phase space :

eg. one particle : six-dim

property : 1° track of different particles don't in intersect.

2° Liouville

ensemble theory :

Hypothesis :

① ergodic hypothesis : (L. Boltzmann 1871)

Condition : isolated system. any initial state time long enough

result : go through any possible microstate

time average = statistical average

② equal probability

Condition : equilibrium state

result : equal probability of all microstates

ensemble :

purpose : to avoid solving hamiltonian equation of 10^{23} particles

method : $\underbrace{A_{宏}(t) = \frac{1}{\tau}\int_{t}^{t+\tau} A_{微}(t')\,dt'}_{\text{time average}}$ to statistical average over

mechanical rules to statistical rules.

an ensemble.

ensemble :

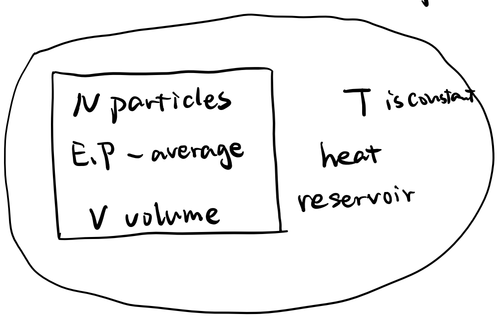
1. M systems with same macroscopically constrained parameters (E, V, N)
2. with different microstates , each represents a point in phase space
3. all points in same plane with same energy

Common ensembles (different constrain) :

systems with different restrictions bound with different heat reservoir to build isolated systems.

① canonical ensemble NVT.

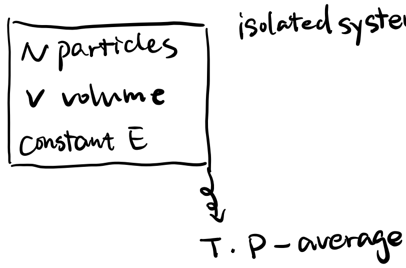
- classical representation of monte carlo simulation.



characteristic function :
F (N, V, T)

② micro - canonical ensemble NVE

- used in molecular dynamics simulation



isolated system (no energy nor particle exchange)

characteristic function :
S (N, V, E)

③ constant - pressure constant - temperature ensemble NPT or T-P ensemble.

N particle
P pressure
T temperature

movable wall
Constant T

monte carlo simulation E. V -

characteristic function : G(N. P. T)

④ grand canonical ensemble VTμ Monte carlo simulation

E. P. N — average E. N. μ exchange

characteristic function : J(μ, V, T)

Choice of ensemble

X choice of fluctuation anyone

④ is most common

① micro-canonical ensemble :

- independent. identical. localized particles
- every particle only two different possible states.
  eg. ferromagnetic . paramagnetic model.

② canonical when micro-canonical is hard to solve

③ grand canonical in replace of canonical

Classical statistical ensemble (density function) :

- Integrate $D(q, p, t)$ over the whole space = the number of particles
- $\frac{\partial D}{\partial t} + \{D, H\} = 0 \Rightarrow D(q_i, p_i, t_i) = D(q_{i+1}, p_{i+1}, t_{i+1})$

if in equilibrium , $D(q, p, t) = D(q, p)$

Quantum case:

N $|\psi\rangle$ ensemble

expectation$(F(A))$ = $\mathrm{tr}(\rho F(A))$

if in $|\psi\rangle$ with probability p and in $|\phi\rangle$ with probability $1-p$,

then $\rho = p|\psi\rangle\langle\psi| + (1-p)|\phi\rangle\langle\phi|$

eg. For non-polarization light, density matrix is

$$\rho = \frac{1}{2}|R\rangle\langle R| + \frac{1}{2}|L\rangle\langle L|$$

Definition:

for finite-dimensional space, density matrix is:

$$\rho = \sum_j p_j |\psi_j\rangle\langle\psi_j|$$

by $|1\rangle, \dots, |k\rangle$ and $p_j \Rightarrow \rho = |i\rangle\langle i|$

$\not\Leftarrow$

- different mixture can form same density matrix
- cannot be differentiate by observables.
- $\Leftrightarrow$ there exist $U^*U = I$ and $|\psi_i'\rangle\sqrt{p_i'} = \sum_j u_{ij}|\psi_j\rangle\sqrt{p_j}$

pure $\Leftrightarrow$ $\rho^2 = \rho$

geometry: when ρ can not be represented as a convex combination, it's a pure state; ... can , ... mix

pure states are convex set's extreme points.

$$\rho = \sum_i p_j |\psi_j\rangle\langle\psi_j|$$

$$\langle A\rangle = tr(\rho A)$$

$$A = \sum_i a_i |a_i\rangle\langle a_i| = \sum_i a_i P_i$$

after measurement : $\rho' = \sum_i P_i \rho P_i$

$$\rho_i' = \frac{P_i \rho P_i}{tr[\rho P_i]}$$

$$\rho = \sum_i p_j |\psi_j\rangle\langle\psi_j| \longrightarrow \rho = \sum_i \lambda_i |\varphi_i\rangle\langle\varphi_i| \quad |\varphi_i\rangle \text{ orthonormal}$$

$$S = -\sum_i \lambda_i \ln \lambda_i = -tr(\rho \ln \rho)$$

or $S = H(p_i) + \sum_i p_i S(\rho_i)$

ρ_i : orthonormal $\Rightarrow H(p)$: shannon entropy

time-evolving :

$$i\hbar \frac{d\rho}{dt} = \sum p_i H |\psi_i\rangle\langle\psi_i| - \sum p_i |\psi_i\rangle\langle\psi_i| H = [H, \rho]$$

Quantum Liouville , Moyal's equation :

wigner picture :

$$W(x,p) \stackrel{def}{=} \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \psi^*(x+y)\, \psi(x-y)\, e^{2ipy/\hbar}\, dy$$

time - evolving :

$$\frac{\partial W(q,p,t)}{\partial t} = -\{\{ W(q,p,t), H(q,p) \}\}$$

Paramagnetism

eg. ① atoms or molecules with odd number. (total spin $\neq 0$)

② has electronic shell that's not full

Langevine paramagnetism

- paramagnetic substance with inherent magnetic moment of μ_J
- without interaction
- magnetic moments in chaos in equilibrium without outside field.

$$E_I = -\mu_J \cdot H = -\mu_J H \cos\theta_i$$

N atoms in unit volume. by H, μ_J's distribution of angle relative to H obey Boltzmann statistical distribution, the system's distribution function:

$$Z(H) = \left[\int_0^{2\pi} d\varphi \int_0^{\pi} e^{\mu_J H \cos\theta / k_B T} \sin\theta \, d\theta \right]^N$$

$$= \left[\frac{4\pi k_B T}{\mu_J H} \operatorname{sh}\left(\frac{\mu_J H}{k_B T} \right) \right]^N$$

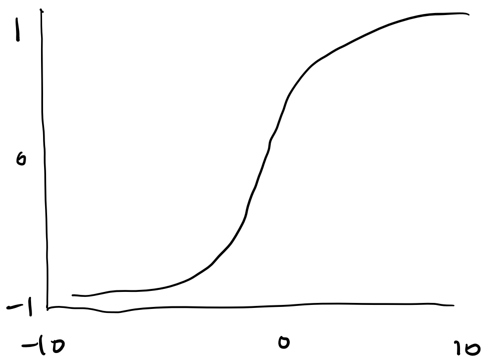
$F = \phi = -k_B T \ln Z(H)$ and $M = -\left(\frac{\partial \phi}{\partial H} \right)_{T,P} = -\left(\frac{\partial F}{\partial H} \right)_{T,P}$

$$\therefore \ln Z(H) = N \ln \left[\frac{4\pi k_B T}{\mu_J H} \operatorname{sh}\left(\frac{\mu_J H}{k_B T} \right) \right]$$

$$\therefore \frac{\partial \ln Z(H)}{\partial H} = N \frac{\frac{4\pi k_B T}{\mu_J H} \cdot \frac{\mu_J}{k_B T} \operatorname{ch}\left(\frac{\mu_J H}{k_B T} \right) - \frac{4\pi k_B T}{\mu_J H^2} \operatorname{sh}\left(\frac{\mu_J H}{k_B T} \right)}{\frac{4\pi k_B T}{\mu_J H} \operatorname{sh}\left(\frac{\mu_J H}{k_B T} \right)}$$

$$= \frac{N \mu_J}{k_B T} \left[\operatorname{cth}\left(\frac{\mu_J H}{k_B T} \right) - \frac{k_B T}{\mu_J H} \right]$$

Langevine function : $L(x) = \coth(x) - \frac{1}{x} L(x)$



$$\therefore M = k_B T \frac{\partial}{\partial H}\left[\ln Z(H)\right]$$

$$= N\mu_J \left[\operatorname{cth}\left(\frac{\mu_J H}{k_B T}\right) - \frac{k_B T}{\mu_J H} \right]$$

$$\alpha = \mu_J H / k_B T$$

$$\Rightarrow M = N \mu_J L(\alpha)$$

$$L(\alpha) = \operatorname{cth}\alpha - \frac{1}{\alpha} \rightarrow \text{Langevine function}$$

two cases :

1. High T :

$$k_B T \gg \mu_J H, \ \alpha \ll 1$$

then $\operatorname{cth}\alpha = \dfrac{e^{\alpha}+e^{-\alpha}}{e^{\alpha}-e^{-\alpha}} = \dfrac{1}{\alpha} + \dfrac{\alpha}{3} - \dfrac{\alpha^2}{45} + \cdots \approx \dfrac{1}{\alpha} + \dfrac{\alpha}{3}$

$$\therefore L(\alpha) = \frac{\alpha}{3}$$

$$\therefore M = \frac{N\mu_J \alpha}{3} = \frac{N\mu_J^2 H}{3k_B T}$$

also $\because \mu_J = g_J \sqrt{J(J+1)}\,\mu_B$

$$\therefore M = \frac{N g_J^2 H}{3k_B T} J(J+1)\mu_B^2$$

$$\therefore \chi_p = \frac{M}{H} = \frac{N\mu_J^2}{3k_BT} = \frac{C}{T}$$

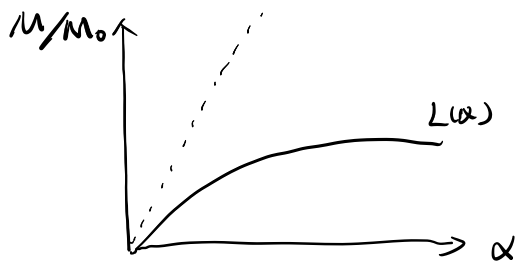
then $\chi_p = \frac{C}{T}$

$$C = \frac{N\mu_J^2}{3k_B} = \frac{N}{3k_B} g_J^2 J(J+1)\mu_B^2$$

2. low T :

$k_BT \ll \mu_J H$, $\alpha \gg 1$, $\coth\alpha \to 1$, $L(\alpha) \to 1$

$\therefore M = N\mu_J = M_0$



Correction on Langevine function — brillouin function :

- magnetic moment's spatial orientation is quantized

Let $\alpha' = m_J g_J \vec{\mu}_B \cdot \vec{H}/k_BT = \mu_z H/k_BT$,

$\mu_z = [(\mu_J)_H]_{max} = J g_J \mu_B$

let $x = g_J \mu_B H/k_BT$

then $Z(H) = \left(\sum_{m_J=-J}^{J} e^{m_J x}\right)^N$

$$\therefore M = k_BT \frac{\partial}{\partial H} \ln Z(H) = Nk_BT \frac{\partial}{\partial H}\left(\sum_{m_J=-J}^{J} e^{m_J x}\right)$$

$$= Nk_BT \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x} \cdot \frac{g_J \mu_B}{k_BT}}{\sum_{m_J=-J}^{J} e^{m_J x}} = Ng_J\mu_B \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x}}{\sum_{m_J=-J}^{J} e^{m_J x}}$$

and $\sum_{m_J=-J}^{J} A^{m_J} = A^{-J}\left(1+A+A^2+\cdots\cdots+A^{2J}\right) = \frac{A^{-J}-A^{J+1}}{1-A}$

let $A = e^x$:

$$\sum_{m_J=-J}^{J} e^{m_J x} = e^{-Jx}\left(1+e^x+e^{2x}+\cdots+e^{2Jx}\right)$$

$$= \frac{e^{-Jx}-e^{(J+1)x}}{1-e^x}$$

$$= \frac{e^{-(J+\frac{1}{2})x}-e^{(J+\frac{1}{2})x}}{e^{-\frac{1}{2}x}-e^{\frac{1}{2}x}} = \frac{sh\left[(J+\frac{1}{2})x\right]}{sh(\frac{1}{2}x)}$$

$$\sum_{m_J=-J}^{J} m_J e^{m_J x} = \frac{d}{dx}\left(\sum_{m_J=-J}^{J} e^{m_J x}\right) = \frac{d}{dx}\left(\frac{sh\left[(J+\frac{1}{2})x\right]}{sh(\frac{1}{2}x)}\right)$$

$$= \frac{\left\{(J+\frac{1}{2})\, ch\left[(J+\frac{1}{2})x\right] sh(\frac{1}{2}x) - \frac{1}{2}\, sh\left[(J+\frac{1}{2})x\right] ch(\frac{1}{2}x)\right\}}{sh^2(\frac{1}{2}x)}$$

$$\therefore \frac{\sum_{m_J=-J}^{J} m_J e^{m_J x}}{\sum_{m_J=-J}^{J} e^{m_J x}} = (J+\tfrac{1}{2})\, cth\left[(J+\tfrac{1}{2})x\right] - \tfrac{1}{2}\, cth(\tfrac{1}{2}x)$$

$\because x = \frac{\alpha'}{J}$ then : $M = NJ g_J \mu_B\left[\frac{2J+1}{2J}\, cth\left(\frac{2J+1}{2J}\alpha'\right) - \frac{1}{2J}\, cth\frac{\alpha'}{2J}\right]$

let $B_J(\alpha') = \frac{2J+1}{2J}\, cth\left(\frac{2J+1}{2J}\alpha'\right) - \frac{1}{2J}\, cth\frac{\alpha'}{2J}$, $\mu_z = J g_J \mu_B$

$\therefore M = N\mu_z B_J(\alpha')$, $B_J(\alpha')$ is then called brillouin function

for high T (feeble field) :

$\mu_z H \ll k_B T$, $\alpha' \ll 1$

$$B_J(\alpha') = \frac{2J+1}{2J}\left(\frac{2J}{2J+1}\cdot\frac{1}{\alpha'} + \frac{1}{3}\cdot\frac{2J+1}{2J}\alpha'\right) - \frac{1}{2J}\left(\frac{2J}{\alpha'} + \frac{\alpha'}{6J}\right)$$

$$= \frac{(2J+1)^2\alpha'}{12J^2} - \frac{\alpha'}{12J^2} = \frac{J+1}{3J}\alpha'$$

$$\therefore M = N\mu_z \frac{J+1}{3J}\alpha'$$

$$= N g_J^2 J(J+1)\mu_B^2 \cdot \frac{H}{3k_BT}$$

$$= \frac{C}{T}H$$

$$\therefore \chi_p = \frac{M}{H} = \frac{C}{T}$$

$$C = N g_J^2 J(J+1)\mu_B^2/3k_B = N\mu_z^2/3k_B$$

$\mu_z H \gg k_BT$, $\alpha' \gg 1$, $B_J(\alpha') \to 1$

$$\therefore M = N\mu_z$$

$$= N g_J J \mu_B = M_0$$

if $J \to \infty$, $B_J(\alpha') = L(\alpha)$