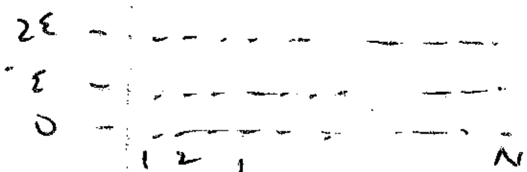
$$A = N \cdot A_1$$

$$-k_B T \ln Z = -N k_B T \ln Z_1$$

$$\ln Z = N \ln Z_1$$

Expanding Z:

$$= \sum_{\{n_i\}} e^{-\beta\varepsilon n_1} e^{-\beta\varepsilon n_2} \ldots e^{-\beta\varepsilon n_N}$$



$\downarrow$

"Very hard to solve in microcanonical ensemble".

$$= (1+e^{-\beta\varepsilon})(1+e^{-\beta\varepsilon}) \ldots (1+e^{-\beta\varepsilon})$$

$$= \prod_i \left(\sum_{n_i} e^{-\beta\varepsilon n_i} \right) \qquad (1+e^{-\beta\varepsilon})^N$$

$$Z(T,N) = \ldots$$

$$= (1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})(\ldots)$$

$$= (1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})^N$$

2/17/2025 Problem Session

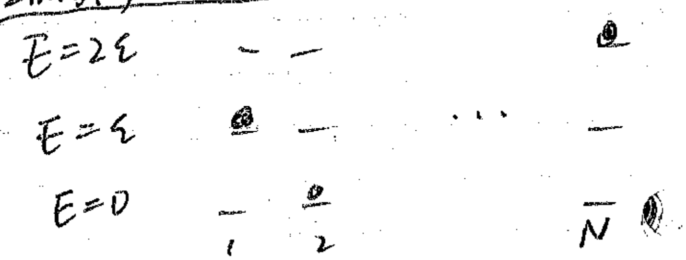
Ideal Gas.

$$Z = \frac{1}{N!}\frac{1}{h^{3N}}\int \prod_{i=1}^{3N} dq_i\, dp_i \exp\left(-\frac{\mathcal{H}(\{q_i\},\{p_i\})}{k_BT}\right).$$

$$\mathcal{H} = \sum_i \frac{|P_i|^2}{2m}.$$

$$Z = \frac{V^N}{N!\,h^{3N}}\int_{-\infty}^{\infty} dp_i \exp\left(-\frac{P_i^2}{2mk_BT}\right)$$

$$= \frac{V^N}{N!\,h^{3N}}(2\pi m k_BT)^{3N/2}$$

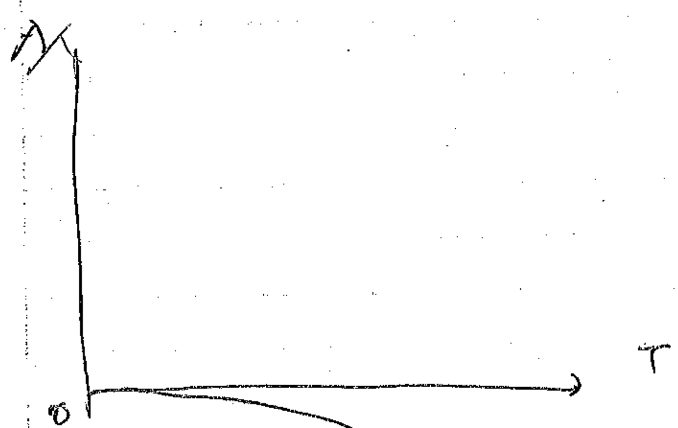


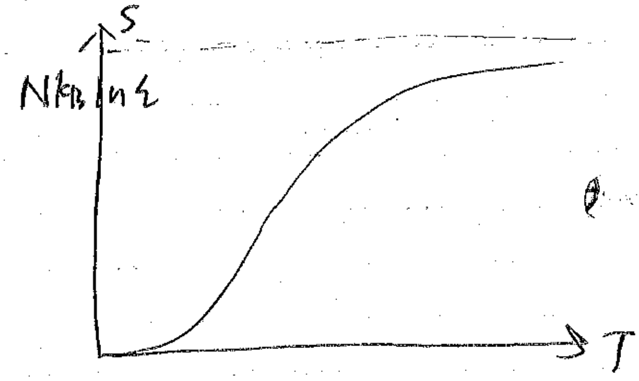
$$Z = (1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})^N$$

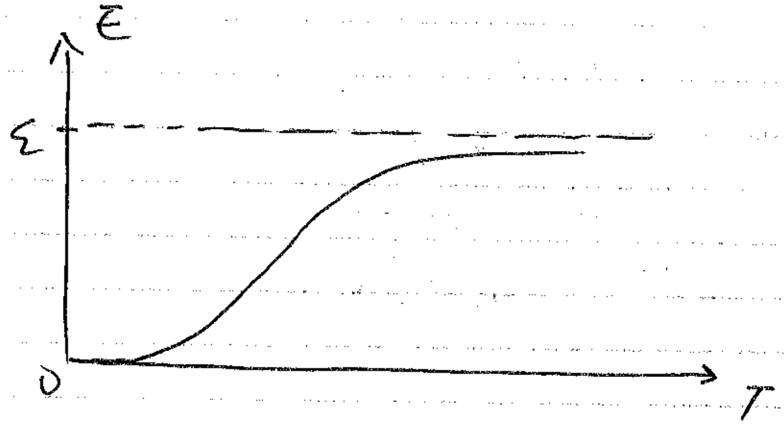
$$A = -k_BT\ln Z = -Nk_BT\ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})$$

$$S = -\frac{\partial A}{\partial T} = Nk_B\ln(1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon})$$

$$+Nk_B\,\frac{\varepsilon e^{-\beta\varepsilon}+2\varepsilon e^{-2\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}\,\frac{1}{k_BT}$$







(a) $E_S = -\varepsilon n_s$

$S_s = k_B \ln \Omega_s \quad \binom{N_s}{n_s}$

$A_s = E - TS = -\varepsilon n_s - k_B T \ln(\quad)$

(b) $E_B = 0$

$S_B = k_B \ln\binom{N_B}{n_B}$

$A_B = E - TS = -k_B T \ln\binom{N_B}{n_B}$

(c). $A = A_s + A_B \longrightarrow \frac{\partial A}{\partial n_s} = 0$ find wrt. n_s.

Stirling: $\log(N!) = N\ln N - N$.

$$\log\left(\frac{N_s!}{n_s!(N_s-n_s)!}\right) = N_s \log N_s - N_s - (n_s \log n_s - n_s) - \left((N_s - n_s)\log(N_s - n_s) - (N_s - n_s)\right)$$

$\frac{\partial A}{\partial n_s} = -\log n_s + \log(N_s - n_s) \cancel{-1+1}$

$\frac{\partial A}{\partial n_B} = \log N_B$

$$-\varepsilon - k_BT \ln\left(\frac{(n-n_s)N_s}{n_s \cdot N_B}\right) = 0$$

$$-\varepsilon - k_BT \ln\left(\frac{(N_s-n_s)(n-n_s)}{n_s(N_B-n_B)}\right) = 0$$

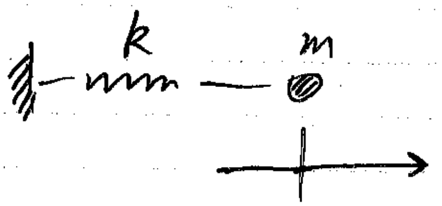
(d). $\frac{\partial A}{\partial n_s} = \mu_s$

$\frac{\partial A}{\partial n_B} = \mu_B$ $\qquad \mu_s = \mu_B$

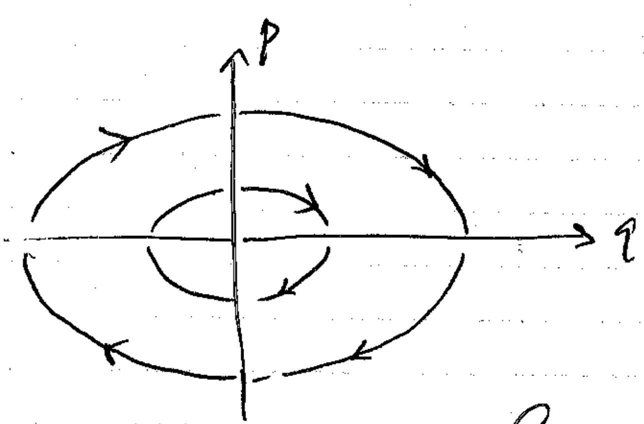
2/10/2025 Lecture 11.

- Classical harmonic oscillator
- Quatum H. O.
- Cooling towards Zero K.
- Einstein model of Solid.
- Debye model of Solid
- Hessian matrix. phase spectrum

- Classical harmonic oscillator 1D.



$$\mathcal{H}(q,p) = \frac{p^2}{2m} + \frac{1}{2}kq^2.$$



partition function.

$$Z_1 = \frac{1}{h}\int dq\,dp.\exp\left[-\beta\left(\frac{p^2}{2m}+\frac{1}{2}kq^2\right)\right]$$

each q & p have units of h

Gaussian integral ... important!

$$= \frac{1}{h}\int dp.\, e^{-\frac{p^2}{2k_BTm}}\int dq.\, e^{-\frac{kq^2}{2k_BT}}$$

Gaussian

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{x^2}{2\sigma^2}}$$

$$= \frac{1}{h}\sqrt{2\pi k_B T m}\sqrt{\frac{2\pi k_B T}{k}}.$$

"angular frequency"

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

$$\omega = \sqrt{\frac{k}{m}}$$

$e^{i\omega t}$ (sol'n)

$= 2\pi\nu$

$$= \frac{k_B T}{\hbar\omega}$$

$\hbar\omega = h\nu$

$\hbar = \frac{h}{2\pi}$ ← Planck const.

Helmholtz free energy.

$$A = -k_B T \ln Z = -k_B T \ln\frac{k_B T}{\hbar\omega}.$$

$$S = -\frac{\partial A}{\partial T} = \frac{\partial}{\partial T}\left(k_B T \ln\frac{k_B T}{\hbar\omega}\right)$$

$$S = k_B \ln\frac{k_B T}{\hbar\omega} + k_B \cancel{T}\cdot\frac{1}{\cancel{T}}$$

units of energy

$$= k_B\left(\ln\frac{k_B T}{\hbar\omega} + 1\right)$$

$h = 6.626\times10^{-34}\ J\cdot Hz^{-1}$

units of energy. $k_B = 1.38\times10^{-23}\ J\cdot K^{-1}$

$$= -\frac{\partial}{\partial\beta}\ln Z \quad \text{(the other way to calculate).}$$

$$= -k_B T \ln\frac{k_B T}{\hbar\omega} + k_B T \ln\frac{k_B T}{\hbar\omega} + k_B T$$

$$= k_B T.$$

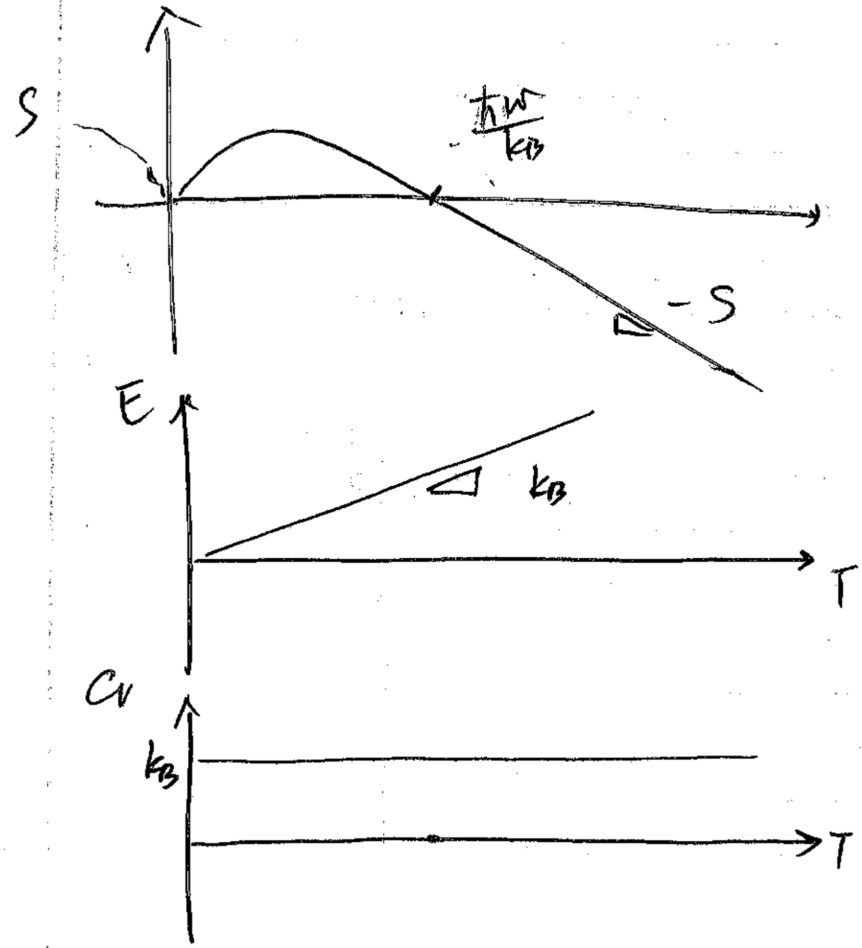
$$C_V = \frac{\partial E}{\partial T} = k_B$$

if we have 3N H.O.

$\bar{E} = 3Nk_BT$, $C_V = 3Nk_B$.

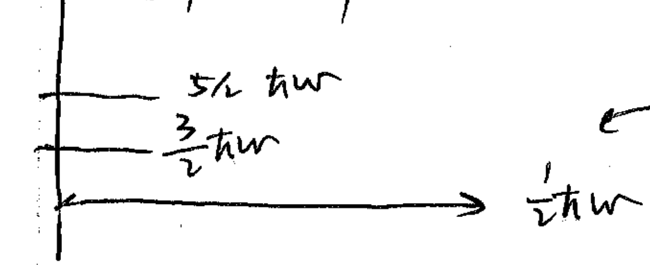
compare w/ ideal gas.

$\bar{E} = \frac{3N}{2}k_BT$, $C_V = \frac{3}{2}Nk_B$



Quantum harmonic oscillator. 1D.

$\mathcal{H}\psi = E\psi$



phenomenon only satisfied when $E_n = (n+\frac{1}{2})\hbar\omega$

$n = 0, 1, 2, \ldots$

Step 1: partition function.

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta E_1} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

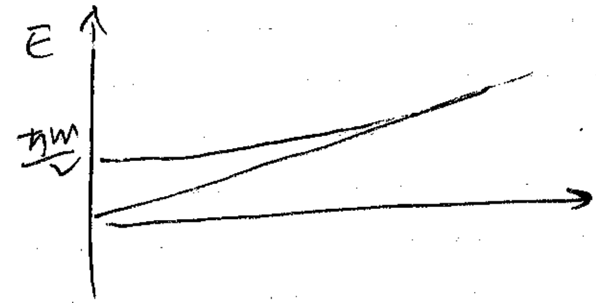
$$= e^{-\beta\frac{\hbar\omega}{2}}\left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots\right)$$

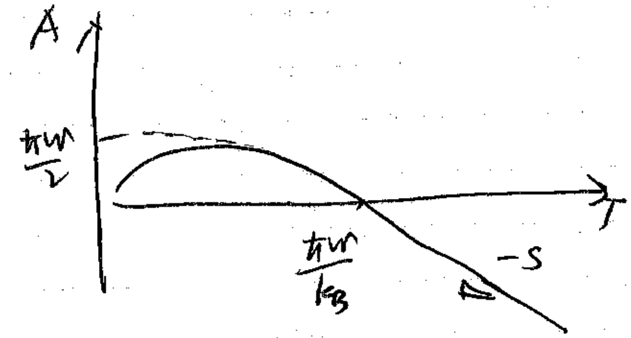
$$= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

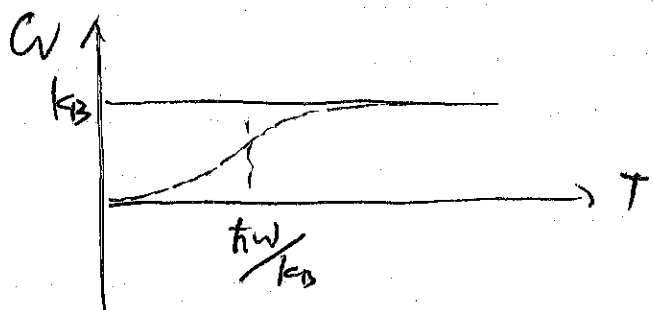
Helmholtz free energy.

$$A = -k_BT\ln Z = \frac{\hbar\omega}{2} + k_BT\ln\left(1-e^{-\frac{\hbar\omega}{k_BT}}\right)$$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$







"transition happening"

$T \to 0$

$A \to \frac{\hbar\omega}{2}$

$E \to \frac{\hbar\omega}{2}$

$S \to 0$

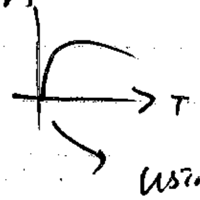
$A = E - TS$

3rd law of thermodynamics. $T \to 0: \; S \to 0$

$$S(T) - S(0) = \int_0^T \frac{C_V}{T} \, dT \qquad C_V(T)$$

$$\left(dS = \frac{đQ}{T} \right)$$

if C_V const.



using slope. $S \to -\infty$

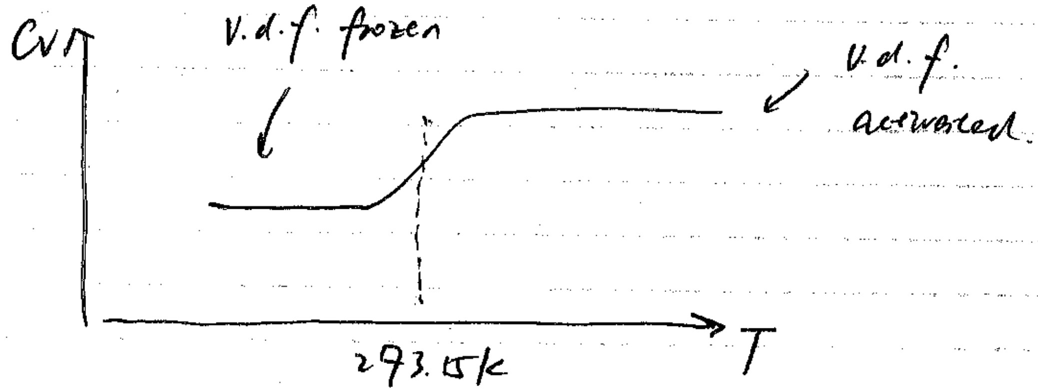
$C_V \sim e^{-\frac{\hbar\omega}{k_B T}}$ as $T \to 0$

Example $O - O$ O_2 molecule.

vibrational frequency $\nu = 4.67 \times 10^{13}$ Hz.

$h\nu = \hbar\omega = 3.09 \times 10^{-20}$ J.

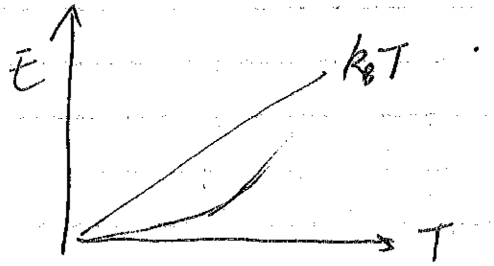
$$\frac{h\nu}{k_B} = \frac{\hbar\omega}{k_B} = \frac{3.09 \times 10^{-20} \text{J}}{1.38 \times 10^{-23} \text{J}} \text{K} = 2.2 \times 10^3 \text{K}.$$

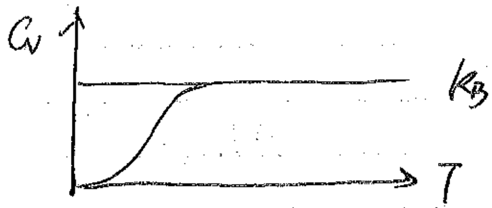


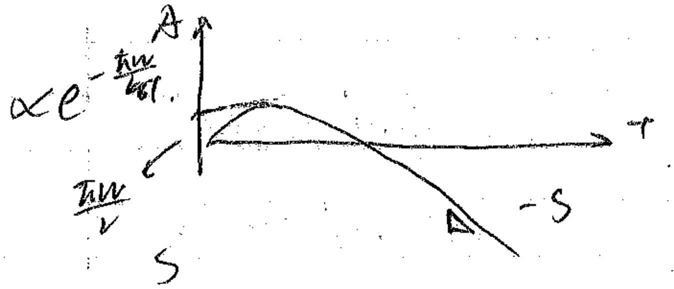
2/12/2025 Week 6 Lecture 2.

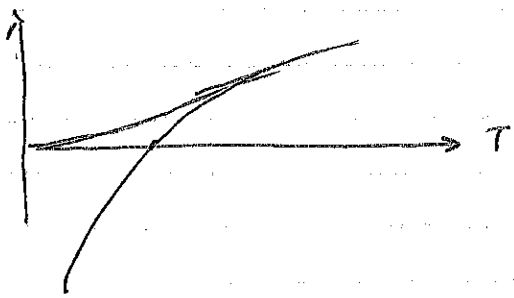
Today
- cooling toward 0 K
- Debye model of solid
- Hessian matrix & density of states

Classical harmonic oscillator





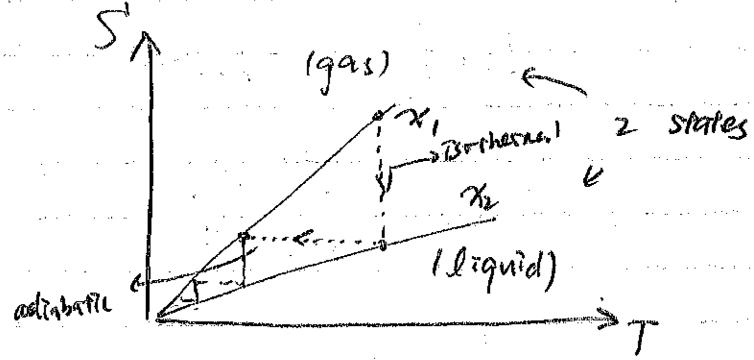


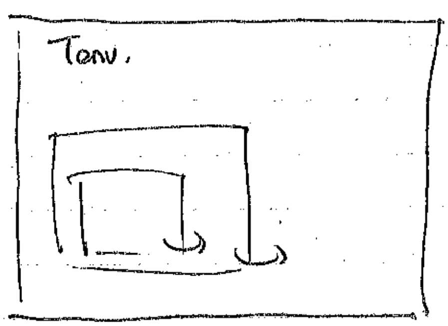


Third law of thermodynamics

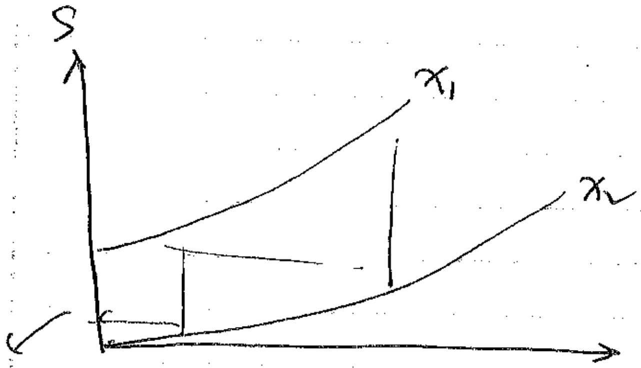
$S \to 0$ (as $T \to 0$)

Consequence: cannot cool to zero K in finite steps



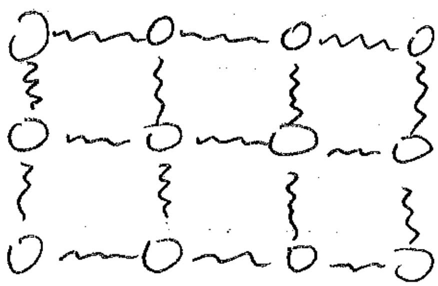


rooms in rooms to dump heat into the outside room



can go to zero temperature

Debye model of solid



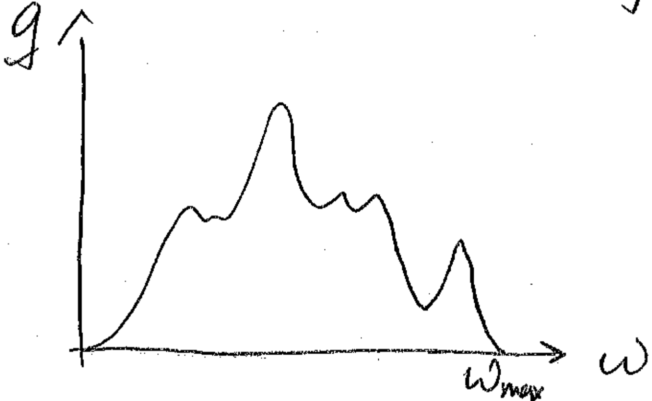
diagonalize $\longrightarrow$ new coordinates. 3N independent harmonic oscillators

$N \to \infty$

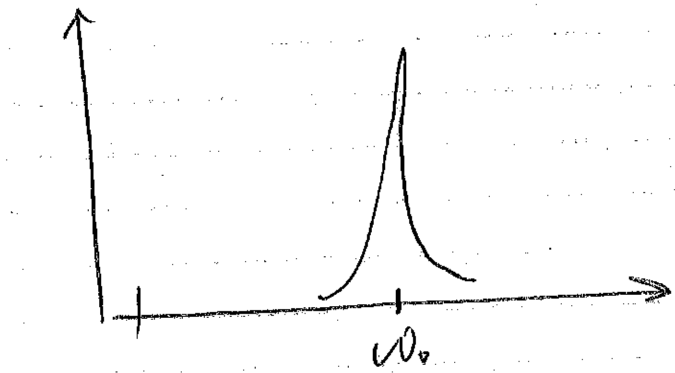
density of states

$g(\omega)\,d\omega$ = # of modes (harmonic oscillator) frequency in $[\omega, \omega+d\omega]$.

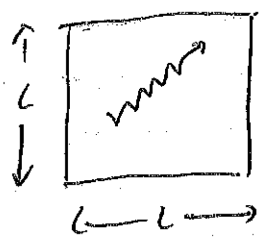
$$\int_0^\infty g(\omega)\,d\omega = 3N$$



Einstein model.



Assume P.B.C.



$e^{i(kx-\omega t)}$

$(\underline{k}, \omega)$

$V = L^3$

"not all $\underline{k}$ are allowed".

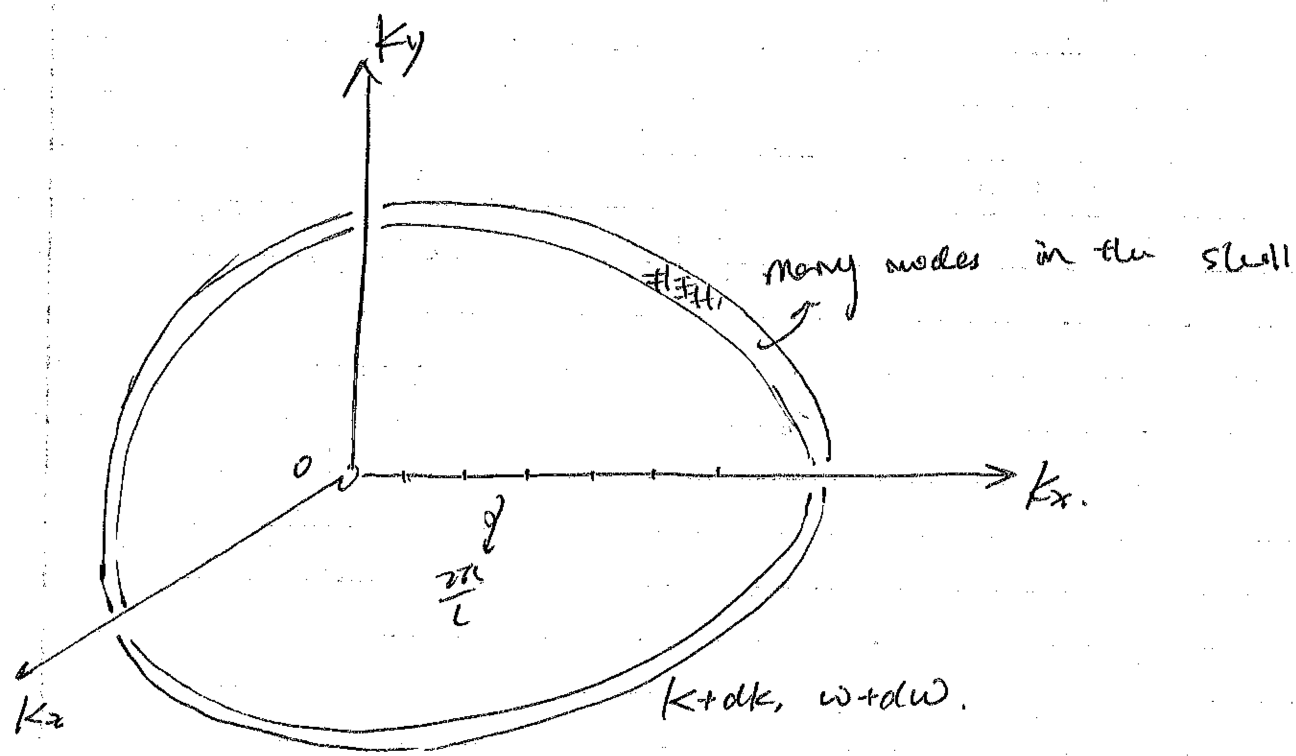
$\underline{k} = k_x, k_y, k_z$.

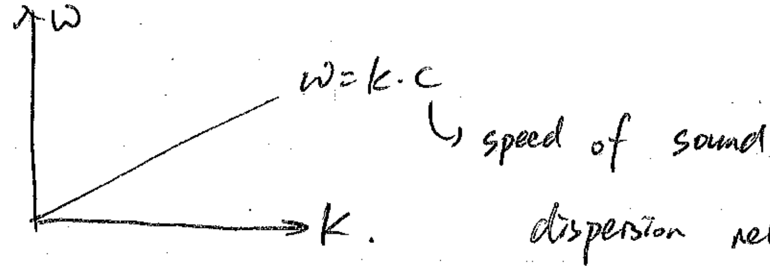
$$\begin{cases} k_x = \frac{2\pi}{L} n_x, \\ k_y = \frac{2\pi}{L} n_y, \\ k_z = \frac{2\pi}{L} n_z \end{cases}$$

In other words, L is a multiple of wave length,

n_i is the number of multiples

$e^{ik_x L} = 1$ to satisfy P.B.C.s





dispersion relation. $c = \frac{\omega}{K}$

$$e^{i(kx-\omega t)} = e^{i(kx-kct)}$$

$$= e^{ik(x-ct)}$$

Consider shell K, $K+dK$.

$$g(\omega)\,d\omega = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3}$$

volumes in the fourier space.

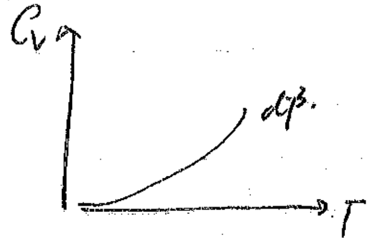
$\omega = kc$. $k = \frac{\omega}{c}$. $dk = \frac{d\omega}{c}$.

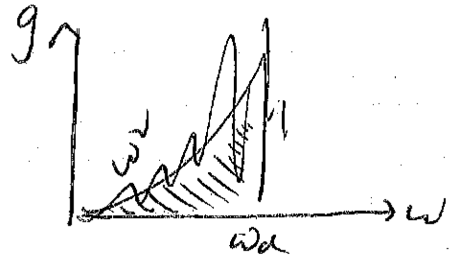
$$g(\omega)d\omega = \frac{4\pi\left(\frac{\omega}{c}\right)^2 \frac{d\omega}{c}}{\left(\frac{2\pi}{L}\right)^3} = \frac{4\pi\omega^2}{c^3\left(\frac{2\pi}{L}\right)^3}d\omega$$

$$= \frac{4\pi\omega^2 L^3}{c^3(2\pi)^3}$$

$$= \frac{\omega^2 L^3}{c^3 2\pi^2}$$

$$g(\omega) = \frac{L^3}{2\pi^2 c^3}\omega^2$$





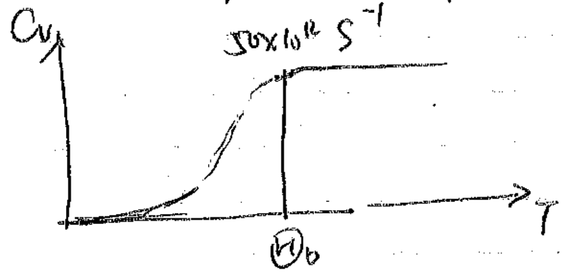
↓
maximum frequency.

$\hbar\omega_D = k_B \Theta_D$

debye temperature

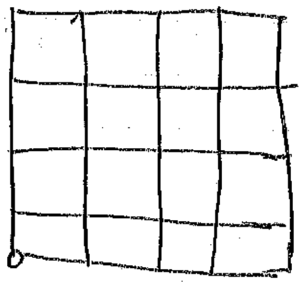
where you start to see

quantum effect !!



TA

Example

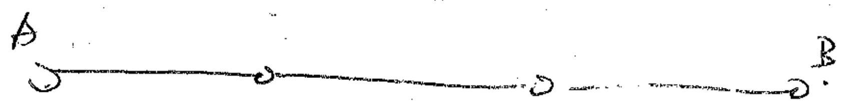


2D discrete energy problem.

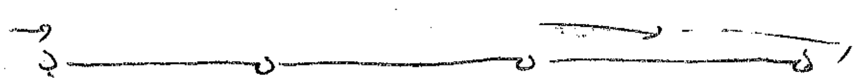
Overlap	✓	✓	✗	✗
Distinguish	✗	✓	✓	✗
	$\binom{25}{2}+\binom{25}{1}$	$(25)^2$	25×24	$\frac{25\cdot 24}{2}=\binom{25}{2}$

distinguishable by positions

Cannot be distinguished by the positions

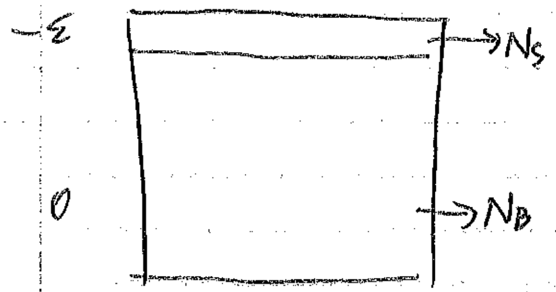


No PBC



PBC

Midterm Review



there are 14 N_s sites

14×14 N_B sites

* No two molecules can occupy same surface / bulk sites.

$n = n_s + n_B$ $\longrightarrow$ find n_s by minimizing free energy.

(a) find E_s, S_s, A_s of surface

$\nwarrow$ n_s surfactant molecules

Partition function.

1. S molecule: $\exp(-\beta(-\varepsilon))$

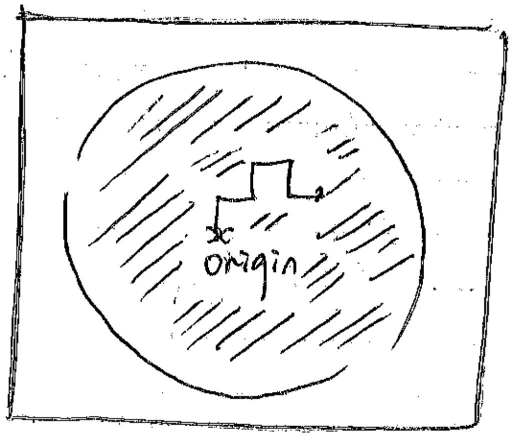
cannot distinguish: $\binom{25}{2}$

$E_s = -\varepsilon n_s$.

$S_s = k\ln\binom{N_s}{n_s}$

$A_s = E_s - TS_s$

Chain of 2D lattice



N links $\begin{cases} (a,0) \\ (0,a) \\ (-a,0) \\ (0,-a) \end{cases}$

$\downarrow$

distributions of these vectors are independent

apply force field $\underline{f} = f\underline{e}_x$

Hamiltonian $\mathcal{H}(\vec{l}_i) = -f \cdot (\vec{l}_i \cdot \vec{e}_x)$

partition function for whole chain

$\rightarrow$ due to independence

for one link. $Z_1 = \sum_{i=1}^{4} \exp(-\beta \mathcal{H}_i)$

$$Z_N = (Z_1)^N$$

2/19/2025 Week 7 Lecture 2 (1 skipped).

Today

- NPT ensemble
- Grand canonical ensemble
- Bosé - Einstein distribution
- Fermi - Dirac distribution.

Grand canonical ensemble

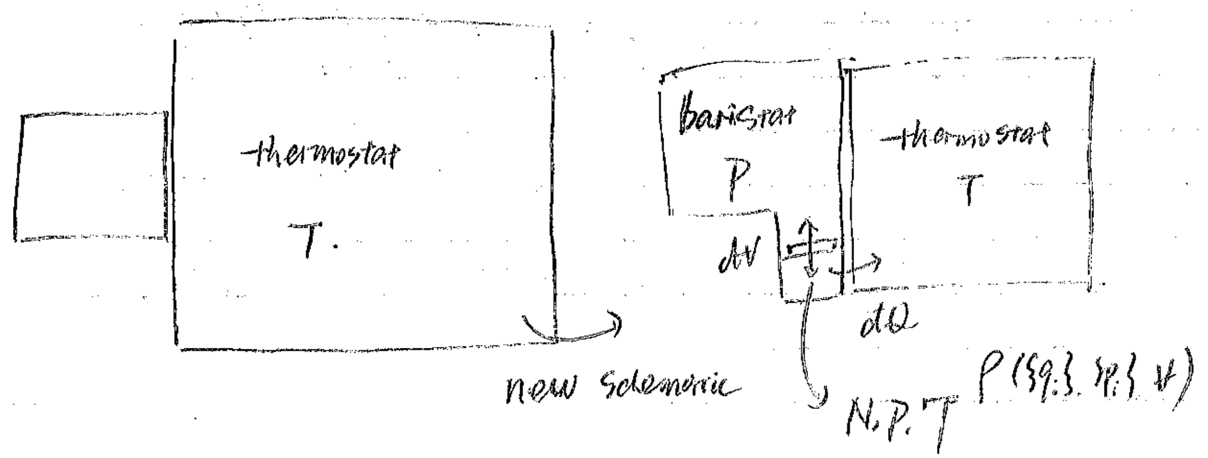
microcanonical ensemble

Canonical ensemble

$$
\begin{tikzcd}
 & \Phi(T,V,\mu) \\
E(S,V,N) \arrow[r, "-TS"] \arrow[d, "+pV"'] & A(T,V,N) \arrow[u, "-\mu N"'] \arrow[d, "+pV"] \\
H(S,p,N) \arrow[r, "-TS"] & G(T,p,N)
\end{tikzcd}
$$

N, p, T ensemble

- NPT ensemble



take the whole system as the micro canonical

$\rho(\{q_i\}, \{p_i\}, V) \rightarrow$ # of states barostat & thermostat can rearrange themselves s.t.

Ω_s

$V_0 - V \quad E_0 - \mathcal{H}(\{q_i\}, \{p_i\})$

$\mathcal{H}(\{q_i\}, \{p_i\}, V) + \mathcal{H}_s(\cdots) = \text{const.} = E_0$

$S_s(N_s, V_s, E_s)$

$V + V_s = \text{const.} = V_0$

$$S_s = S_s(N_s, V_0, E_0) - \frac{\partial S_s}{\partial V_s} \cdot V - \frac{\partial S_s}{\partial E_s} \mathcal{H}(q_i, p_i, V)$$

$$- \frac{P}{T} V - \frac{\mathcal{H}}{T}$$

Taylor's expansion

$$\propto \exp\left(- \frac{\mathcal{H}(q_i, p_i, V) + pV}{k_B T} \right)$$

$$\rho(\{q_i\}, \{p_i\}, V) = \frac{1}{\Xi} \exp\left[-\beta \left(\mathcal{H}(\{q_i\}, \{p_i\}, V) + pV \right) \right]$$

or $\tilde{\Xi}$ (quantum correction)

normalization constant

$$\tilde{\Xi} = \frac{1}{N! \, h^{3N}} \int_0^\infty dV \cdot \int \prod_{i=1}^{3N} dq_i \, dp_i \, e^{-\beta[\mathcal{H}(q_i, p_i, V) + pV]}$$

do the algebra

$$G(N, p, T) = -k_B T \ln \Xi$$

μN

$$\boxed{\Xi(N,p,T) = \int_0^\infty dV\; Z(N,V,T)\; e^{-\beta p V}}$$

Laplace transform

$$\langle V \rangle = -k_BT \frac{1}{\Xi} \frac{\partial \Xi}{\partial p}$$

$$\langle V^2 \rangle = -(k_BT)^2 \frac{1}{\Xi} \frac{\partial \Xi}{\partial p^2}$$

$$(\Delta V)^2 = \langle V^2 \rangle - \langle V \rangle^2 = -k_BT \frac{\partial \langle V \rangle}{\partial p}$$

Compressibility

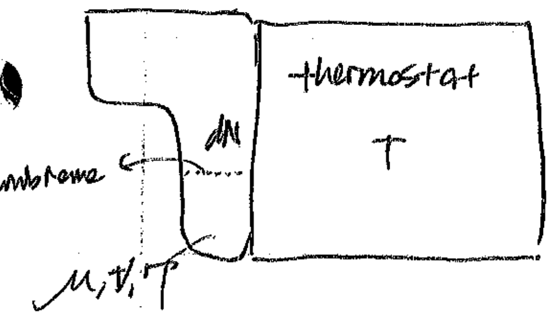
$$\beta_c = -\frac{1}{V}\frac{\partial V}{\partial p} \quad \rightarrow \text{substitute}$$

$$(\Delta V)^2 = k_BT \beta_c V \quad (\text{variance})$$

$$\Delta V = \sqrt{k_BT \beta_c V}.$$

"volume fluctuation is related to $\sqrt{V}$, In the thermodynamic limit it should $\rightarrow 0$".

Grand canonical ensemble



$$\rho(\{q_i\},\{p_i\},N) = \underbrace{\frac{1}{\tilde{Z}}}_{\text{grand partition function}} e^{-\beta(H(q_i,p_i,\mu) - \mu N)}$$

Continue ...

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

$$\Phi(\mu, V, T) = -k_BT \ln \mathcal{Z}(\mu, V, T) = -pV.$$

andau tential"

... trying all the ideal gas example !!

$$\sum_{N=0}^{\infty} Z(N, V, T)\, z^N$$ "z-transform"

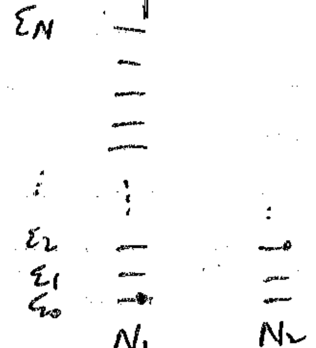
$z = e^{\beta\mu}$ "fugacity".

$$\boxed{\text{in dilute (ideal solution), } \mu = k_BT \ln C. \text{ ... chemistry}}$$

... ← $\mu = k_BT \ln z$

$$\Delta N \propto \sqrt{N}, \quad \frac{\Delta N}{N} \propto \frac{1}{\sqrt{N}} \to 0, \text{ as } N \to \infty$$

* System of non-interacting particles.



... → $\alpha = 1, 2, \ldots$

$\{S_\alpha\}$, $\mathcal{H}(\{S_\alpha\}) = \sum_{\alpha=1}^{N} \varepsilon_{S_\alpha}$.

$\{S_\alpha\} = \{0, 2, \cdots\}$ → overcounting !!!

$\{2, 0, \cdots\}$ they are indistinguishable

instead, we should :

← how many particles in each state

$\{n_i\} = \{2, 0, 1, \cdots\}$

total number of particles.

$$N = \sum_{i=0}^{\infty} n_i$$

$$\mathcal{H}(\{n_i\}) = \sum_{n=0}^{\infty} n_i \varepsilon_i$$

in canonical ensemble.

$$Z_1 = \sum_{\{n_i\}} e^{-\beta \sum_{i=0}^{\infty} n_i \varepsilon_i}$$

$\hookrightarrow$ s.t. $\sum n_i = N$.

$Z(N, T)$

not!

after derivation:

$\langle N \rangle(\mu) = N$

Lagrange multiplier control the n fluc.

$$\mathcal{Z}(\mu, T) = \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \varepsilon_i - \mu \sum_i n_i)}$$

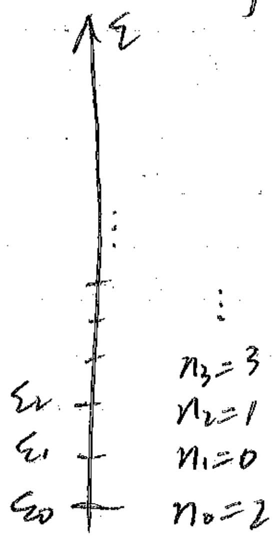
Today

- Bose - Einstein distribution.
- Fermi- Dirac distribution.

Application.

- Black - body radiation
- Electrons in semiconductors,

non-interacting particles



specify microscopic states by $\{n_i\}$.

$$\mathcal{H}(\{n_i\}) = \sum_i n_i \varepsilon_i$$

Canonical ensemble

$$Z(N,T) = \sum_{\{n_i\}} e^{-\beta \mathcal{H}(\{n_i\})}$$

s.t. $\sum_i n_i = N$

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

s.t. $\sum_i n_i = N$

in Grand - Canonical Ensemble.

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

$$= \sum_{N=0}^{\infty} \sum_{\substack{\{n_i\} \\ \text{s.t. } \sum_i n_i = N}} e^{-\beta \sum_i n_i \varepsilon_i} e^{\beta \mu \sum_i n_i}$$

$$\mathcal{Z}(\mu, T) = \sum_{\{n_i\}} e^{-\beta \sum_i n_i (\varepsilon_i - \mu)}$$

$$= \sum_{\{n_i\}} \prod_i e^{-\beta n_i (\varepsilon_i - \mu)}.$$

Boltzmann factor

$$= \prod_i \left(\sum_{n_i} e^{-\beta n_i (\varepsilon_i - \mu)} \right)$$

$$\parallel$$

$$\Big(\underbrace{1 + e^{-\beta(\varepsilon_0 - \mu)} + e^{-2\beta(\varepsilon_0 - \mu)} + \cdots}_{n_0 = 0, 1, 2, \cdots} \Big)$$

$$\Big(\underbrace{1 + e^{-\beta(\varepsilon_1 - \mu)} + e^{-2\beta(\varepsilon_1 - \mu)} + \cdots}_{n_0 = 0, 1, 2, \cdots} \Big)$$

$$= \prod_i \mathcal{Z}_i$$

Bose - Einstein (Boson)

$$\mathcal{Z}_i = 1 + e^{-\beta(\varepsilon_i - \mu)} + e^{-2\beta(\varepsilon_i - \mu)} + \cdots = \frac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}}$$

$$\mathcal{Z}(\mu, T) = \prod_i \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}$$

Fermi-Dirac. (Fermion). $\sum_{n_i=0,1}$.

$$\mathcal{Z}_i = 1 + e^{-\beta(\varepsilon_i-\mu)}$$

$$\mathcal{Z}(\mu, T) = \prod_i \left(1 + e^{-\beta(\varepsilon_i-\mu)}\right)$$

Bose-Einstein distribution

$$p(n_i = n) = \frac{\prod_i e^{-\beta n_i(\varepsilon_i-\mu)}}{\mathcal{Z}_i}$$

$$\langle n_i \rangle = \frac{0 + 1\cdot e^{-\beta(\varepsilon_i-\mu)} + 2\cdot e^{-2\beta(\varepsilon_i-\mu)} \dots}{1 + e^{-\beta(\varepsilon_i-\mu)} + e^{-\beta(\varepsilon_i-\mu)} + \dots} \qquad p(\{n_i\}) = \frac{\prod_i e^{-\beta n_i(\varepsilon_i-\mu)}}{\prod_i \mathcal{Z}_i}$$

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

$n_0 = 1$, $n_1 = 2 \cdots$

Summing over all possible states

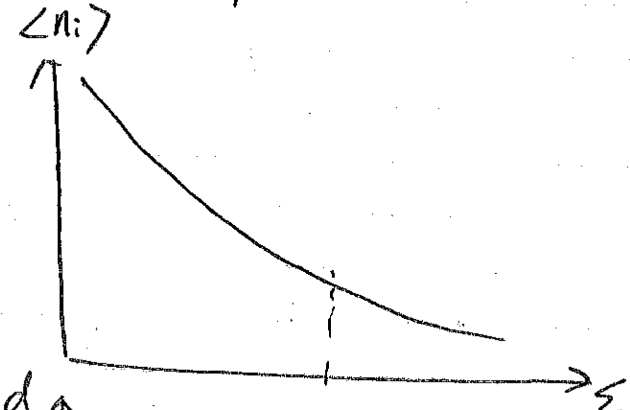
$1 + e^{-\beta(\varepsilon_i-\mu)} + e^{-2\beta(\varepsilon_i-\mu)} + \dots$

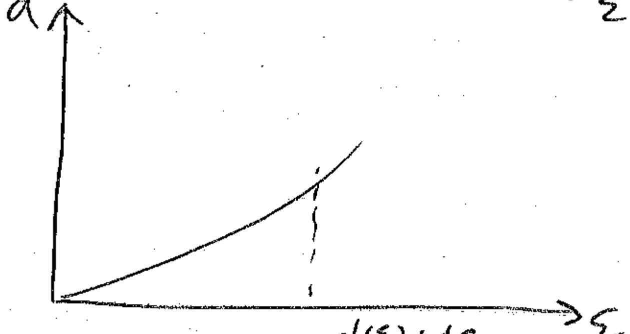
$$= \frac{1}{\mathcal{Z}_i}(-k_B T)\frac{\partial}{\partial \varepsilon_i}\mathcal{Z}_i$$

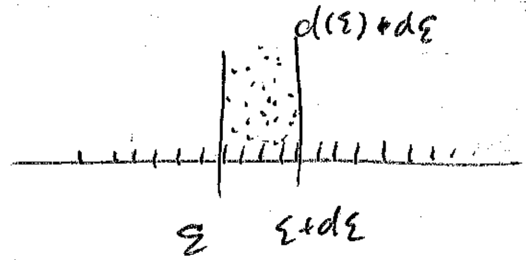
$$= -k_B T \cdot \frac{\partial}{\partial \varepsilon_i} \ln\left(\frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}\right)$$

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

↳ Bose-Einstein equation.







Fermi-Dirac

n does not go to ∞.

$$p(n_i = n) = \frac{e^{-\beta n_i(\varepsilon_i - \mu)}}{1 + e^{-\beta(\varepsilon_i - \mu)}}$$

$n_i = 0, 1.$

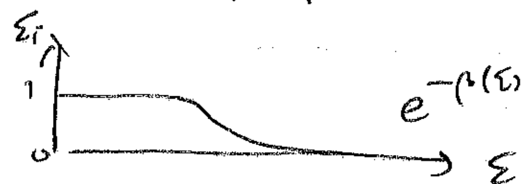
$$\langle n_i \rangle = \frac{e^{-\beta(\varepsilon_i - \mu)}}{1 + e^{-\beta(\varepsilon_i - \mu)}}$$

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

at a particular energy level, there are (could) more than one energy state!

"at high temperature, different ensembles should converge to the same."

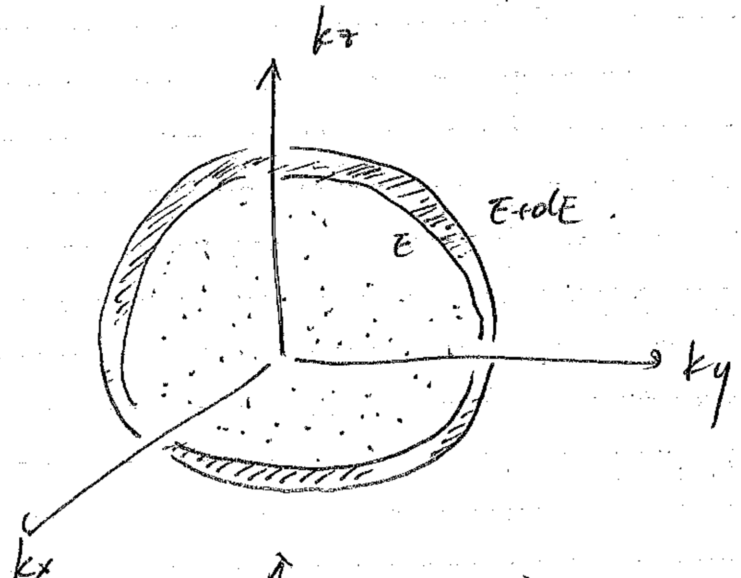
Multiplying the two we have the number of particles.



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

What is μ?

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



$\varepsilon(k)$.

count number of states.

What if num. particles not conserved?

$\downarrow$

let $\mu = 0$

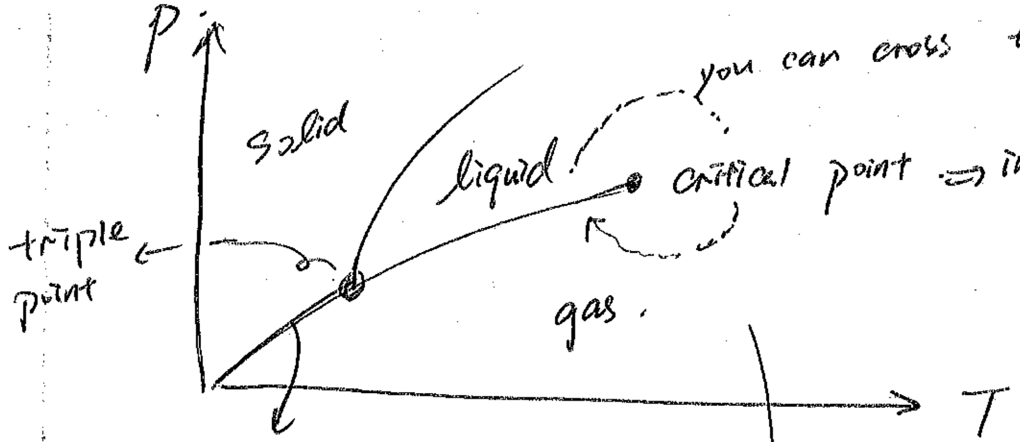
2/24/2025 Week 8 Lec 1.

- Phase diagram.

  phase transitions, critical point.

- van der Waals model.
- Virial expansion
- Virial coefficients from molecular interactions.

Start from a phase diagram



you can cross this many times

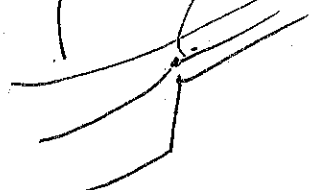
critical point ⇒ implying liquid & gas are not really two phases

first order phase transition

so, we can just call this the "fluid phase".

continuous

slope goes to infinity.



phase transition: discontinuous

Ideal gas review

$PV = Nk_BT$.

"fundamental equation of state".

$$\boxed{A(T,V,N) = -Nk_BT\left[\ln\left(\frac{V}{N\Lambda^3}\right)+1\right], \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}}$$

find p from A.

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

$E(S,V,N)$

$dE = TdS - pdV + \mu dN$.

$A(T,V,N) = E - TS$.

$dA = -SdT - pdV + \mu dN$

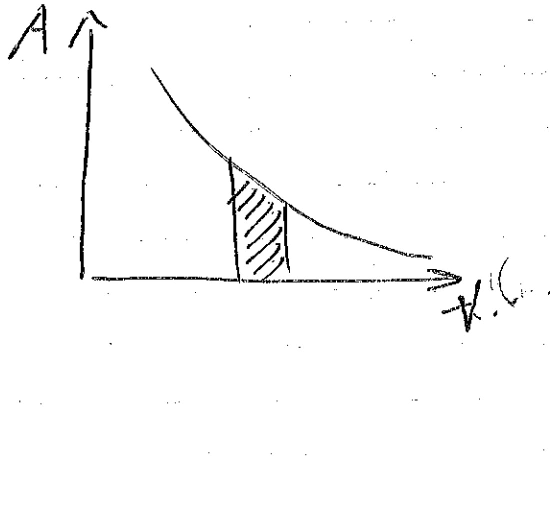
$A(T,V,N) = \quad \dots$

$$A(T,V_0,N) - \int_{V_0}^{V} p\,dV \quad . -Nk_BT \ln\frac{V}{V_0}$$

heat capacity of ideal gas.

$E = \frac{3}{2}Nk_BT$.

$C_V = \frac{3}{2}Nk_B$.



Non-ideal gas. (van der Waals)

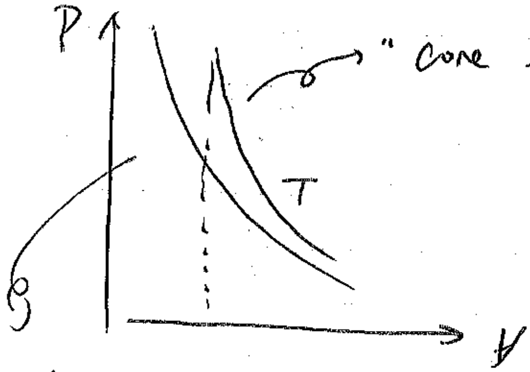
$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = N k_B T$$

expand it, goes to infinite order

a: pairwise attraction.

b: exclusion volume.

$$P = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}$$



"Core electron, finite size effects".

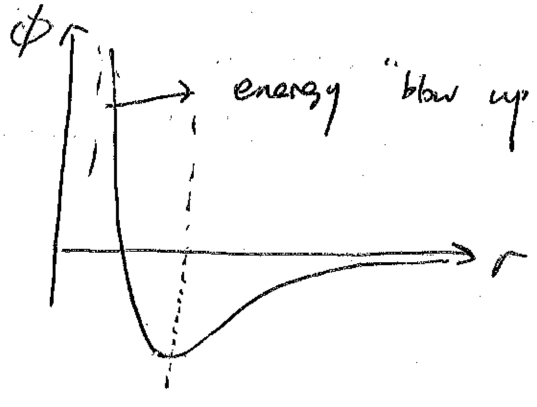
⇓

"ideal gas". account for pair-wise attraction

only blow up when $V \to 0$

in real gas, all "molecule" has some sort of exclusion volume, they "blow up" when T = some val.

Molecular attraction in reality



⇒ because it's pair-wise, the energy will depend on the "density-square". n^2

One further derives:

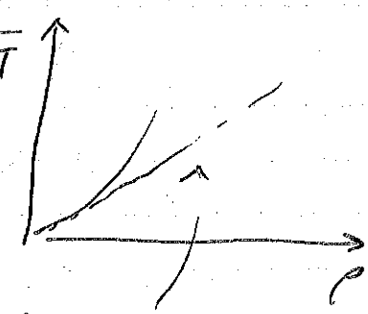
$$A(T, V, N) = -Nk_BT\left[\ln\left(\frac{V - Nb}{N\Lambda^3}\right) + 1\right] - \frac{N^2 a}{V}$$

$$\Downarrow$$

"connected to smaller image (molecular), but not quite the final answer".

one defines $\rho \equiv \frac{N}{V}$.

take ideal gas. $\frac{P}{k_BT} = \rho$



deviation should be the difference from ideal gas.

Virial expansion.

$$\frac{P}{k_BT} = \rho + B_2^{(T)}\rho^2 + B_3^{(T)}\rho^3 + \ldots \quad \text{H.O.T.}$$

$B_i(T)$. virial coefficients. "fit for the experimental fact."

Van der Waals (can be interpreted in terms of the virial coefficients)".

$$\frac{P}{k_BT} = \rho + \left(b - \frac{a}{k_BT}\right)\rho^2 + \ldots$$

do the algebra, one finds that

$$B_2(T) = b - \frac{a}{k_B T}.$$

$$B_3(T) = b^2$$

$$B_4(T) = b^3.$$

$\vdots$

a simple model.

"the more correct way is to start with the partition function".

$$Z(N, V, T) \Rightarrow A(N, V, T) = -k_B T \ln Z.$$

$$Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dp_i \, dq_i \, e^{-\beta \mathcal{H}(\{q_i, p_i\})}.$$

$$\mathcal{H}(\{q_i, p_i\}) = \sum_i \frac{p_i^2}{2m} + U(\{\underline{r}_i\})$$

$$U(\{\underline{r}_i\}) = \sum_{i=j} \phi(r_{ij}) \qquad r_{ij} = |\underline{r}_i - \underline{r}_j|.$$

pair num. $\frac{N(N-1)}{2}$

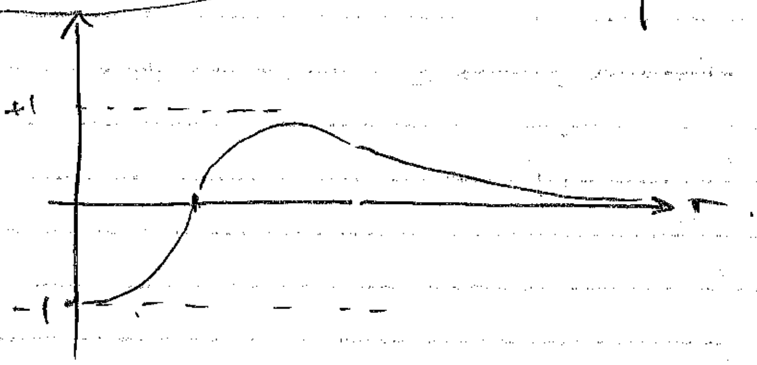
$$Z_1 = Z_1^{i.g.} \cdot \underbrace{\int \prod_{i=1}^{3N} dq_i \, e^{-\beta U(\{\underline{r}_i\})}}.$$

$$Z_u = \int d^3\underline{r}_1 \, d^3\underline{r}_2 \cdots d^3\underline{r}_N \, e^{-\beta U(\underline{r}_1, \underline{r}_2, \ldots \underline{r}_N)}.$$

$$Z_u = \int d^3\underline{r}_1 \cdots d^3\underline{r}_N \prod_{i<j} e^{-\beta \phi(r_{ij})}.$$

... (cont.)

$\boxed{f(r) = e^{-\beta\phi(r)} - 1}$ → $r \to \infty$, $f \to 0$.



...

$$= \int d^3 r_1 \dots d^3 r_N \prod_{i<j} (1 + f(r_{ij})).$$

Expand this:

$$1 + (f(r_{12}) + f(r_{13}) + \dots)$$
$$+ (f(r_{23}) + \dots).$$

One of the low-order results.

$$B_2(T) = -2\pi \int_0^\infty [e^{-\beta\phi(r)} - 1] r^2 dr$$

$f(r)$ is a transformation of the interatomic potential (a mathematical tool) to represent the partition function that connects theory with experiments.

2/26/2025 Week 8. lec 2.

Today

1. virial coefficient from molecular interactions

2. liquid - gas phase transitions
   (with van der Waals model)

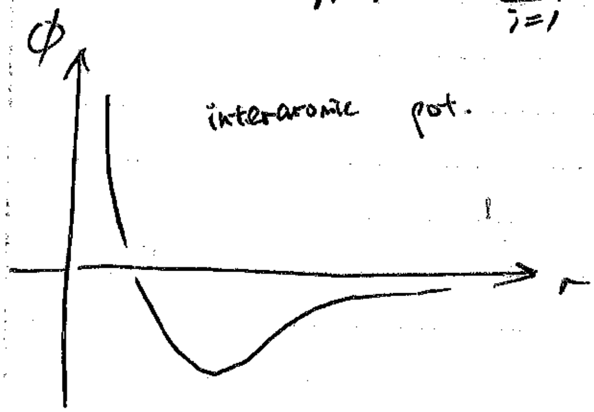
3. Maxwell construction

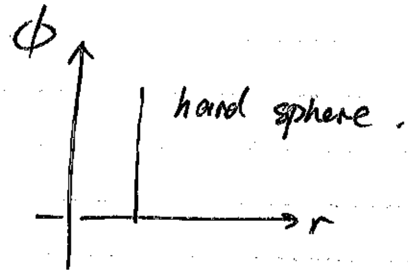
4. Critical exponents
   (with van der Waals model).

Nonideal gas

Hamiltonian.

$$\mathcal{H}(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{r_i\}).$$





$$U(\{r_i\}) = \sum_{i<j} \phi(r_{ij}).$$

$$r_{ij} = |\underline{r}_i - \underline{r}_j|$$

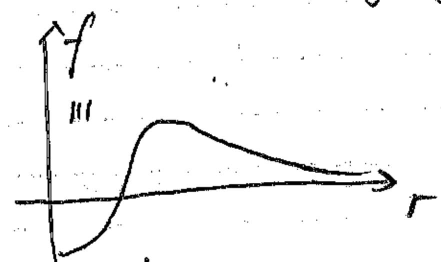
partition function

$$Z = \frac{1}{N!\,h^{3N}} \int \prod_{i=1}^{3N} dq_i\, dp_i\; e^{-\beta \mathcal{H}(\{q_i\}, \{p_i\})}, \quad \beta \equiv \frac{1}{k_B T}$$

$\nearrow$ kinetic part goes away for ideal gas

$$= \frac{Z^{i.g.}}{V^N} \int \prod_{i=1}^{3N} dq_i \, e^{-\beta U(\{\underline{r}_i\})}$$

$$Z_u = \int \underline{d^3 r_1} \, \underline{d^3 r_2} \cdots \underline{d^3 r_N} \prod_{i<j} e^{-\beta\phi(r_{ij})} \rightarrow [1 + f(r_{ij})]$$



$e^{-\beta\phi(r)} - 1$

Product of all pairs.

$$\prod_{i<j} [1 + f(r_{ij})] = [1 + f(r_{12})] \, [1 + f(r_{13})] \cdots [1 + f(r_{1N})] \cdots [1 + f(r_{21})] \cdots [1 + f(r_{2N})] \cdots [1 + f(r_{N-1} r_N)]$$

$\frac{N(N-1)}{2}$ # pairs.

$2^{\frac{N(N+1)}{2}}$ terms.

$\frac{N(N+1)}{2}$ terms.

$$= 1 + [f(r_{12}) + f(r_{13}) + \cdots + f(r_{N-1} r_N)]$$

$$+ [f(r_{12}) f(r_{13}) + f(r_{12}) f(r_{14}) + \cdots]$$

perturbative approach $\hookrightarrow$

$$+ [f(r_{12}) f(r_{13}) f(r_{14}) + \cdots$$

$$+ \cdots$$

$$+ f(r_{12}) f(r_{13}) f(r_{14}) \cdots f(r_{N-1\,N}).$$

pure ideal gas effect

pure internal energy effect

$$Z_1 = Z_1^{i.g.} \frac{Z_u}{V}.$$

$\frac{N(N-1)}{2}$ terms.

$$\frac{Z_u}{V^N} = 1 + \frac{1}{V^N}\int d^3\underline{r}_1 \cdots d^3\underline{r}_N \sum_{i<j} f(r_{ij}) + \cdots$$

$$\frac{1}{V^N}\int d^3\underline{r}_1 \cdots d^3\underline{r}_N \sum_{i<j}\sum_{k<l} f(r_{ij}) f(r_{kl}) + \cdots$$

$\cdots (*)$

$\phi = \phi(r_{ij})$

central potential assumption.

All THE TERMS ARE THE SAME !!!

(1st order)

we eliminate H. O. T.

Further simplifying eqn. (*)

$$= 1 + \frac{\frac{N(N-1)}{2}}{V^N}\int \cdots$$

$$\frac{Z_u}{V^N} = 1 + \frac{N(N-1)}{2V^2}\int d^3\underline{r}_1\, d^3\underline{r}_2\, f(r_{12}) + \cdots$$

* Assumptions: ① all particles are the same

$\Rightarrow$ All terms are the same : $f(x) = x^2 + \sin x.$

This is a mathematical statement, not a physical assumption !!!

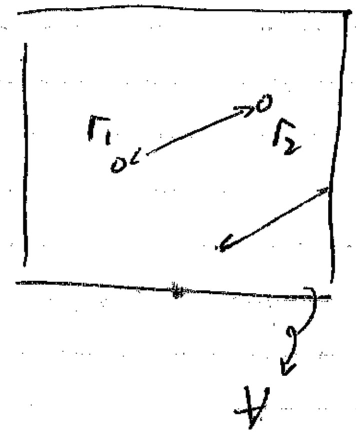
$$\int_a^b f(x)\,dx = \int_a^b f(\xi)\,d\xi$$

one can further simplify $\frac{Z_N}{V^N}$

$$\int d^3 r_1\, d^3 r_2\, f(r).$$

$\Downarrow$

V



exactly the same!

$$= 1 + \frac{N(N-1)}{2V^2} V \cdot \int d^3 r_{12}\, f(r_{12}).$$

$\Downarrow$

$\to 10^{23}$ very large

~ "approximate" density ρ

$$\int_0^\infty r^2 dr \underbrace{\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi}_{4\pi} f(r)$$

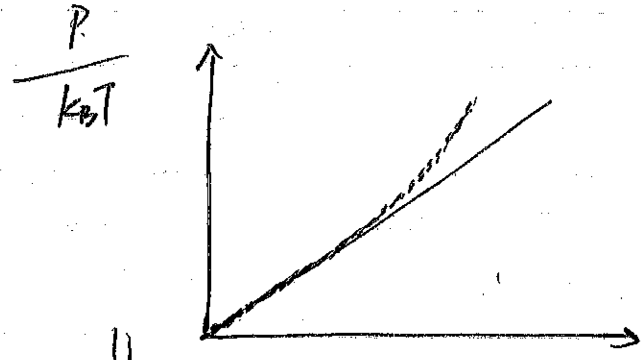
$$= 1 + \frac{N(N-1)}{2V^2} V \, 4\pi \int_0^\infty dr\, r^2 f(r) + \cdots \quad (\text{H. O. T.})$$

$$B_2(T) = -2\pi \int_0^\infty r^2 f(r)\, dr = -2\pi \int_0^\infty \left[e^{-\beta\phi(r)} - 1\right] r^2 dr + \cdots$$

$\Downarrow$

"deviation from ideal gas"

$\to$ molecular interactions taken into account.

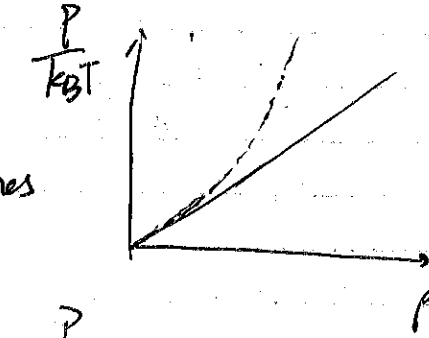


you'll have $B_3, \ldots$

$\Downarrow$

this model gives similar "physical results" as the vdW model.

macroscopically measurable B_2, B_3 ...



Connect the macroscopic properties with the molecular interactions

...

$$\frac{P}{k_BT} = \rho + B_2\rho^2 + B_3\rho^3 + \cdots$$

You can macroscopically measure B_2 ... ⇐ fit for polynomial

in van der Waals model : $B_2 = b - \frac{a}{k_BT}$

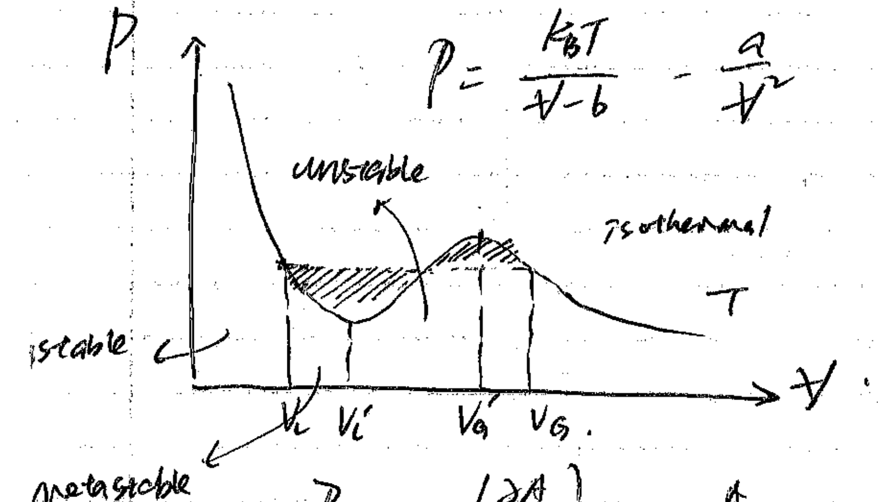
Boyle temperature ρ^2 term cancels.

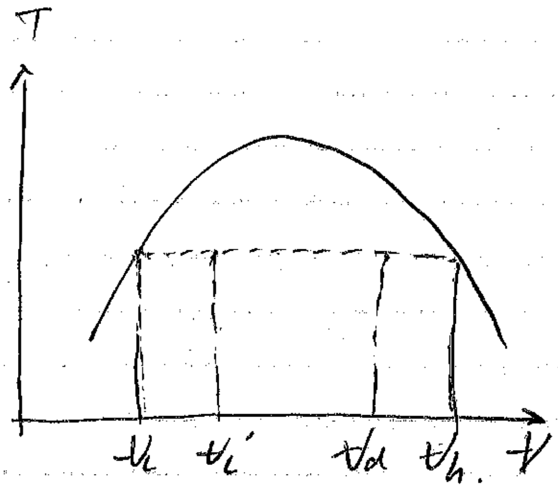
for B_n: find all 2-connected graphs with n vertices.

Problem Session Week 8.

Van der Waals Model.

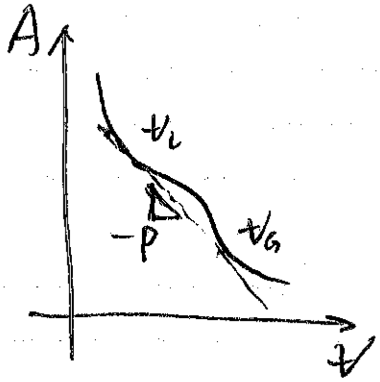
$$P = \frac{k_B T}{V - b} - \frac{a}{V^2}$$

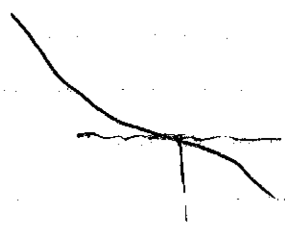


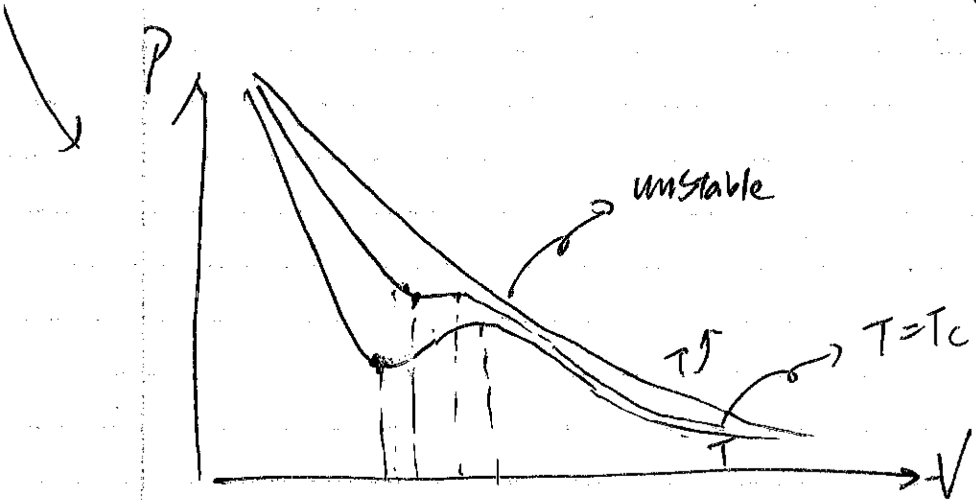


$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

Maxwell's construction for phase transition







at critical point.

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}$$

① $\left.\partial P / \partial V\right|_{V_c} = 0 \rightarrow 2a V_c^{-3} = k_B T_c (V_c - b)^{-2}$.

② $\left.\partial^2 P / \partial V^2\right|_{V_c} = 0 \rightarrow 6a V_c^{-4} = 2 k_B T_c (V_c - b)^{-3}$

$$V_c = 3b.$$

$$k_B T_c = \frac{8a}{27b}$$

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

$$\left.\begin{aligned} \hat{P} &= P / P_c \\ \hat{V} &= V / V_c \\ \hat{T} &= T / T_c \end{aligned}\right| \rightarrow \left(\hat{P} + \frac{3}{\hat{V}^2}\right)\left(3\hat{V} - 1\right) = 8\hat{T}$$

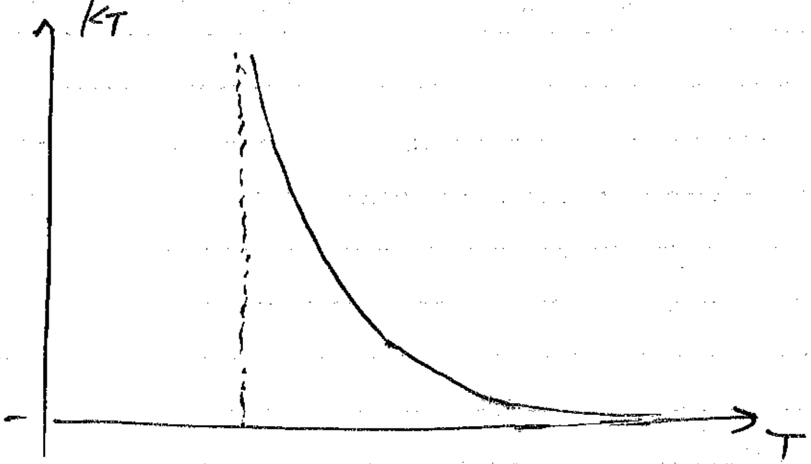
Continue with $k_T = \ldots$

$$-\frac{\partial P}{\partial V} = -k_B T (V - b)^{-2} + 2aV^{-3}.$$

$$\frac{\partial V}{\partial P} = \frac{1}{-k_B T (V-b)^{-2} + 2aV^{-3}}$$

$$\kappa_T = -\frac{1}{V}\cdot\frac{\partial V}{\partial p} = \frac{1}{k_B T V (V-b)^{-2} - 2aV^{-2}}$$

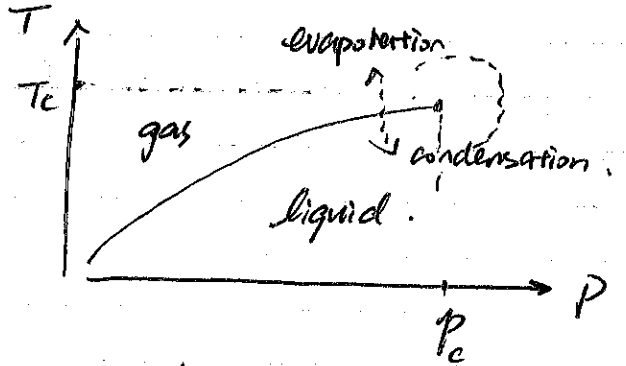
$$= \frac{4b}{3k_B}\,(T - T_c)^{-1} \qquad T > T_c$$



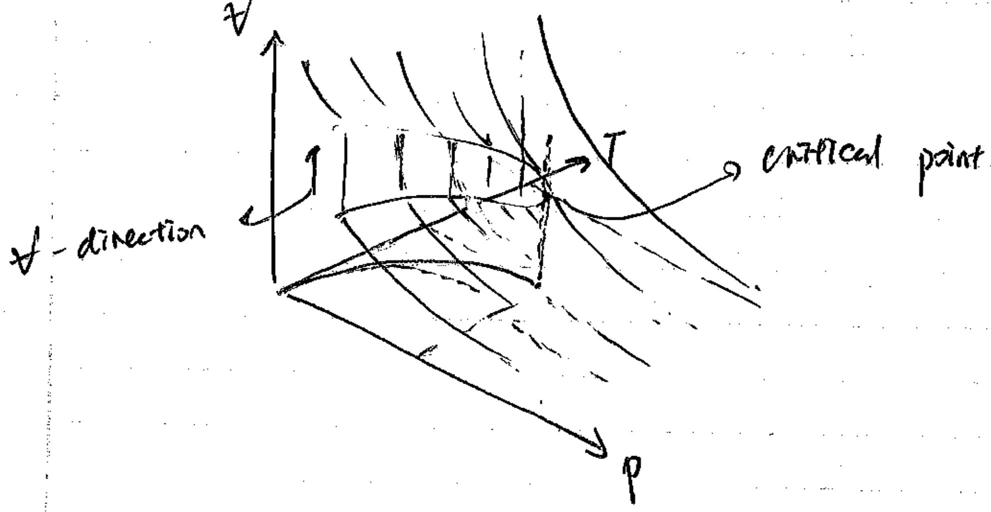
3/3/2025 Week 9. Lecture 1.

Ising Model.

1. General behavior
2. Solution in 1D.
3. Solution in 2D.



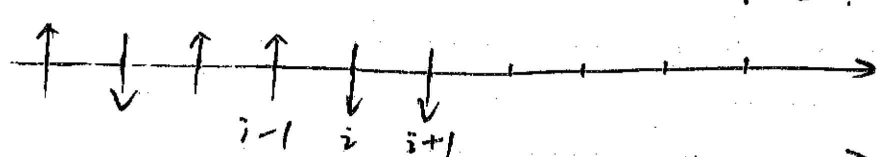
Water
$T_c = 647K$.
$P_c = 22MPa$



Definition - Ising model.

$S_i = \pm 1$.

1D.

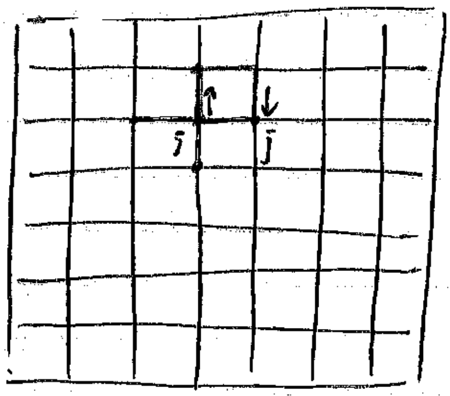


$$\mathcal{H}(\{S_i\}) = -J\sum_{\langle i,j\rangle} S_i S_j \xrightarrow{1D} -J\sum_i S_i S_{i+1}$$

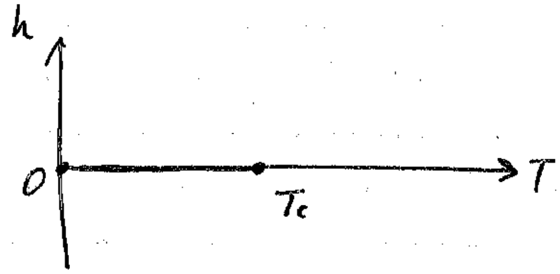
external magnetic field → $-h\sum_i S_i$

if $J > 0$: neighboring spin tend to be parallel / aligned.

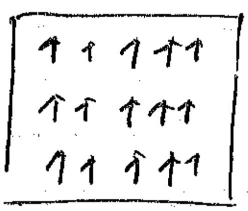
2D Ising model



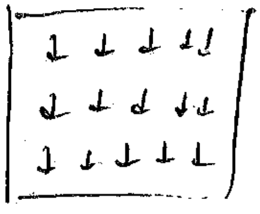
Ernst Ising, 1925



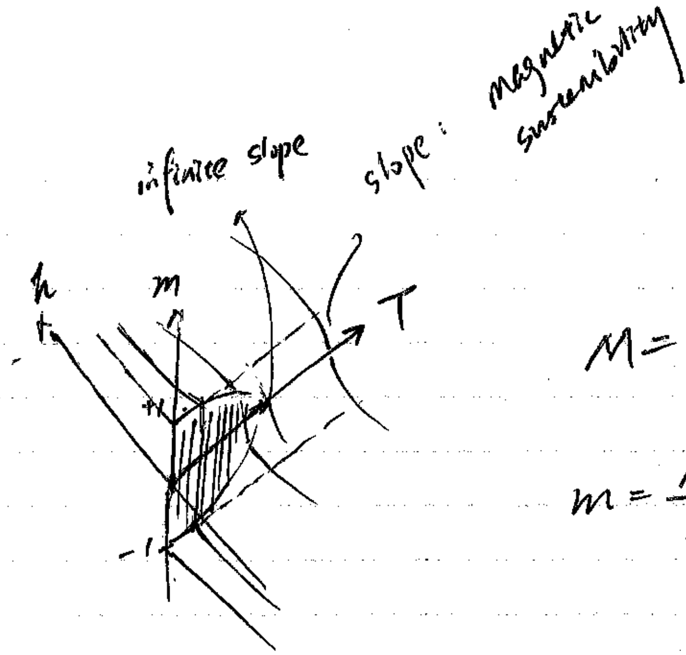
$T << T_c$ $(T \to 0)$



↳ only 2 states: all spins are up / down



degeneracy will be broken by "h".



$$M = \sum_i S_i$$

$$m = \frac{M}{N} = \frac{1}{N} \sum_i S_i$$

if h is "slightly" non-zero

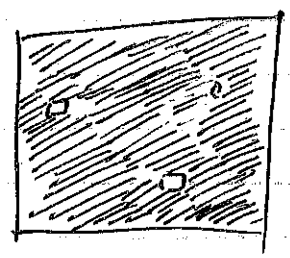
$T < T_c$

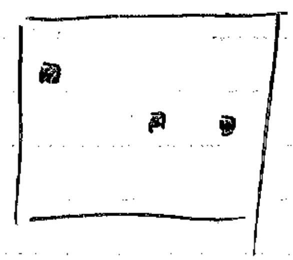
$T = T_c$

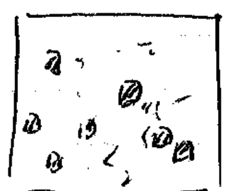
$T > T_c$ ($T \to \infty$)

"completely random"

no patterns







when T is slightly lower than ∞, there are still Some patterns in it.

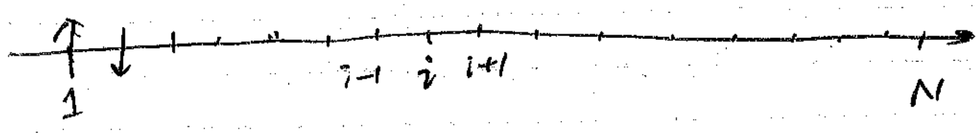
@ $T = T_c$ → weird distribution of "clusters".

fractal pattern (fluctuations @ all scales)

$T = T_c$ critical point

↳ critical region

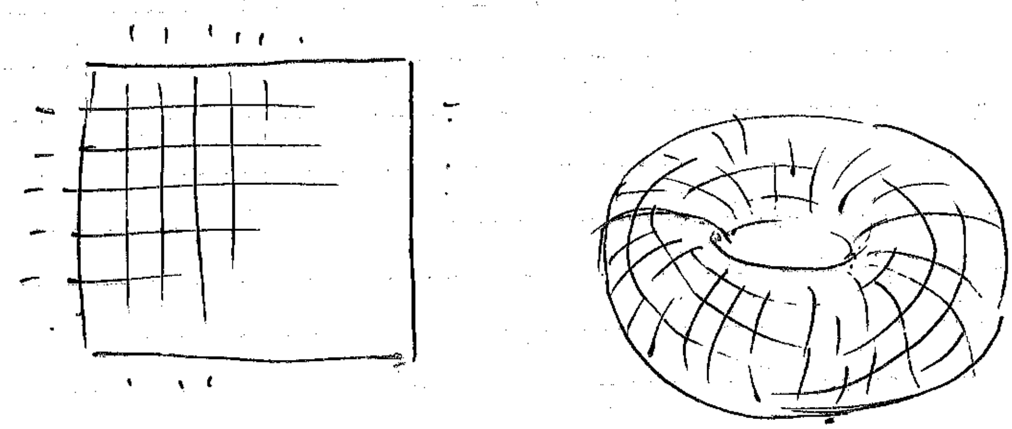
Solution in 1D



Boundary conditions.

free B.C.s: $S_1S_2 + S_2S_3 + \cdots + S_{N-1}S_N$

P.B.C.s: $S_1S_2 + S_2S_3 + \cdots + S_{N-1}S_N + S_NS_1$



2.1. $T=0.$ $h \neq 0.$

$$Z = \sum_{\{S_i\}} \exp(\beta h \textstyle\sum_i S_i)$$

$$= \sum_{\{S_i\}} \prod_i \exp(\beta h S_i) \xrightarrow[\text{non-interacting}]{} \prod_i \sum_{\{S_i\}} e^{\beta h S_i}$$

$$= \left(\exp(+\beta h) + \exp(-\beta h) \right)^N$$

$$= (2 \cosh \beta h)^N$$

↪ Helmholtz free energy. ...

A, E, C_V, ...

"Non-interacting model, no phase transition".

2.2. $J \neq 0$, $h = 0$.

$$\mathcal{H}(\{S_i\}) = -J\,(S_1 S_2 + S_2 S_3 + \cdots S_{N-1} S_N) \quad \text{free B.C.}$$

$$S_1, S_2, \ldots, S_N = \pm 1$$

$$S_1, P_2, P_3, \ldots, P_N$$

$$S_1 S_2 \quad S_2 S_3. \quad S_{N-1} S_N$$

$$\mathcal{H}(S_1, P_2, \ldots P_N) = -J\,(P_2 + \cdots + P_N).$$

$$Z_1 = 2\left(e^{\beta J} + e^{-\beta J} \right)^{N-1} \quad (\text{free B.C.}).$$

P.B.C.

$$Z_1 = (2 \cosh \beta J)^N \left[1 + (\tanh \beta J)^N \right].$$

2.3 $J \neq 0$, $h \neq 0$.

3/5/2025 . Week 9. Lec 2.

Today

1. 1D Ising model ($J \neq 0$, $h \neq 0$).

   Transfer matrix method

2. 2D Ising model.

   Onsager Solution.

3. Monte Carlo Simulation.

   Detailed balance.

$S_i = \pm 1$.

N spins.

$$1D. \quad \mathcal{H}(\{S_i\}) = -J \sum_i S_i S_{i+1} - h \sum_i S_i$$

$$Z = \sum_{\{S_i\}} \exp\left(-\beta \mathcal{H}(\{S_i\})\right)$$

2^N terms

$$e^{\beta h S_1} e^{\beta h S_2} \cdots e^{\beta h S_N}$$

$$e^{\beta J S_1 S_2} e^{\beta J S_2 S_3} \cdots e^{\beta J S_N S_1}$$

$2N$ terms.

Transfer matrix method.

$e^{\beta h S_1}$ $e^{\beta h S_2}$ ... $e^{\beta h S_i}$ $e^{\beta h S_{i+1}}$.

$e^{\beta J S_1 S_2}$ $e^{\beta J S_i S_{i+1}}$

$e^{\beta \frac{h S_i}{2}}$ $e^{\beta \frac{h S_{i+1}}{2}}$

$e^{\beta J S_i S_{i+1}}$

$$Z = \sum_{\{S_i\}} \prod_i e^{\beta\left(\frac{h}{2} S_i + J S_i S_{i+1} + \frac{h}{2} S_{i+1}\right)} \quad (PBC)$$

We define the pattern as P.

$$\Updownarrow$$

$$e^{\beta\left(\frac{h}{2}S_i + JS_iS_{i+1} + \frac{h}{2}S_{i+1}\right)}$$

$$\Updownarrow$$

$$P(S_i, S_{i+1}) = \begin{array}{c|cc} S_i \backslash S_{i+1} & + & - \\ \hline + & e^{\beta(h+J)} & e^{-\beta J} \\ - & e^{-\beta J} & e^{\beta(J-h)} \end{array}$$

↳ partition function in a matrix form. $P_{S_i, S_{i+1}}$.

$$Z_1 = \sum_{\{S_i\}} P_{S_1 S_2} P_{S_2, S_3} \cdots P_{S_{N-1}, S_N} P_{S_N S_1}.$$

called the "transfer matrix".

$$= \mathrm{Tr}\,(P^N).$$

product of N terms

element of $\mathbb{R}^{2\times 2}$ P matrix

$\sum_{S_1} (P^N)_{S_1}$ equivalent to $\sum_{S_2} (P^N)_{S_2}$

... How to compute $\mathrm{Tr}(P^N)$?

↳ brute force $P^2 = P \cdot P$. $(\quad)\cdot(\quad)\cdots$

does not go to any new expression, "reprove" the original expression

→ Exactly the same ...

Second way.

$$P = V D V^T \qquad D = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

↳ similarity transformation does not change the trace

$$Tr(P) = \lambda_1 \lambda_2$$

$$P^2 = V D V^T V D V^T \cdots$$

$$= V D^2 V^T \qquad D^2 = \begin{bmatrix} \lambda_1^2 & \\ & \lambda_2^2 \end{bmatrix}$$

$$P^N = V D^N V^T \qquad D^N = \begin{bmatrix} \lambda_1^N & \\ & \lambda_2^N \end{bmatrix}$$

$$Tr(P^N) = \lambda_1^N + \lambda_2^N$$

$$\equiv$$

$$Z_1$$

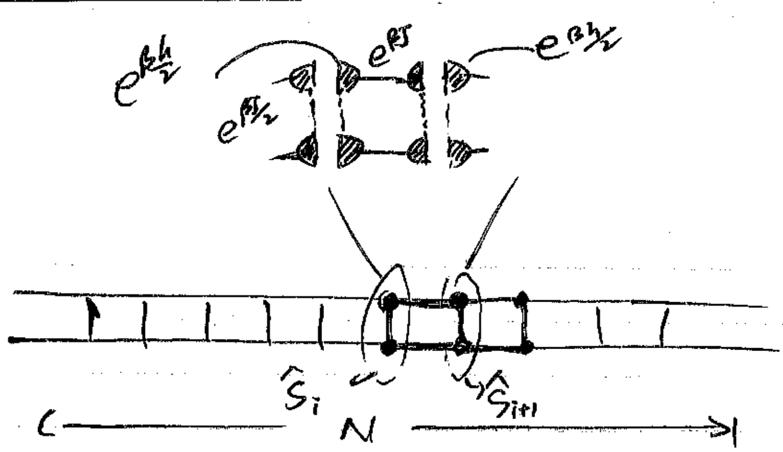
when $N \to \infty$. $Z_1 = \lambda_1^N$.

$$A = -k_BT \ln Z_1 = -k_BT \ln(\lambda_1^N + \lambda_2^N)$$

$$\cong -N k_BT \ln \lambda_1$$

$$Z_1 = Tr(P^N). \cong \lambda_{max}^N$$

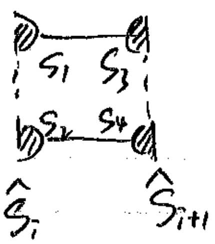
$$P_{s_i s_j} = e^{\frac{\beta}{2} h s_i} e^{\beta J s_i s_j} e^{\beta \frac{h}{2} s_i}.$$



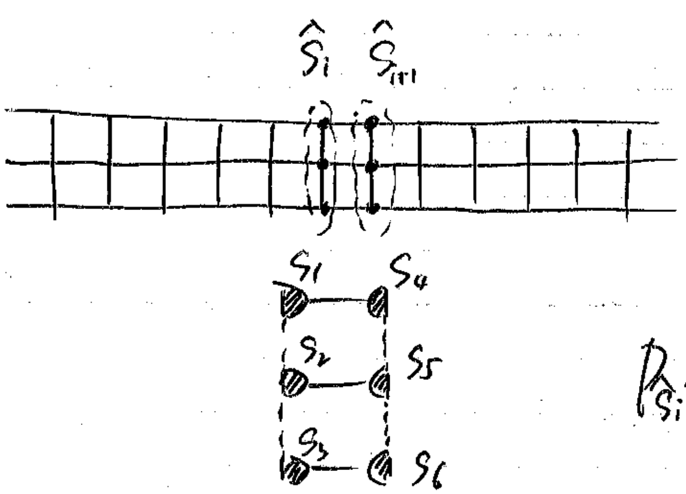
$\mathcal{H}(\{\hat{S}_i\})$ $\quad \hat{S}_i = \begin{cases} ++ \\ +- \\ -+ \\ -- \end{cases}$

2 rows of 1D Ising model.

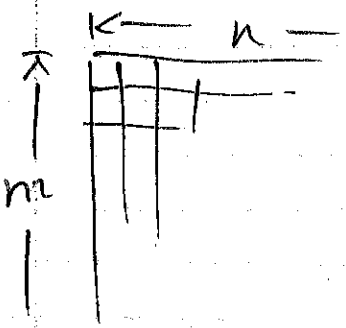
$$P_{\hat{S}_i \hat{S}_{i+1}} = \begin{array}{c|c} {}_{\hat{S}_i}\backslash^{\hat{S}_{i+1}} & \begin{array}{cccc} ++ & +- & -+ & -- \end{array} \\ \begin{array}{c} ++ \\ +- \\ -+ \\ -- \end{array} & \left(\begin{array}{c|c|c|c} & & & \\ \hline & & & \\ \hline & & & \\ \hline & & & \end{array} \right) \end{array}$$



$$P_{\hat{S}_i \hat{S}_{i+1}} = e^{\beta \frac{h}{2} s_1} e^{\beta \frac{h}{2} s_2} e^{\beta \frac{h}{2} s_3} e^{\beta \frac{h}{2} s_4} \cdot e^{\beta J s_1 s_3} e^{\beta J s_2 s_4} \underbrace{e^{\beta \frac{J}{2} s_1 s_2} e^{\beta \frac{J}{2} s_3 s_4}}_{\text{on the edges}}$$



$$P_{\hat{S}_i \hat{S}_{i+1}} = \begin{array}{c|c} & \begin{array}{cccc} +++ & ++- & \cdots & --- \end{array} \\ \begin{array}{c} +++ \\ ++- \\ \vdots \\ --- \end{array} & \left(\begin{array}{c} \\ 8 \times 8 \\ \\ \end{array} \right) \end{array}$$



Extend the framework to $n \times m$,

let $n \to \infty$, $m \to \infty$, observes phase transition.

transfer matrix. $P_{\hat{S}_i \hat{S}_{i+1}} = 2^m \times 2^m$ matrix

diagonize

↓

and solve the partition function.

- Onsager
- Kaufman. → Simplify the diagonization

↓

gives another matrix R $2m \times 2m$.

the eigenvalues of $P_{..}$ & R

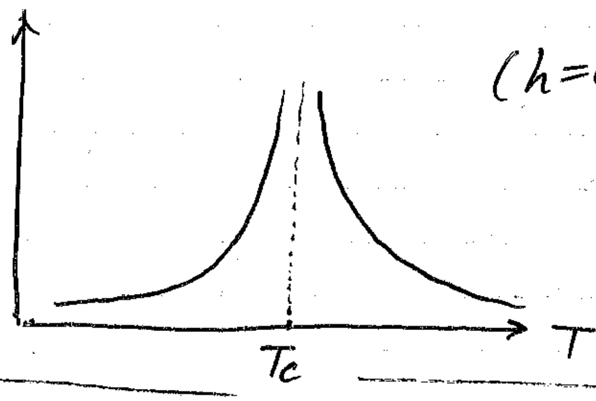
are related.

Week 10 Lecture 1.

Today.

- critical exponents
- Renormalization.

$c_v = \frac{C_v}{N}$



$(h=0)$

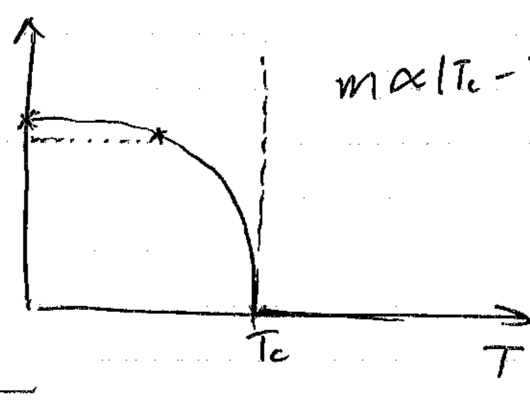
2D: ($\alpha = 0$: $C_v \propto \ln\left|\frac{1}{T-T_c}\right|$).

$$\boxed{* \text{ heat capacity. } \quad C_v \propto |T-T_c|^{-\alpha}}$$

	2D	3D
$\tilde{\beta}$	$1/8$	0.3264.
α	0	0.1101
γ	$7/4$	1.2371
y_t	1	1.5874.
y_h	$15/8$	2.4818
d	2	3

<······ $\alpha = 2 - \frac{d}{y_t}$

$m = M/N$



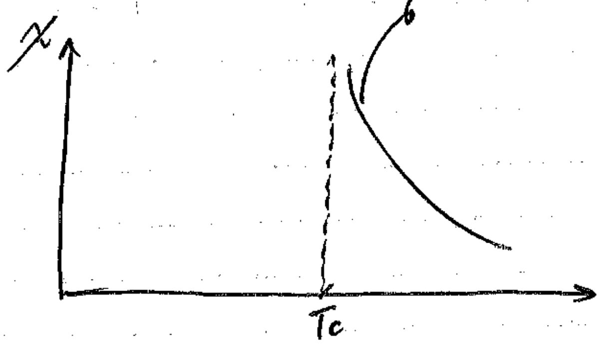
$m \propto |T_c - T|^{\tilde{\beta}}$

* spontaneous magnetization.

$$m \propto |T-T_c|^{\tilde{\beta}} \qquad \tilde{\beta} = \frac{d-y_h}{y_t}.$$

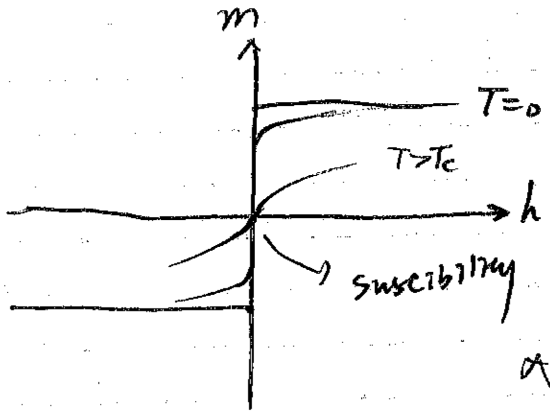
* Q why slope not negative?

value of the slope



$$\chi = \frac{\partial m}{\partial h}$$

$$\chi \propto |T - T_c|^{-\gamma}$$



susceptibility is the slope.

$\propto$ when $T \to T_c$

spontaneous magnetization is gone

* magnetic susceptibility.

$$\chi \propto |T - T_c|^{-\gamma}$$

$$\gamma = \frac{2y_h - \alpha}{y_t}$$

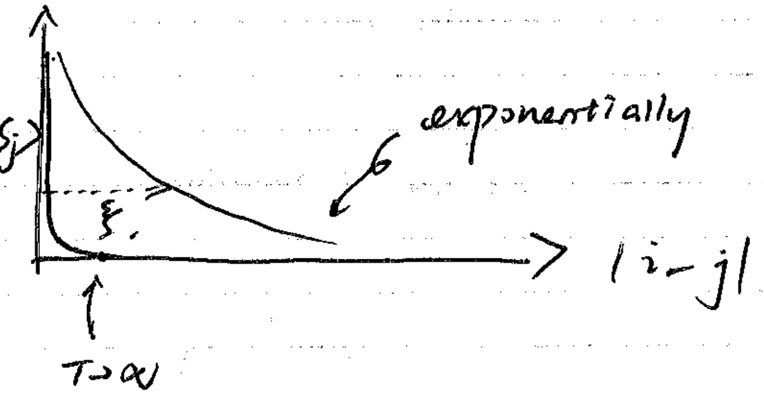
$$\dots \alpha + 2\tilde{\beta} + \gamma = 2$$

$$\alpha = 2 - d \cdot \nu .$$

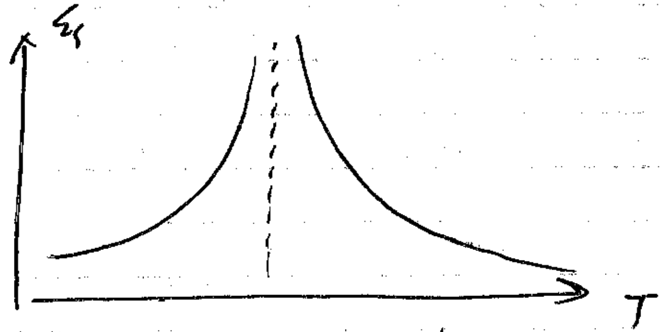
Correlation length.

high temperature: $T > T_c$.

$C_{ij} \equiv \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$



exponentially decaying func.



correlation length $\xi \propto |T - T_c|^{-\nu}$

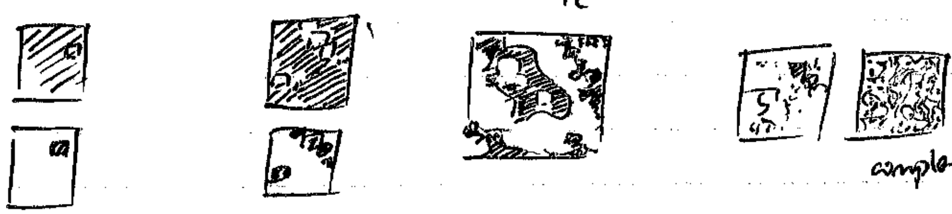
$$\nu = \frac{1}{y_T}$$

	2D	3D.
ν	1	0.63

Recall Ising model

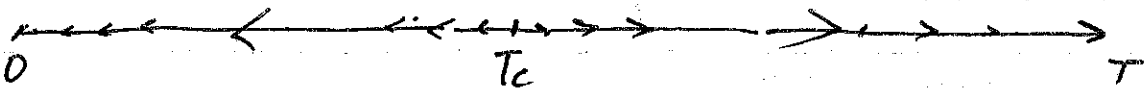
$h = 0$

$T < T_c$ $\quad$ $T = T_c$ $\quad$ $T > T_c$



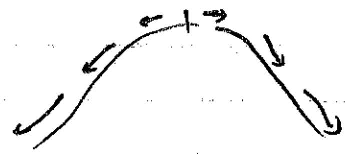
(gray sparks)

completely random



zooming out
⇕
lower temperature

Zooming out
⇕.
higher temperature

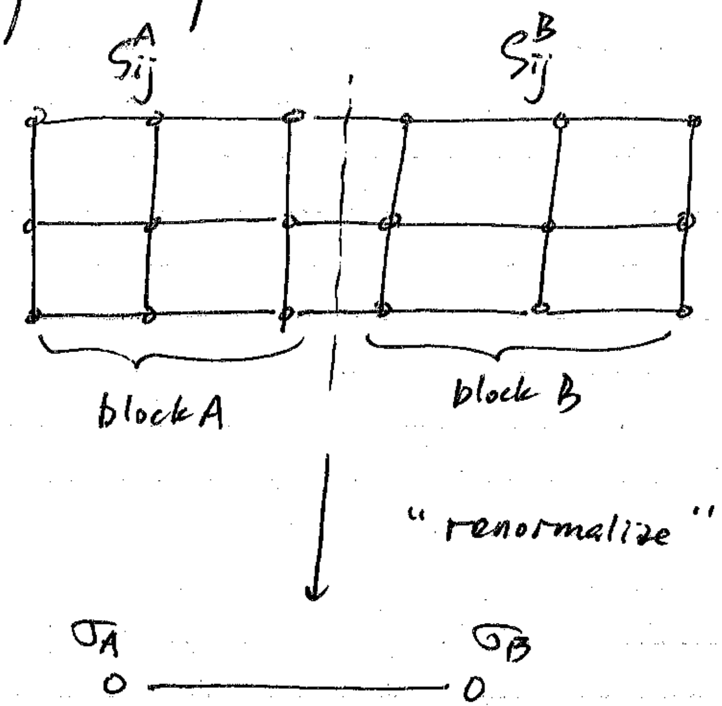


connecting the qualitative results and numerical values from the exponential coeff.

↓

renormalization group.

"Baby Ising model #2".



$$Z_1 = \sum_{\{S_{ij}^A, S_{ij}^B\}} e^{-\beta \mathcal{H}(\{S_{ij}^A\}, \{S_{ij}^B\})} \quad \dots (*)$$

2^{18}

all spins

"renormalized" model.

$$Z_1 = \sum_{\sigma_A, \sigma_B} e^{-\beta \mathcal{H}(\sigma_A, \sigma_B)} \quad \dots (**)$$

$\sigma_A \overset{\tilde{J}}{—} \sigma_B$

$\pm 1 \qquad \pm 1$

in the model, lower the T $\equiv$ increase βJ.

lowest energy

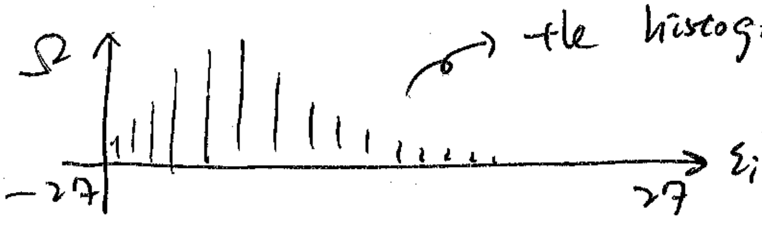
12 vertical bonds.

15 horizontal bonds.

$$a\, e^{27\beta J} + b\, e^{25\beta J} + \dots + z\, e^{-27\beta J}$$

Some coefficients.

Eqn. $(*)$: $\displaystyle\sum_{\varepsilon_i=-27}^{+27} \Omega(\varepsilon_i)\, e^{-\beta\varepsilon_i}$



the histogram is the symbolic expression.

Eqn. (**)

$$Z_1 = e^{-\beta \hat{\mathcal{H}}(++)} + e^{-\beta \hat{\mathcal{H}}(+,-)}$$

$$+ e^{-\beta \hat{\mathcal{H}}(-+)} + e^{-\beta \hat{\mathcal{H}}(--)}$$

$$= \tilde{Z}_1(++) + \tilde{Z}_1(+-) + \tilde{Z}_1(-+) + \tilde{Z}_1(--)$$

$$\Omega(\mathcal{E}) = \Omega_{++}(\mathcal{E}_i) + \Omega_{+-}(\mathcal{E}_i) + \Omega_{-+}(\mathcal{E}_i)$$

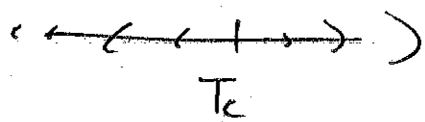
$$+ \Omega_{--}(\mathcal{E}_i).$$

...

e.g., $\tilde{Z}_1(++) = \sum \Omega_{++}(\mathcal{E}_i) . e^{-\beta \mathcal{E}_i}$

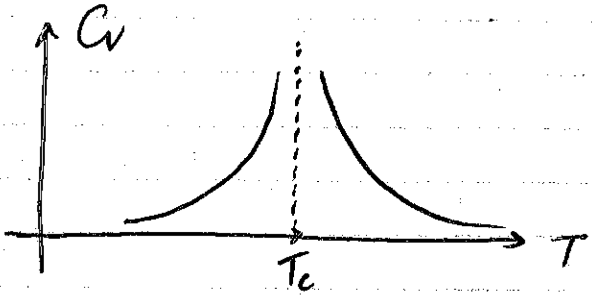
$$\beta \tilde{J} = f(\beta J).$$

having the property of



Week 10 Lecture 2. 3/12/2025

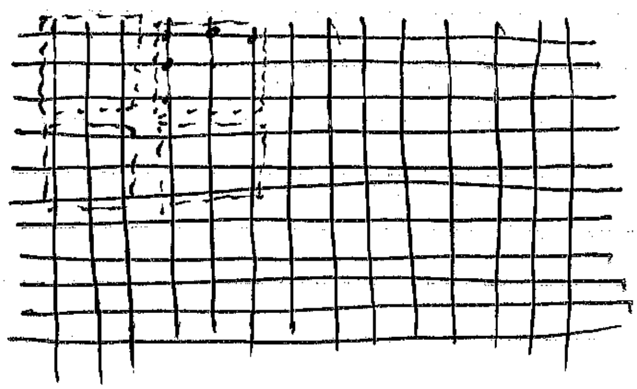
review.



$$C_v \propto |T - T_c|^{\alpha}$$

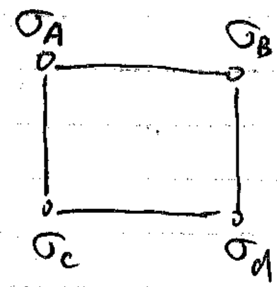
$$\alpha = 2 - \frac{d}{y_c}.$$

	2D	3D
α	0	0.1101
y_t	1	1.5879.



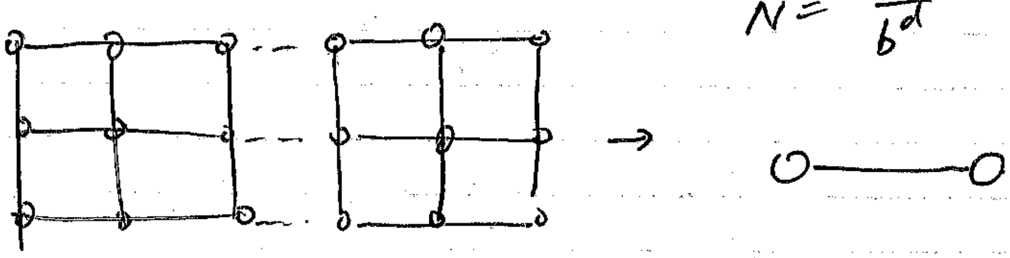
N spins

$b = 3.$



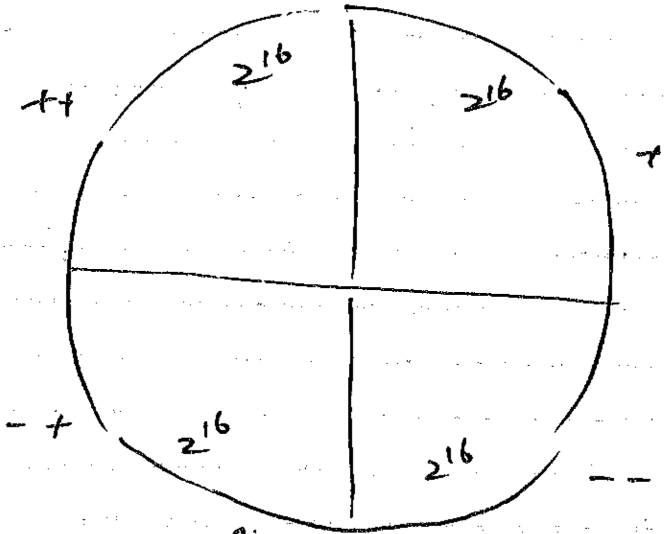
$\tilde{N}$ spins.

$$\tilde{N} = \frac{N}{b^d}$$



$$Z = \sum_{\{s_{ij}\}} e^{-\beta \mathcal{H}(\{s_{ij}\})}.$$

↳ 2^{18} terms: $e^{-\beta \varepsilon_i}$



partition into 4 regions (σ_A, σ_B).

$\downarrow$

σ regions ξ_i

$$Z = \sum_{\xi_i = -2q_j}^{+2q_j} \Omega(\xi_i) e^{-\beta \xi_i}.$$

$$= Z_{++} + Z_{+-} + Z_{-+} + Z_{--}$$

$$Z_{++} = \sum_{\xi_i = -2q_j}^{+2q_j} \Omega_{++}(\xi_i) e^{-\beta \xi_i}$$

$$= \sum_{\{\xi_{ij}\}} e^{-\beta \mathcal{H}(\{s_{ij}\})}.$$

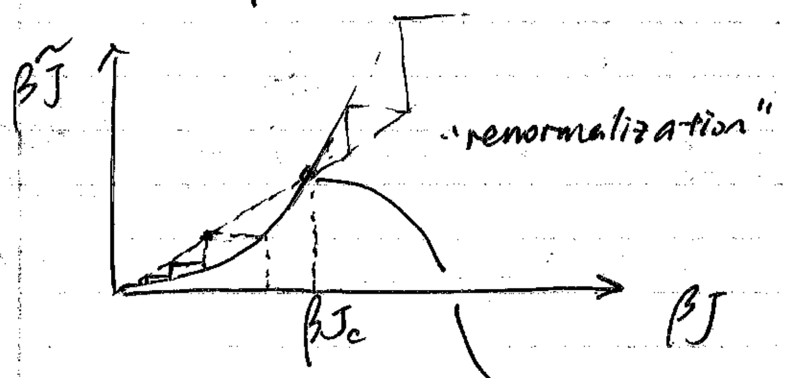
s.t. maj. $s_{ij}^A = +1$

maj $s_{ij}^B = +1$.

$$\Omega(\xi_i) = \Omega_{++}(\xi_i) + \Omega_{+-}(\xi_i) + \Omega_{-+}(\xi_i) + \Omega_{--}(\xi_i).$$

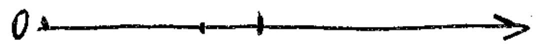
$$Z_{++} = e^{-\beta \tilde{\mathcal{H}}(++)}$$
$$Z_{+-} = e^{-\beta \tilde{\mathcal{H}}(+-)}$$
$$Z_{-+} = e^{-\beta \tilde{\mathcal{H}}(-+)}$$
$$Z_{--} = e^{-\beta \tilde{\mathcal{H}}(--)}$$

$$\beta\tilde{J} = f(\beta J).$$



$\rightarrow \beta J_c = 0.504$

from the slope,



$T \to \infty$ limit. $T \to 0$ limit

$\tilde{J} = f(J)$

$J_c = f(J_c)$

$$\delta\tilde{J} = f'(J_c)\,\delta J \qquad J_c + \delta\tilde{J} = J_c + f'(J_c)\,\delta J.$$

$$f'(J_c) = b^{y_t}$$

$y_t > 0$

$J = J_c + \delta J$

$\downarrow$

$\tilde{J} = J_c + \delta\tilde{J}$

free energy density function (per spin)

$$f_s(t, h) = b^{-d} f_s(b^{y_t} t, b^{y_h} h). \quad \begin{aligned} J &= J_c + t. \\ h &= 0 + h. \end{aligned}$$

" similar to the homogeneous function def'n "

the function has to be like this near the critical point.

Final Review.

1. connection with thermodynamics. (Axioms).

~ Equation of state.

$S(N, V, E)$ or $E(S, V, N)$. homogeneous function of order 1.

$dE = TdS - pdV + \mu dN.$

T, p, μ as partial derivatives.

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

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

canonical ensemble

$A = -k_BT \ln Z.$ … (Δ)

microcanonical ensemble

$S = k_B \ln \Omega$

$$\begin{tikzcd}
\begin{array}{c} S(N,V,E) \\ E(S,V,N) \end{array} \arrow[r, "-TS"] \arrow[d, "+pV"] & \begin{array}{c} A(T,V,N) \\ A = -N + \mu N \end{array} \arrow[d, "+pV"] \\
H(S,p,N) \arrow[r, "-TS"] & \begin{array}{c} G(T,p,N) \\ G = \mu N \end{array}
\end{tikzcd}$$

(D)

$\rightarrow$ (Δ) … $Z = \frac{1}{N! h^{3N}} \int \prod dp_i\, dq_i\, e^{-\beta\mathcal{H}(\{q_i, p_i\})}$

$Z = \sum_{\{S_i\}} e^{-\beta\mathcal{H}(\{S_i\})}$

NPT ensemble

(D) $G = -k_B T \ln \Xi$

$$\Xi = \int_0^\infty dV \cdot Z(N, V, T)$$

2. Mathematical Identities

$$\langle aX + bY \rangle = a\langle X \rangle + b\langle Y \rangle.$$

$$\langle XY \rangle = \langle X \rangle \langle Y \rangle.$$

if X, Y independent.

$\langle X^2 \rangle \geq \langle X \rangle^2$ $\quad V(X) \equiv \langle X^2 \rangle - \langle X \rangle^2$

Variance $\quad \sigma_x = \sqrt{V(x)}$

Standard deviation.

$$C_n^m = \frac{n!}{m!(n-m)!}$$

→ $\ln N! \approx N\ln N - N.$ $\quad tr(AB) = tr(BA).$

$\lim_{n\to\infty} (1 + \frac{x}{n})^n = e^x.$ $\quad P = UDU^T$

diagonal $\begin{pmatrix} \lambda_1 & & 0 \\ 0 & \lambda_2 & \\ & & \ddots \end{pmatrix}$

$$\int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} dx = 1$$

$UU^T = I$

$tr(P) = \sum_i \lambda_i$

$$\mathrm{tr}(P^N) = \mathrm{tr}(D^N) = \Sigma_i \lambda_i^N$$

3. Useful relations.

for N- noninteracting subsystems.

$$Z_1 = (Z)^N.$$

$$E = \langle H \rangle = \frac{\int dp_i\, dq_i \quad e^{-\beta H(q_i, p_i)} \; H(q_i p_i)}{\int dq_i\, dp_i \; e^{-\beta H(q_i p_i)}}$$

Canonical

$$= -\frac{1}{Z_1} \cdot \frac{\partial}{\partial \beta} Z$$

$$= -\frac{\partial}{\partial \beta} \ln Z$$

$$(\Delta E)^2 = \langle H^2 \rangle - \langle H \rangle^2$$

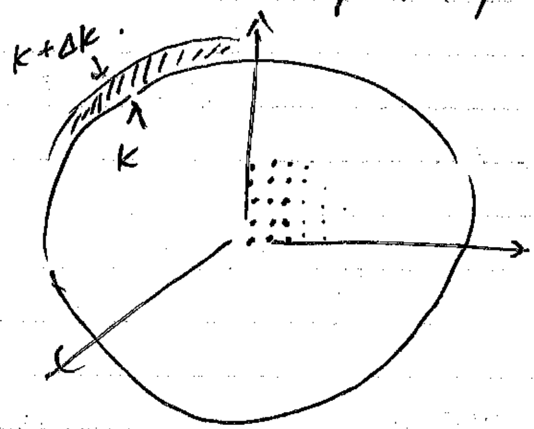
$$= \frac{\partial}{\partial \beta}\left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)$$

$$= k_B T^2 \frac{\partial E}{\partial T}$$

$(\Delta E)^2 \propto N$.

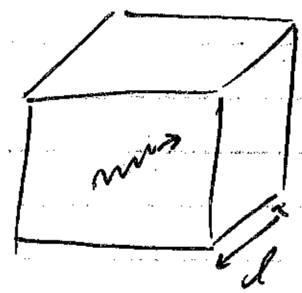
$\Delta E \propto \sqrt{N}$ $\qquad \dfrac{\Delta E}{E} \propto \dfrac{1}{\sqrt{N}}$

4. How to count properly.



$g(\varepsilon)$.

non-interacting particles.
↳ occupy states.



$\underline{k} = k_x k_y k_z$.

$k_x = n_x \frac{2\pi}{L}$

$k_y = n_y \frac{2\pi}{L}$

$k_z = n_z \frac{2\pi}{L}$.