

theory behind thermodynamics
based on mechanical ... of a system, calculate ...

macroscopic properties

↓
statistical
physics

microscopic

Boltzmann

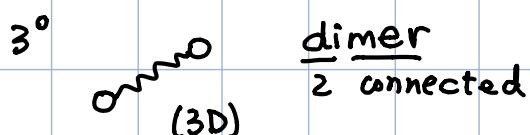
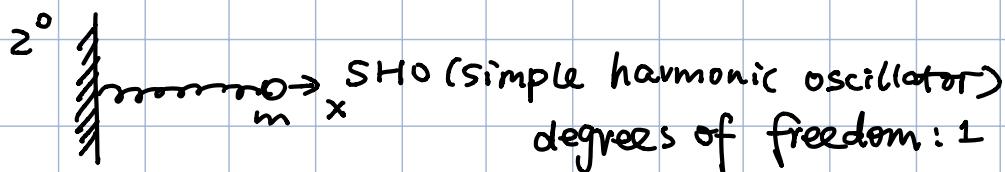
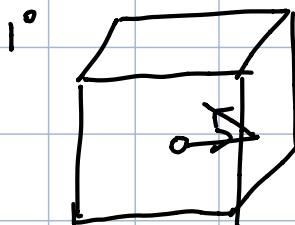
Microstates } 1. microscopic states
 } 2. classical - phase space
 } 3. QM $\rightarrow \equiv$

1. From classical dynamics to microstates

(a) one particle: point like one particle

6 variables } $\vec{r}(t)$: position, trajectory \rightarrow not present everything
 } \rightarrow generalised coordinate / momentum
 } $\vec{p}(t)$: momentum

Degrees of freedom: [3D] 3 single-point-like-particle



$$DOF = 6$$

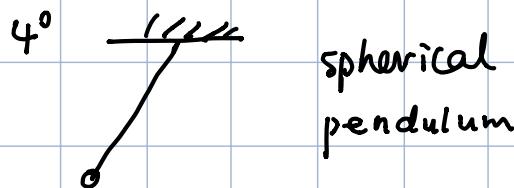
$$(x_1, y_1, z_1, x_2, y_2, z_2)$$

$$(\vec{r}_c, \theta, \varphi, r)$$

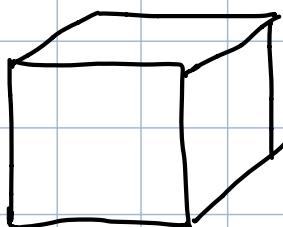
↑
distance

$$\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2$$

or $\vec{r}_c, \vec{p}_c, \vec{p}_\theta, \vec{p}_\varphi, p_r$



(b) N particle



$$i = 1, 2, 3, \dots, N$$

$$DDF = 3N - 1 \quad (\text{Energy conserved})$$

$$\text{Variable} = 3N \times 2$$

$$\begin{aligned} (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) &\rightarrow (\vec{r}^N) \\ (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) &\rightarrow \vec{p}^N \end{aligned} \quad \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} (\vec{r}^N, \vec{p}^N)$$

6N variables

Notes: 1° if $(\vec{r}^N(0), \vec{p}^N(0))$ are given, then $\vec{r}^N(t)$, $\vec{p}^N(t)$, will be determined

2° interactional energy $V = V(\vec{r}^N)$

3° phase space: a generalised coordinate space
(classical)
eg. 1 particle in 1D

Gibbs

$\begin{matrix} P \\ \uparrow \\ \cdot(x, p) \end{matrix} \rightarrow \text{a microscopic state is given.}$

not a picture of the particle

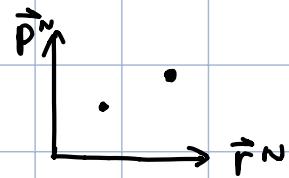
1 particle in 3D $\vec{r}(x, y, z)$

$\vec{p}(p_x, p_y, p_z)$

\vec{P} $\uparrow \cdot$ conceptually $(3+3)D$ space

$$\vec{r}$$

N particle in 3D



2. Quantum state

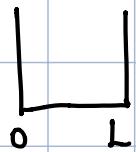
(a) one particle in 1D (x, p)

$$H = \frac{p^2}{2m} + V(x)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\text{Seq. } \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Phi_i(x) = E_i \Phi_i(x)$$

$$i=1, 2, 3, \dots, \infty$$

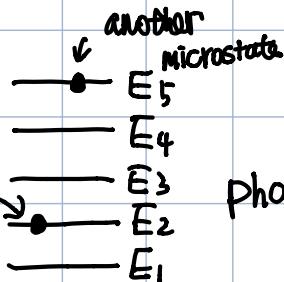


1D-Box

- 1维无限深势阱

$$\{E_i\}$$

$$i=1, 2, 3, \dots, \infty$$



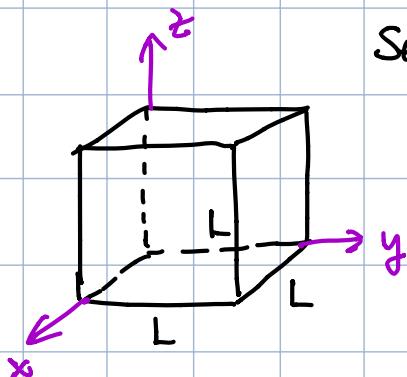
phase space in QM

(b) one particle in 3D $(x_1, p_1), (x_2, p_2), (x_3, p_3)$

$$H = \frac{p_1^2 + p_2^2 + p_3^2}{2m} + V(x_1, x_2, x_3)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$$

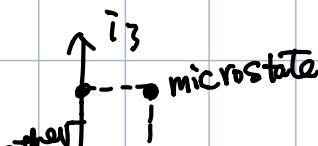
$$\text{Seq. } \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \Phi_i = E_i \Phi_i$$



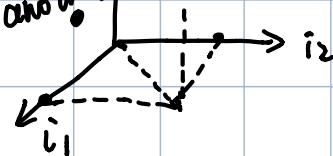
Homework: $\Phi(x, y, z) = \Phi_1(x) \Phi_2(y) \Phi_3(z)$

separation of variables

$$E_{i_1, i_2, i_3}$$



integer



(C) N particles in 3D

$3N$ integers



" i " = i_1, i_2, \dots, i_{3N}

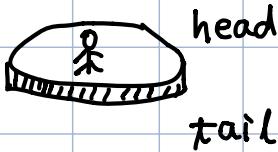
Discrete (discontinuous)

Probability Theory

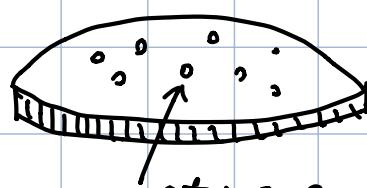
1. Basic Definitions

ensemble (系統): a collection of systems whose statistical properties will be examined.

e.g.



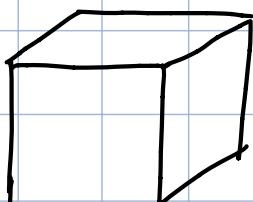
many coins are a system.



atoms even electrons
one coin is a system of conductors

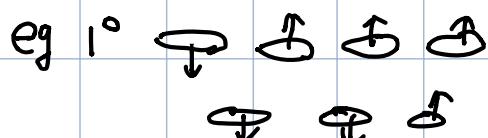
2. Ensemble in Statistical Physics

(a)

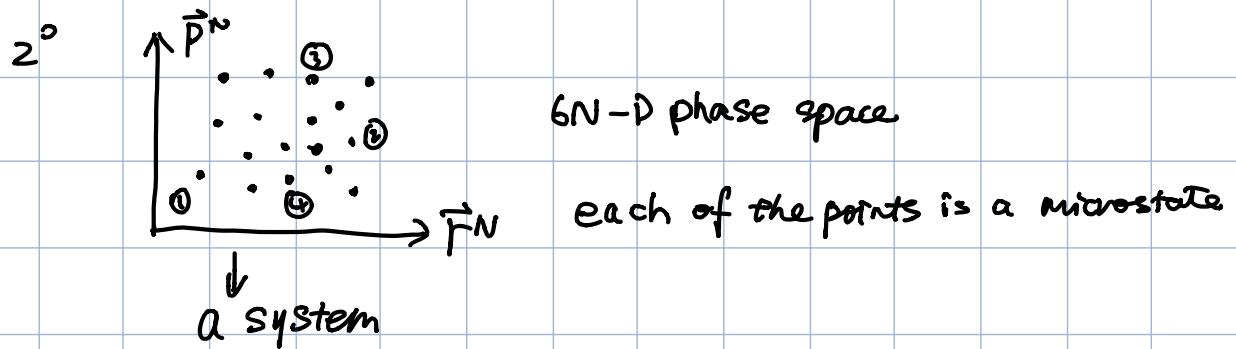
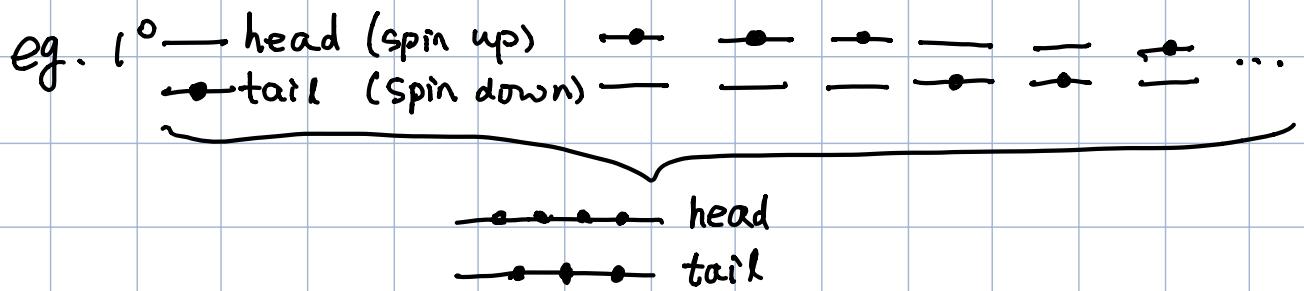


collection of imaginary systems

(b) each system is at a different microstate.
at a particular microstate.



(c) How to represent ensemble in a plot?



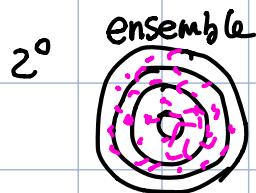
3. Probabilities

eg. 1° two states $\uparrow \downarrow$

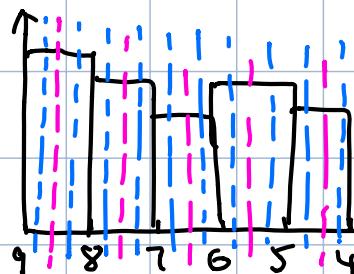
$$P_{\uparrow} = \frac{\# \text{ of those with spin up}}{\text{total number of imaginary systems}}$$

roughly 0.5

$$P_{\downarrow} = \frac{\# \text{ of those with spin down}}{\text{total # of imaginary systems}}$$



dart board 飞镖板

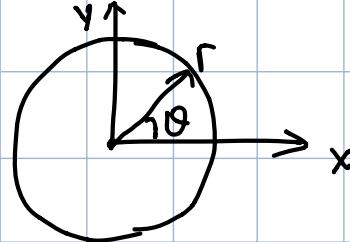
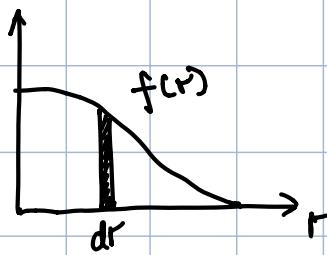


what happened?

$$\left. \begin{array}{l} q \rightarrow 8 \rightarrow q \rightarrow 9.5 \rightarrow 8 \\ p_q^{\text{old}} \rightarrow p_q^{\text{new}} \sim p_q^{\text{old}} \cdot \frac{1}{2} \end{array} \right\}$$

$$\left. \begin{array}{l} q \rightarrow 8 \rightarrow q \rightarrow 8.75 \rightarrow 8.5 \rightarrow 8.25 \rightarrow 8 \\ p_q^{\text{old}} \rightarrow p_q^{\text{new}} \sim p_q^{\text{old}} \cdot \frac{1}{4} \end{array} \right\}$$

For continuum variable Γ : $P(\Gamma \rightarrow \Gamma + d\Gamma) = \underbrace{f(\Gamma)}_{\text{probability distribution function}} d\Gamma$
 times a distance element



In 2D. $(\Gamma, \theta) \rightarrow f(\Gamma, \theta)$

4. Definition of $P_{i..}(Q/m)$: fraction of systems sitting at a quantum state "i".
 ↗ Quantum Numbers.

5. For a classical system (N atoms)

$$P(\vec{\Gamma}^N \rightarrow \vec{\Gamma}^N + d\vec{\Gamma}^N, \vec{p}^N \rightarrow \vec{p}^N + d\vec{p}^N) = f(\vec{\Gamma}^N, \vec{p}^N) d\vec{\Gamma}^N d\vec{p}^N$$

6. Ensemble average [mean, expected value] of a physical quantity

$$g(\vec{\Gamma}^N, \vec{p}^N) \text{ (classical)} \quad g_{i..}(q, m)$$

$$\langle g \rangle = \bar{g} = \sum_{i..} P_{i..} g_{i..}$$

↑ Note: 1° weighted average

2° ensemble average

Remarks: 1° If $P_{i..}$ is normalised: $\sum_{i..} P_{i..} = 1$

$$2° \text{ If } P_{i..} \text{ is not normalised, } \bar{g} = \frac{\sum P_{i..} g_{i..}}{\sum P_{i..}}$$

Don't forget to normalise the probabilities

normalisation

3^o Assume $g^{(i)}$, $h^{(i)}$ are 2 separate physical quantities,

$$\langle g^{(i)} h^{(i)} \rangle \stackrel{\text{generally}}{\neq} \langle g^{(i)} \rangle \langle h^{(i)} \rangle$$

$$\langle p^2 \rangle \neq \langle p \rangle \langle p \rangle = \langle p \rangle^2$$

$$\langle \frac{1}{p} \rangle \neq \frac{1}{\langle p \rangle}$$

$$\underbrace{\langle \alpha g^{(i)} \rangle}_{\text{constant}} = \alpha \langle g^{(i)} \rangle$$

e.g. Find the variance

$\bar{g} \rightarrow \text{average}$

$$\text{Deviation of } \bar{g} \quad \sigma_{(i)} = g^{(i)} - \bar{g} \quad \langle \sigma \rangle = 0$$

$$\langle \sigma^2 \rangle = \langle (g^{(i)} - \bar{g})^2 \rangle = \langle g^{(i)2} + \bar{g}^2 - 2g^{(i)}\bar{g} \rangle$$

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

$$= \langle g^2 \rangle - \bar{g}^2 = \langle g^2 \rangle - \langle g \rangle^2$$

Assume $f(\vec{r}^N, \vec{p}^N)$ is given. Consider a physical quantity $g(\vec{r}^N, \vec{p}^N)$

$$\langle g \rangle = \frac{\iiint d\vec{r}^N d\vec{p}^N f(\vec{r}^N, \vec{p}^N) g(\vec{r}^N, \vec{p}^N)}{\sum_i P_i g_i}$$

Remarks: 1^o if $f(\vec{r}^N, \vec{p}^N)$ is normalised. $\int d\vec{r}^N d\vec{p}^N f(\vec{r}^N, \vec{p}^N) = 1$

\int
6N-dim integral

$$2^o \quad \langle g^2 \rangle \neq \langle g \rangle^2$$

Quantum Mechanically:
 $(\Delta x \Delta p)^3 N$

$\frac{1}{h^{3N}}$ factor (explain later)

7. Ensemble average for an equilibrium state.

$\sim \sim \sim$ / classical

system

$\langle g \rangle$ of a Quantum mechanical system

physical meaning \rightarrow  $\cdot \infty$

P_T	0.501
P_a	0.499

$$\langle S_T \rangle = 0.501 \cdot \frac{\hbar}{2}$$

$$\langle S_a \rangle = 0.499 \left(-\frac{\hbar}{2}\right)$$

Concept of time average

$$P_T = \frac{0 + 0 + 0 + 0 + \dots}{\text{total } \# \text{ of exp.}} = 0.501 \dots$$

time exp.

In a lab, measurement of S_{th} = time-series based ave.

↓
Postulate

Postulation #1 in statistical Mechanics:

$$\langle g \rangle_{\text{ensemble}} = \langle g \rangle_{\text{time}}$$

Isolated systems - microcanonical ensemble

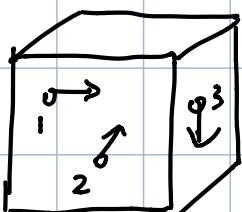
↓
fixed E

1. A system that do not exchange energy nor particle with outside.

N is fixed. E (total energy) inside the box is fixed.

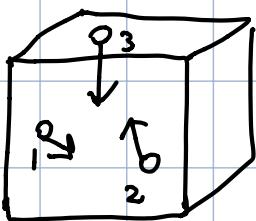
Volume is assumed to be fixed.

2. Ensemble:



V.N.E
fixed

microstate-1



...

microstate-2

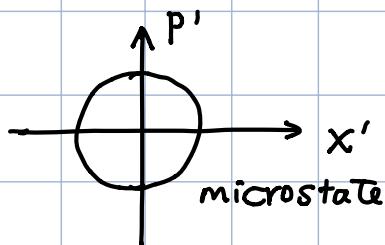
eg. ~~free~~ SHO $x, p.$

$$N=1 \quad E = \frac{1}{2}x^2 + \frac{p^2}{2m} \quad \text{fixed}$$

~~free~~
pressed

~~free~~
stretched

....



put some coefficient
and the ellipse becomes
a circle.

$$\text{Q.M. } E_n = (n + \frac{1}{2}) \hbar \omega \quad \omega^2 = k/m \quad n=0, 1, 2, \dots$$

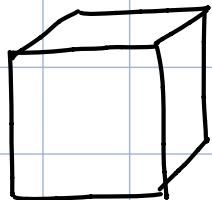
quantum number

⋮
— n=3
— n=2
— n=1
— n=0

for $E_n = E_{\text{total}}$, microstates:

⋮
—
• • •
—
—

eg2.

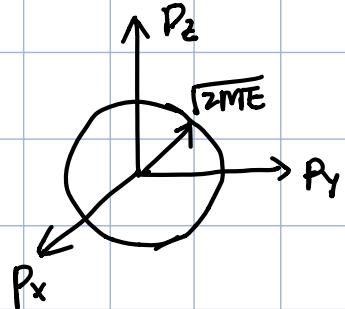


$N=1$

"free" particle (但是被限制在盒子里)

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V = E = \text{fixed.}$$

T_0



microstate: surface of sphere.

3. Postulation #2: All microstates having the same energy are assumed to be equally probable.

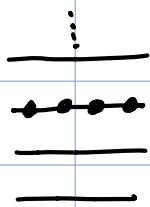
eg.



density of points.

(original p & x)

4. Q.M.



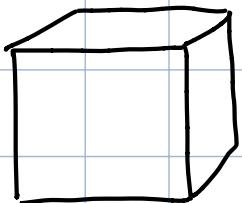
Assume that the system is at the L^{th} energy

level (total energy). All quantum states having the same E_L are equally probable.

Review. Degeneracy. "i" — quantum state label

You might have many states that belong to the same energy level. $E^{(i)} = E_L$. Degenerated states corresponding to E_L .

deg.



$$-\frac{\hbar^2 \nabla^2}{2m} \Psi(x, y, z) = E^{(i)} \Psi(x, y, z)$$

$$\Psi = A \sin \frac{n_1 \pi}{L} x \sin \frac{n_2 \pi}{L} y \sin \frac{n_3 \pi}{L} z.$$

$$E_{n_1, n_2, n_3} = -\frac{\hbar^2}{2m} (n_1^2 + n_2^2 + n_3^2)$$

quantum number
(l_1, l_2, l_3)

Energy level E_L

$(1+1+1)$

degeneracy (w_r) 1

$(4+1+1)$

3

$(1, 1, 2)$ $(1, 2, 1)$ $(2, 1, 1)$

$(4+4+1)$

3

$(2, 2, 1)$ $(2, 1, 2)$ $(1, 2, 2)$

$$P^{(i)} = \begin{cases} a & \text{if } E^{(i)} = E_L \\ 0 & \text{otherwise.} \end{cases}$$

$$\text{eg. } P_{n_1, n_2, n_3} = \begin{cases} a & \dots (n_1^2 + n_2^2 + n_3^2) = E_L \\ 0 & \text{otherwise} \end{cases}$$

What is a ? — Normalization. $\sum_i P_i = 1$

$$a = \frac{1}{\text{Degree of Degeneracy}} = \frac{1}{w_L}$$

$$\text{LHS} = \sum_{E_i=E_L} + \sum_{E_i \neq E_L}$$

$$= \sum_{E_i=E_L} a + \sum_{E_i \neq E_L} 0$$

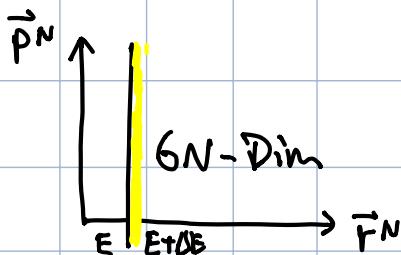
$$= a \sum_i 1$$

$$E_i = E_L$$

= a. degeneracy

$$RHS = 1$$

5. Classical version



$$H(\vec{r}^N, \vec{p}^N)$$

Hamiltonian

$$H(\vec{r}^N, \vec{p}^N) = E$$

↑
6N-dim

total energy, constant

hypersurface in 6N-dim

itself is (6N-1)-dim

$$E \leq H \leq E + \Delta E$$

very small.

not really isolated (能量可以在很小范围内变化)

連續情況下 $f(\vec{r}^N, \vec{p}^N) = \begin{cases} 1, & E \leq H(\vec{r}^N, \vec{p}^N) \leq E + \Delta E \\ 0, & \text{otherwise.} \end{cases}$

find "a" — Normalization

$$\int d\vec{r}^N d\vec{p}^N f(\vec{r}^N, \vec{p}^N) = 1$$

$$\text{LHS} = \int_{E \leq H \leq E + \Delta E} d\vec{r}^N d\vec{p}^N f(\vec{r}^N, \vec{p}^N) + \int_{\text{otherwise}} d\vec{r}^N d\vec{p}^N f(\vec{r}^N, \vec{p}^N)$$

$$= \int_{E \leq H \leq E + \Delta E} d\vec{r}^N d\vec{p}^N a = a \Omega$$

$$a = \frac{1}{\Omega}$$

$\Rightarrow \Omega = \int_{E \leq H \leq E + \Delta E} d\vec{r}^N d\vec{p}^N$ /
Planck constant

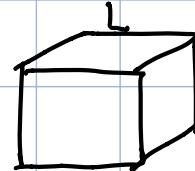
$$\Omega = \Omega(N, V, E)$$

Number of Microscopic states
(Boltzmann)

is dimensionless but $\int d\vec{r}^N d\vec{p}^N |$ isn't. → use h.

what's " Ω "?

e.g. Ideal Gas.
(perfect)



V, N, E

$$H(\vec{r}^N, \vec{p}^N) = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + \dots + \frac{P_N^2}{2m} + V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$$

$$\begin{cases} 0 \leq x_i \leq L \\ 0 \leq y_i \leq L \\ 0 \leq z_i \leq L \end{cases} \dots$$

$$\omega(N, V, E) = \int_{0 \leq E \leq E} d\vec{r}^N d\vec{p}^N = \int d\vec{r}^N \int d\vec{p}^N$$

V^N

$0 \leq p_1^2 + p_2^2 + \dots + p_N^2 \leq 2mE$

$$\omega = V^N \cdot \frac{(\sqrt{2mE})^{3N} C^{3N/2}}{3N \text{ 3维的体积}}$$

3N-Dim
空间

$$\mathcal{L}(N, V, E) = \omega(N, V, E + \Delta E) - \omega(N, V, E)$$

$$\approx \left. \frac{\partial \omega}{\partial E} \right|_{N, V} dE = V^N \left(\frac{3N}{2} \right) \cdot 2m (2mE)^{\frac{3N-1}{2}} C^{3N/2} dE$$

Entropy

In Thermal Dynamics, $TdS = \partial Q$ what is heat?

1. Def: (Boltzmann Entropy)

$$S = K_B \ln \mathcal{L}(E, V, N)$$

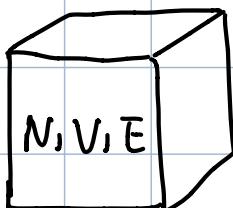
just an assumption

↑
dimension
universal

↑ number of microscopic states

Quantum Mechanical version. $S = k_B \ln W$

↑ # of degeneracy of E_L



E = total energy = internal energy.

$$S = K_B \ln \mathcal{L}$$

2. Combined 1st & 2nd laws of thermodynamics.

$$dU = \partial Q - dW + \mu dN$$

μ = chemical potential

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

pressure acting on the wall.

$$dS = T^{-1}dE + T^{-1}pdV - T^{-1}\mu dN$$

$$\downarrow \text{math: } F(x, y, z) = 0. \quad df = \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz$$

the definition of T : $T^{-1} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$

a derived quantity

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

Ideal gas: $N = CV^N E^{\frac{3}{2}N-1}$

$$S = k_B \ln N = k_B \ln C + k_B N \ln V + k_B \left(\frac{3}{2}N\right) \ln E$$

large N approximation

$$\Rightarrow \frac{\partial S}{\partial V} = \frac{k_B N}{V} \Rightarrow T^{-1}p = \frac{\partial S}{\partial V} = \frac{k_B N}{V} \Rightarrow pV = Nk_B T$$

$$= nRT$$

↑
gas constant
per molar gas

$$\Rightarrow R_N^{-1} = k_B$$

$$T^{-1} = \frac{3}{2}Nk_B \frac{1}{E} \Rightarrow E = \frac{3}{2}Nk_B T \text{ (ideal gas)}$$

$$\Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right) = \frac{3}{2}Nk_B$$

heat capacity

3. Entropy is an extensive thermal dynamics quantity

quantity } intensive 強度易 T. P. μ
 } extensive 幾度易 E. V. N. S

$$\text{Classical: } N = \int d\vec{r}^N d\vec{p}^N \cdot 1 = \int_{H(\vec{r}^{N_1}, \vec{p}^{N_1})} d\vec{r}^{N_1} d\vec{p}^{N_1} \cdot 1 \times \int_{H(\vec{r}^{N_2}, \vec{p}^{N_2})} d\vec{r}^{N_2} d\vec{p}^{N_2} \cdot 1$$

$$= N_1 \cdot N_2$$

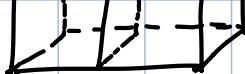
$$\Rightarrow S = S_1 + S_2$$

Quantum Mechanically: $W_L = W_1 W_2$



$$\Rightarrow S = S_1 + S_2$$

□

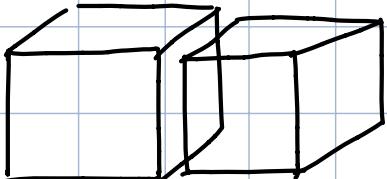


Thermodynamically : $T^{-1} = \left(\frac{\partial S}{\partial E} \right)_{V, N}$

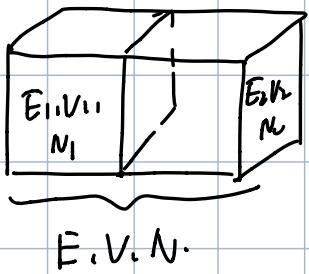
↑ intensive ↑ extensive

extensive (it must be !)

4. The 0th law of thermodynamics.



$$\text{thermal eq.} \Rightarrow T_1 = T_2$$



$$E_1 + E_2 = E = \text{fixed}$$

$$S = S_1(E_1, N_1, V_1) + S_2(E - E_1, N_2, V_2)$$

Second law: Thermal eq. \Rightarrow entropy = max

$$\text{i.e. } \frac{\partial S}{\partial E_1} = 0$$

$$\Rightarrow \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_1} = 0$$

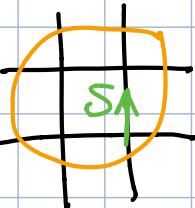
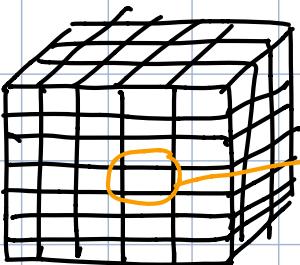
$$\Rightarrow \frac{\partial S_1}{\partial E_1} + \frac{\partial S_2}{\partial E_2} \frac{\partial(E - E_1)}{\partial E_1} = 0$$

$$\Rightarrow \frac{\partial S}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0$$

$$\Rightarrow T_1^{-1} = T_2^{-1} \Rightarrow T_1 = T_2$$

eg. lattice

B↑



spin $\frac{1}{2}$ system of N spins. S_i . $i=1, 2, \dots, N$

$$S_i = \pm 1$$

Energy of i^{th} spin $-\mu_B$ (for +)

$+\mu_B$ (for -)

↑
magnetic dipole moment

i.e. Energy of i^{th} spin $= -S_i \mu_B$

$$\begin{aligned} E_{\text{total}} &= -n\mu_B + (N-n)\mu_B \\ &= (N-2n)\mu_B \end{aligned}$$

if. n up
 $N-n$ down.

$E_{\text{given}} \Rightarrow n$ given (linearly)

degeneracy: $W_n = C_N^n = \# \text{ of different ways of selecting } n \text{-ups from } N \text{ spins.}$

$$= \binom{N}{n} = \frac{N!}{n!(N-n)!}$$

$$\ln W = \ln N! - \ln n! - \ln(N-n)!$$

$$\sim N \ln N - n \ln n - (N-n) \ln(N-n)$$

$$E = (N-2n)\mu_B$$

String approximation

$$\ln(N!) \sim N \ln N$$

$$T = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln W}{\partial E} = k_B \frac{\partial \ln W}{\partial n} \frac{\partial n}{\partial E}$$

$$= k_B (-\ln n - 1 + \ln(N-n) + 1) \cdot \left(-\frac{1}{2\mu_B}\right)$$

$$= -\frac{k_B}{2\mu_B} \ln \frac{N-n}{n}$$

$$\boxed{\frac{n}{N} = \frac{1}{e^{-2\mu_B/k_B T} + 1}}$$

Limiting cases: 1° $\mu_B \rightarrow \infty$, $n/N \rightarrow 1$, all spin up.

2° $\mu_B = 0$, $n/N = \frac{1}{2}$, half up half down

3° $k_B T / \mu_B \rightarrow \infty$, $n/N = \frac{1}{2}$, random arrangement

4° $T \rightarrow 0$, $k_B T / \mu_B \rightarrow 0$, $n/N \rightarrow 1$, all up

{going to have some quantum effect}

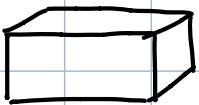
$$S = k_B [N \ln N - n \ln n - (N-n) \ln (N-n)]$$

$$\xrightarrow{T \rightarrow 0} k_B (N \ln N - n \ln n - 0) = 0$$

because no degeneracy

(Third law)

Isolated system



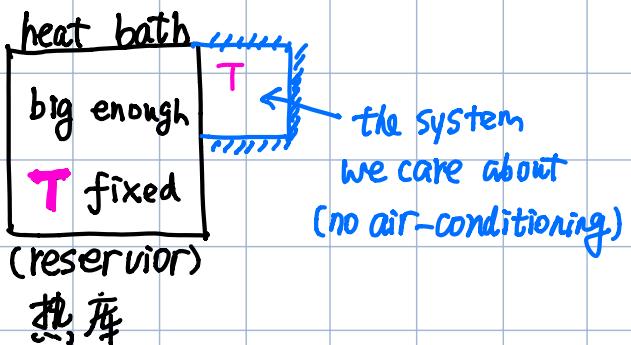
N,V,E fixed

equilibrium is the key to build the concept of temperature

"0th" law

Canonical Ensemble

1. Variables : V, N, T



assume the two systems together are
an isolated system.

1° combined system: isolated

goal : find $P_{ij}^n, f(\vec{r}^n, \vec{p}^n)$

$$E_{\text{total}} = E_{\text{system}} + E_{\text{bath}}$$

exchange

N,V remains the same.

2° $E_{\text{system}} \ll E_{\text{bath}}$

2. Derivation for a quantum mechanical system.

" i " sys \rightarrow quantum # of the system.

" i " bath \rightarrow quantum # of the bath

total: " i " \rightarrow " i "sys " i "bath

P_{sys}

known for the combined system.
(since it is isolated)

$$P_{\text{sys}} = \sum_{\substack{\text{"i"} \\ \text{"i" bath}}} P_{\text{sys "i" bath}} \quad \leftarrow \text{probability reduction}$$

we can set a probability of multivariable

$$\text{e.g. } P(a, h, g) = \sum_{h,g} P(a, h, g)$$

$$P_{\text{sys}} = \sum_{\substack{\text{"i" bath}}} \begin{cases} a & \text{if } E_{\text{sys "i" bath}} = E_L \leftarrow \text{fixed energy level of the combination} \\ 0, \text{others} & \end{cases}$$

$$E_{\text{bath}} = E_L - E_{\text{sys}}$$

$$P_{\text{sys}} = \sum_{\text{all "i" bath}} a, \text{ if } E_{\text{bath}} = E_L - E_{\text{sys}}$$

$$= aW$$

\uparrow # of degeneracy that $E_{\text{bath}} = E_L - E_{\text{sys}}$

$$k_B \ln P_{\text{sys}} = k_B (\ln a + \ln W(E_L - E_{\text{sys}})) \quad \text{Taylor expansion}$$

$$= C + \underbrace{k_B [\ln W(E_L) + \frac{\partial \ln W}{\partial E} (-E_{\text{sys}}) + \dots]}_{\text{still const}}$$

$$= C' + \frac{\partial (\ln W)}{\partial E} \Big|_{E=E_{\text{bath}}} (-E_{\text{sys}})$$

$$= C' + T^{-1} \Big|_{E=E_{\text{bath}}} (-E_{\text{sys}})$$

$$\Rightarrow \ln P_{\text{sys}} = C'' - \frac{1}{k_B T} E_{\text{sys}}$$

$$P_{\text{sys}} \propto e^{-\frac{1}{k_B T} E_{\text{sys}}} = e^{-\beta E_{\text{sys}}}$$

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

$$P_{\text{sys}} \propto e^{-\beta E_{\text{sys}}}$$

Boltzmann-Gibbs distribution

3. Classical [see Notes]

$$f(\vec{r}^N, \vec{p}^N) \propto e^{-\beta H(\vec{r}^N, \vec{p}^N)}$$

4. Normalization

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

$$1 = \sum_{\text{all } i} P_i = A \sum_i e^{-\beta E_i}$$

$$P_i = \frac{1}{Z} e^{-\beta E_i}$$

sometimes Q

\downarrow

define: $Z = \sum_i e^{-\beta E_i}$ (N, V)

partition function

$$Z = Z(\beta, N, V)$$

dimension less

Classical: $f(\vec{r}^N, \vec{p}^N) = A e^{-\beta H(\vec{r}^N, \vec{p}^N)}$

$$1 = \int f(\vec{r}^N, \vec{p}^N) d\vec{r}^N d\vec{p}^N = A \int d\vec{r}^N \vec{p}^N e^{-\beta H(\vec{r}^N, \vec{p}^N)}$$

$$Z(\beta, N, V) = \frac{1}{h^{3N}} \int d\vec{r}^N d\vec{p}^N \cdot e^{-\beta H(\vec{r}^N, \vec{p}^N)}$$

[h] = [xp]

5. Ensemble average of energy

$$\langle E \rangle_{QM} = \frac{1}{Z} \sum_{\text{all } i} E_i \cdot e^{-\beta E_i}$$

$$= \frac{1}{Z} \sum_{\text{all } i} -\frac{\partial e^{-\beta E_i}}{\partial \beta}$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left[\sum_i e^{-\beta E_i} \right]$$

$$\langle E \rangle_{QM} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} (\ln Z)$$

$$\text{Classical: } \langle E \rangle = \frac{1}{Z} \int d\vec{r}^N d\vec{p}^N H(\vec{r}^N, \vec{p}^N) e^{-\beta H} = -\frac{\partial}{\partial \beta} (\ln Z)$$

6. Calculation of $\langle (\Delta E)^2 \rangle$

E is no longer a fixed quantity

fluctuation?

$$E - \langle E \rangle \equiv \Delta E$$

$$\langle \Delta E \rangle = 0$$

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \rangle = \langle E^2 \rangle - 2\langle E \rangle \langle E \rangle + \langle E \rangle^2 \\ &= \frac{\langle E^2 \rangle - \langle E \rangle^2}{?} \end{aligned}$$

$$\frac{\partial \langle E \rangle}{\partial \beta} = + \frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)^2 - \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \langle E \rangle^2 - \langle E^2 \rangle \quad ??? \text{ 没推出来}$$

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = - \frac{\partial \langle E \rangle}{\partial \beta}$$

$$Z = \sum e^{-\beta E_i}$$

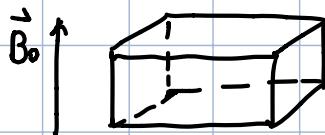
$$\frac{\partial^2 Z}{\partial \beta^2} = \frac{\sum E_i^2 e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \langle E^2 \rangle$$

$$-\frac{\partial \langle E \rangle}{\partial \beta} = - \frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\frac{\partial \langle E \rangle}{\partial T}}{C_V} = k_B T^2 C_V$$

$$C_V$$

Paramagnetic Systems 顺磁

1. Physical picture



paramagnetic

$$\vec{B} = \vec{B}_0 + 4\pi \vec{M} \quad (\text{Gaussian Units})$$

↑
magnetization

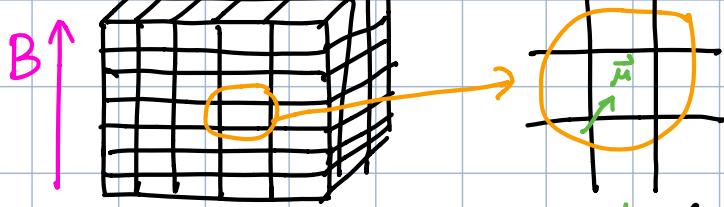
done by experiments $B_0 \uparrow, M \uparrow; B_0 = 0, M = 0;$

$$M = M(B_0) \quad (\text{direction: the same})$$

Now we get $M = M(B_0)$ by theoretical approach.

Model: Assumptions: ① solid lattice





- ② $\vec{\mu}_l$'s don't interact with each other.
 - ③ The dipoles are distinguishable.
(The direct consequence is that we can label them)
 - ④ dipoles (without B_0) can freely rotate.
-

What is a dipole moment?

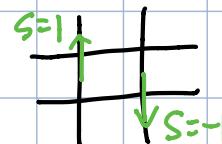
$$I \leftarrow \vec{n} \quad \vec{\mu} = I \vec{A}$$

Energy of a single dipole $E_l = -\vec{\mu} \cdot \vec{B}_0$
we want $\vec{\mu}$ to align with \vec{B}_0

Quantum Mechanics for spin- $\frac{1}{2}$ system.

$$E_l = -S_l \mu_B B_0 \quad S_l = \pm 1$$

Basic dipole moment



Energy of the system:

$$E_{\text{"i"}} = E(S_1, S_2, \dots, S_N) = -S_1(\mu_B B_0) - S_2(\mu_B B_0) - \dots - S_N(\mu_B B_0)$$

\downarrow
1st spin

$$= -\mu_B B_0 \sum_{l=1}^N S_l \quad \text{spin is the quantum number}$$

2. System's partition function

$$\begin{aligned} Z = \sum_{\text{"i"}} e^{-\beta E_{\text{"i"}}} &= \sum_{\substack{\uparrow \\ \text{All possible quantum states}}} e^{\beta(\mu_B B_0) \sum S_l} \\ &= \sum e^{\beta(\mu_B B_0) S_1} \cdot e^{\beta(\mu_B B_0) (S_2 + S_3 + \dots + S_N)} \\ &= \boxed{\sum e^{\beta(\mu_B B_0) S_1} \sum e^{\beta(\mu_B B_0) (S_2 + \dots + S_N)}} \end{aligned}$$

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

$$Z_1 = \sum_{S_1=\pm 1} e^{\beta \mu B_0 S_1} = e^{\beta \mu B_0} + e^{-\beta \mu B_0} = 2 \cosh(\beta \mu B_0)$$

one particle

$$Z = Z_1^N$$

- Average Energy of the System $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{N \partial \ln Z}{\partial \beta}$

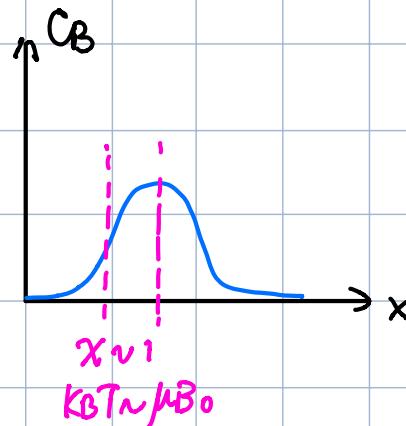
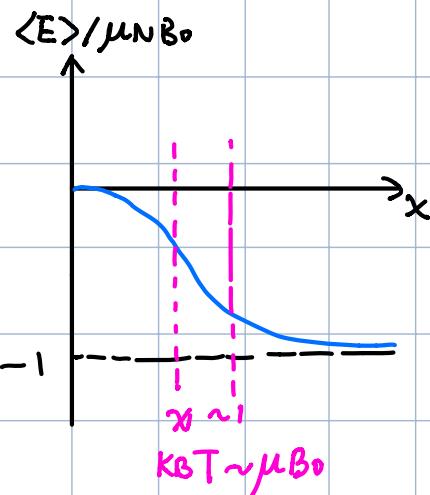
$$= -N \frac{\partial \ln Z_1}{\partial x} \frac{\partial x}{\partial \beta} \quad (x = \beta \mu B_0)$$

$$= -N \frac{2}{Z} \sinh(\beta \mu B_0) \cdot \mu B_0$$

$$= -N \mu B_0 \tanh(\beta \mu B_0)$$

$$\langle M \rangle = \langle S_1 + S_2 + \dots + S_N \rangle \mu = -\frac{\langle E \rangle}{B_0} = N \mu \tanh(\beta \mu B_0)$$

what's this M ? $-MB_0 = E$



$x = \mu B_0 / k_B T$	μB_0	$k_B T$	$\langle E \rangle = -N \mu B_0 \tanh x$	$\langle M \rangle$	C_B
large x	All spin will be forced to point up	\downarrow	$-\mu B_0 N$	μN	0
small x	spin: be themselves	\uparrow	0	0	0

C_B : heat capacity with B_0 fixed $C_B = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial x} \frac{\partial x}{\partial T} = -\frac{\partial \langle E \rangle}{\partial x} \frac{\mu B_0}{k_B T^2}$

canonical: $\langle E \rangle = -\mu N B_0 \tanh(x) = -\mu N B_0 \frac{e^{-2x} - 1}{e^{-2x} + 1}$ calculated fixed T . distribution $\rightarrow \beta \rightarrow x$ $\langle (\Delta E)^2 \rangle \neq 0$

$$\text{microcanonical: } \langle E \rangle = \mu N k_B \frac{e^{-\beta E}}{e^{-\beta E} + 1} \quad \beta = \mu k_B / k_B T \quad \text{we got } T \text{ from the entropy } S$$

$$\langle \Delta E \rangle^2 = 0$$

At the level of fixed average.

No matter the way we do the statistics,
The physics doesn't change.

$$\text{Microcanonical: } P_i \rightarrow S = k_B \ln W \rightarrow \text{All (Thermodynamics)}$$

$$\text{Canonical: } P_i \rightarrow ? ? ? \text{ Bridge} \rightarrow \text{All (Thermodynamics)}$$

for microcanonical only

bridge (Based on Boltzmann's definition)

Thermodynamics (Review or Preview)

1. Entropy redefined

$$\text{General Def: } S = -k_B \sum P_i \ln P_i \quad (\text{general definition})$$

$$\text{Homework: if we use } P_i \text{ (microcanonical)} = \begin{cases} 1/Z, & \text{if } \dots \\ 0, & \text{otherwise} \end{cases} \quad (*),$$

then $S = k_B \ln Z$ is recovered.

$$\text{Now in canonical ensemble, } S = k_B \ln Z + \langle E \rangle / T$$

$$\text{Pf: } P_i = \frac{1}{Z} e^{-\beta E_i} \Rightarrow \ln P_i = -\ln Z - \beta E_i$$

$$\text{According to } (*), \quad S = -k_B [\sum -P_i \ln Z + \sum P_i (-\beta E_i)]$$

$$\text{which one?} \quad = k_B \ln Z + \frac{1}{T} \sum P_i E_i = k_B \ln Z + \frac{\langle E \rangle}{T}$$

2. Thermodynamics

$$1^{\text{st}} + 2^{\text{nd}} \text{ laws: } dU = TdS - pdV + \mu dN$$

internal energy chemical potential variation
 ↓ ↗
 heat transfer work done

$$dS = T^{-1} dU + p dV - \mu dN \quad (\text{just rewrite})$$

$$\text{microcanonical: } U = E, \quad V, N \text{ variables}$$

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