Course 2 Basic postulates and concepts in thermodynamics

(1) Isolated system – basic postulate : equal a priori probability
- equilibrium
- reversible / irreversible process

(2) Composite system (Thermal contact : reservoir, temperature, heat
Mechanical " : generalized force, work
quasi static process
entropy

(3) Thermodynamic laws

*(4) Others

*: Skip : Heat capacity (chaps. 4-5)

$$C_y \underset{\delta T \to 0}{=} \left(\frac{dQ}{dT}\right)_y = C_y(T, y)$$

Maxwell relation

$$dQ = TdS = dE + pdV$$

indep. two variable

$(S, V) \rightarrow dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right) dV$

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

$(S, P) \rightarrow$ enthalpy $H \equiv E + pV = H(S, P)$

$(T, V) \rightarrow$ Helmholtz free energy $F = E - TS = F(T, V)$

$(T, P) \rightarrow$ Gibbs free energy $G = E - TS + pV = G(T, P)$

(1) Isolated system

① state ; quantum mechanics : $\psi(n_1, \cdots, n_f)$

$n_i \sim$ quantum number

classical — : eg. cell of phase space

$$\delta q\, \delta p = h_0 \quad , \quad h_0 \to 0$$

$$\delta q_1 \cdots \delta q_f\, \delta p_1 \cdots \delta p_f = (h_0)^f$$

(cf) $\delta q\, \delta p \geq \hbar$

> $f \sim$ total # of degrees of freedom
> (independent coordinates)

(ex) a particle in a rectangular box (L_x, L_y, L_z)

$$\psi \sim \sin\frac{\pi n_x x}{L_x} \sin\frac{\pi n_y y}{L_y} \sin\frac{\pi n_z z}{L_z}$$

$$E(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

$$\rightsquigarrow \psi_{n_x, n_y, n_z}(x, y, z)$$

(ex2) three spins : $n_i = \pm\frac{1}{2}$, $i = 1, 2, 3$

(ex3) N classical particles in three dimension : $f = 3N$

② Statistical ensemble and accessible states

To discuss a system in terms of probability concepts,

we need ~~its~~ ensemble rather than its full dynamics.

(ex) three spins ⊕ magnetic field H

(+, +, +) } $E = -3\mu H$

(+, +, −) }
(+, −, +) } $-\mu H$
(−, +, +) }

(+, −, −) }
(−, +, −) } μH
(−, −, +) }

(−, −, −) $3\mu H$

accessible states

if the total energy is $-\mu H$.

(Other restriction on total (angular) momentum ...)

∴ total energy conservation in isolated systems

⊙ Equilibrium

In equilibrium, the probability of finding a given (isolated) system in any one state (thus its all macroscopic parameter) is independent of time.

⊙ Postulate of equal a priori probabilities

An isolated system in equilibrium is equally likely to be in any of its accessible states.

(ex) ~~three~~ three spins with energy $-\mu H$

- The laws of mechanics do not prefer any one among accessible states.
- Once one achieves the situation of equal a priori probabilities, it remains forever. (∵ Louville th.)

microcanonical ensemble

P_r (probability of finding a given system in state r)

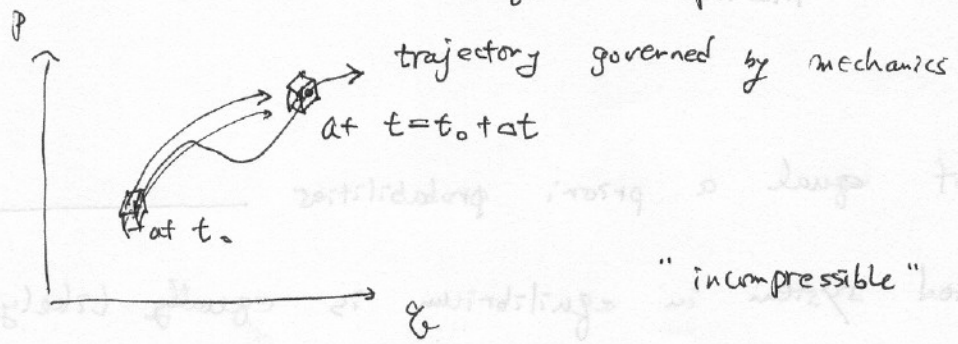
$$= \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

·※· Liouville th.

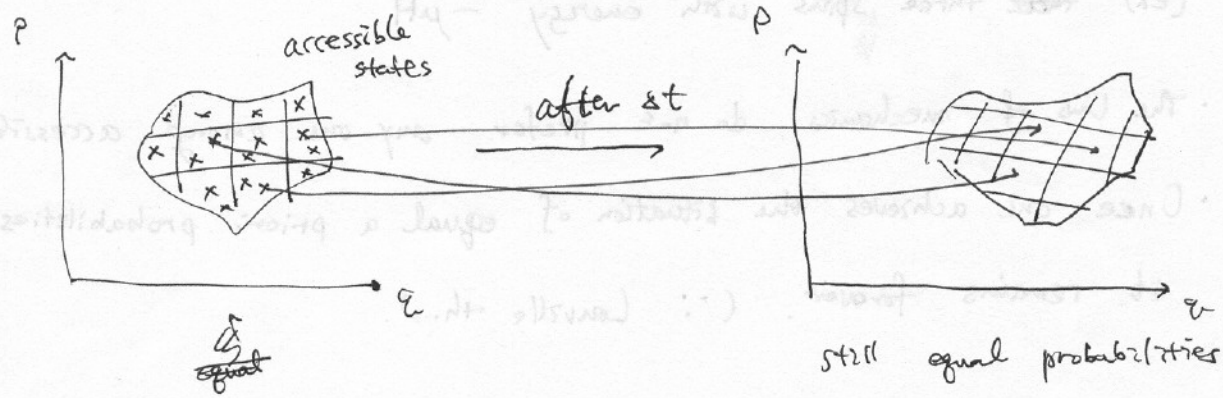
classical mechanics : the conservation of phase space density ρ.

(ensemble distributions in phase space)

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$$



If we start the situation of equal a priori probabilities,



Q.M. density matrix $\hat{\rho}$

$$i\hbar \frac{d\hat{\rho}}{dt} = [H, \hat{\rho}].$$

(∵ ensemble density is conserved at each modified cells)

Skip

·※· Ergodic hypothesis / theorem. → kinetic th. / irreversible process.

(Under some conditions) If one waits a sufficiently long time, the state of a given system will cover the entire accessible phase space.

(classical chaos, random impurities)

~~※ ergodic theory~~.

$\langle f \rangle_{time} = \langle f \rangle_{ensemble}$

⇒ The system is ergodic

Ergodic system

→ it ~~spen~~ spend equal times in equal areas of the energy surface.

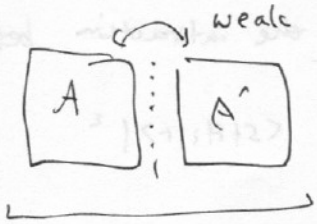
consistent with equal a priori probability.

① Non equilibrium ⟶ equilibrium

※ note first what the ~~state~~ we are dealing is :

- It is not an exact eigenstate. (We can not solve it for the system with huge # of degrees of freedom.)
- instead, we have interested in "approximate" quantum states.

(eg. 1)



(eg. 2) particles in a volume ⊕ weak interactin between them.

Start with a statistical ensemble where the systems are initially distributed over ~~their accessible s~~ only in some particular subset of accessible states.

↓ time evolution with transitins between accessible states due to the weak interaction.

The transitin rate (relaxatin time) depends on the detailed nature of the interactions.

Equilibrium situation

→ Another important hypothesis

(cf) H theorem — it tries to explain this hypothesis on microscopic basis.

→ it can not cover all cases (subjected to some assumption)

eg. Markov processes

(The future of the system is ~~exist~~ determined entirely by its present state, and not by its past.)

- $H \leftrightarrow -S$ (entropy x-1)

For H theorem,

One can read chapter 1.9.5 (pages 40 - 43) of the book

"statistical thermophysics" by Harry S. Robertson.

H theorem: (skip at this moment)

$P_r(t)$: probability that the system is at the state r.

$$\sum_r P_r(t) = 1$$

$W_{r\to s}$: transition rate due to the interaction bet. particles

$$W_{r\to s} = W_{s\to r} \quad ; \quad W_{r\to s} \propto |\langle s|H_i|r\rangle|^2$$

$$\frac{dP_r}{dt} = \sum_s P_s W_{sr} - P_r W_{rs}$$

~~density matrix~~

rate eq. (master eq.)

~it is basically assumed that the transition process is Markov process.

(ignoring previous history of scatter

(derivation of master eq.

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{\mathcal{H}}, \hat{\rho}]$$ ⊕ markov ⊗ perturbation)

$$H \equiv \overline{\ln P_r} \equiv \sum_r P_r \ln P_r$$

Then one can show $\frac{dH}{dt} \le 0 \Rightarrow$ H theorem.

$$\left(\because \frac{dH}{dt} = \sum_r \frac{dP_r}{dt}(\ln P_r + 1) = \sum_r \sum_s W_{rs}(P_s - P_r)(\ln P_r + 1)\right.$$

↓ (r↔s)

$$= -\frac{1}{2}\sum_{r,s} W_{rs}\underbrace{(P_r - P_s)(\ln P_r - \ln P_s)}_{\ge 0}$$

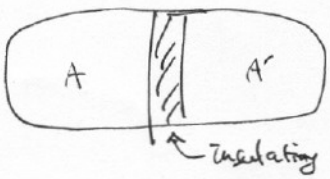
$$\Rightarrow \frac{dH}{dt} \le 0 \leftrightarrow \text{entropy} \propto H \quad . \quad \frac{dS}{dt} \ge 0$$

$$\left(\frac{dH}{dt} = 0 \leftrightarrow \text{the postulate of equal a priori probabilities.}\right.$$

① Equilibrium condition and irreversible processes

$\Omega(y_1, y_2, \cdots, y_n)$: # of accessible states subjected to a set of constraints $\{y_i\}$

eg. $y_i \sim$ volume. energy of subsystem.



$\{y_i\} \ni E_A, E_{A'}$

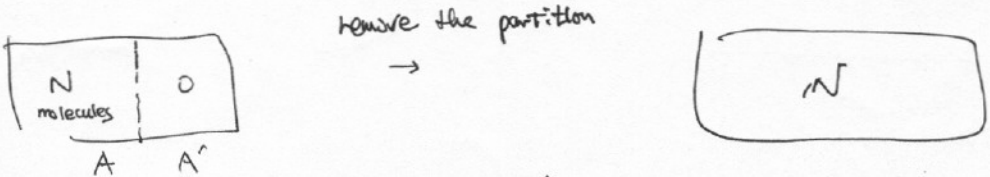
Start with Ω_i accessible states. And then, remove some constraints

$\Rightarrow$ the resulty # of accessible states, Ω_f. is larger than Ω_i.

$\Rightarrow$ not an equilibrium.

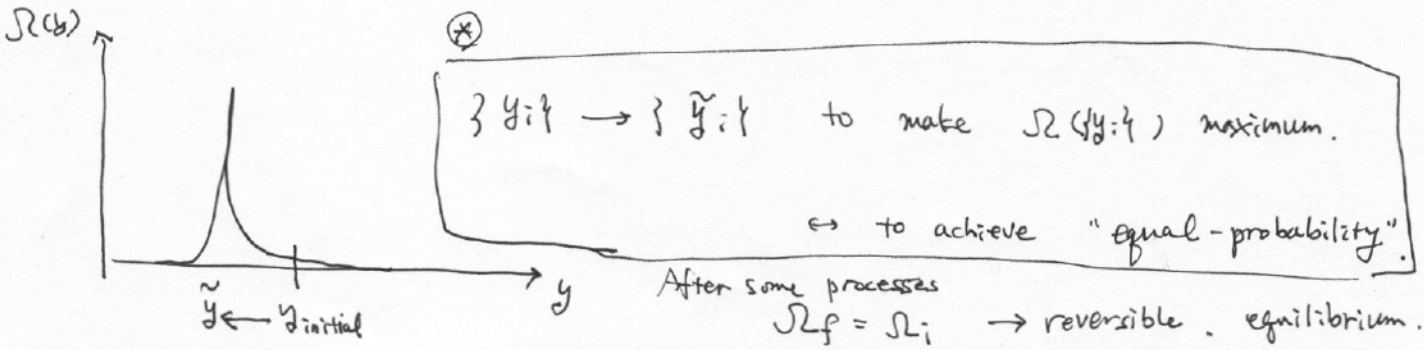
$\Rightarrow$ equally distributed over the Ω_f states.

eg.



$$\frac{\Omega_i}{\Omega_f} = \left(\frac{V_A}{V_A + V_{A'}}\right)^N \ll 1 \quad \text{if } N \to \infty$$

The removal of some constraints allows the chage of correspondig parameter y_i's.



• Quasi-static process :

A system interacts with environments in a process.

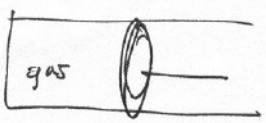
The process is carried out so slowly that the system remains arbitrarily close to equilibrium at all stage of process.

(characteristic time scale of process t_{ch}.

relaxation time τ

$$t_{ch} \gg \tau$$

(ex)



The piston is withdrawn very slowly.

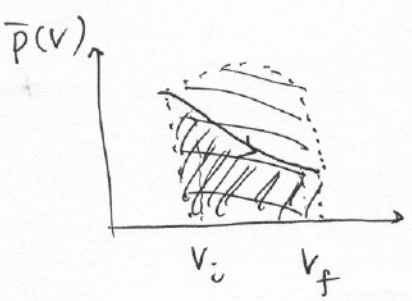
$$\Rightarrow \quad đW_r = \sum_{\alpha=1}^{n} X_{\alpha,r}\, dx_\alpha \qquad X_{\alpha,r} \equiv -\frac{\partial E_r}{\partial x_\alpha}$$

$$\Downarrow$$ quasi-static $\Rightarrow$ We can use mean values!

$$đW = \sum_{\alpha=1}^{n} \bar{X}_\alpha\, dx_\alpha$$

$\bar{X}_\alpha$: mean generalized force conjugate to x_α.

(ex) $đW = p\,dV$



$$W_{if} = \int_{V_i}^{V_f} \bar{p}\, dV$$

~ depends on the path.

(inexact differential)