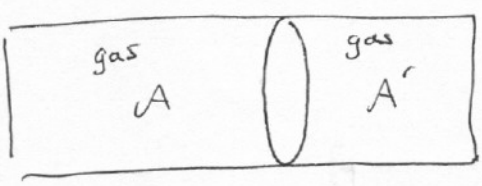
(2) Composite system



a. The piston is thermally insulating and has a fixed position.

→ A and A' do not interact

b. not insulating but fixed ~ purely thermal interaction

c. not fixed but insulating ~ " mechanical "

d not insulating nor fixed ~ both thermal and mechanical

$$\Delta \bar{E} = Q - W$$

$\Delta \bar{E}$: mean energy change due to interaction

Q : mean energy transfer from environment to the system due to pure thermal.
("heat absorbed")

W : work done by system.

$W = -\Delta_x \bar{E}$. $\Delta_x \bar{E}$: energy change due to the change of external parameters.

$$\Rightarrow \quad đQ \equiv d\bar{E} + đW$$

※ exact differential $d\bar{E}$. (see problem 2.5)

vs

inexact differential $đW_{i \to f}$ ~ it is not the difference between two numbers characterizing the two neighboring state but an infinitesimal quantity characterizing the process from i to f.

$đQ = d\bar{E} + đW$

① $đQ = 0$ (adiabatic) ⇒ W_{if} ~ indep. of the path

② $đW = 0$ (no work) ⇒ $đQ$ becomes exact differential

◎ Thermal interaction between macroscopic systems : temperature and entropy

$A^{(0)} \equiv A + A'$

isolated total

$\downarrow \quad \downarrow$

$E^{(0)} = E + E'$

Assumption
(※ the interaction U is neglected. $U \ll E, E'$)

$\underline{\Omega^{(0)}(E^{(0)}) = \Omega(E) \times \Omega'(E')}$

$\Rightarrow \quad \Omega^{(0)}(E) = \Omega(E)\,\Omega'(E^{(0)} - E)$

$P(E)$: probability of finding $A^{(0)}$ in the configuration where $E \in [E, E+\delta E]$

$\rightarrow \quad P(E) = C\,\Omega^{(0)}(E) = \dfrac{\Omega^{(0)}(E)}{\Omega^{(0)}_{tot}}$

$\boxed{\Omega^{(0)}_{tot} = \sum_E \Omega^{(0)}(E) \text{ restricted by total energy } = E^{(0)}}$

(∵ postulate of equal a priori probability.)

$\Rightarrow P(E) = C\,\Omega(E)\,\Omega'(E^{(0)} - E)$

※ $\Omega(E)$ ~ rapidly increasing with E

$\Omega(E) \sim E^f$ $\quad f$: # of degrees of freedom.

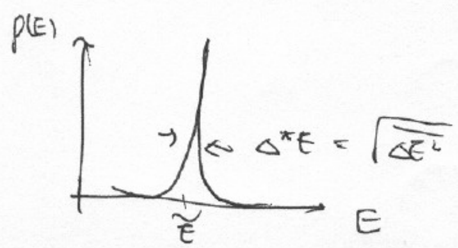
(∵ $\Omega(E) \sim \prod_{i=1}^{f} \Omega_i(E)$, $\Omega_i(E) \sim E$

(eg) $E = \sum_i \dfrac{p_i^2}{2m} \rightarrow |\vec{p}| \sim \sqrt{E}$

$\Rightarrow$ total # of state below E $\propto (\sqrt{E})^f$

$\Rightarrow \Omega(E) \propto \dfrac{d}{dE}(\sqrt{E})^f \sim E^f$ roughly)

$\Rightarrow P(E)$ has a very sharp maximum.



$\dfrac{\Delta^* E}{\tilde{E}} \sim \dfrac{1}{\sqrt{f}}$ $\quad$ (see ~~p. 110~~) Section 3.7

At equilibrium, $E \to \tilde{E}$.

$$\Rightarrow \left.\frac{\partial \ln P}{\partial E}\right|_{\tilde{E}} = 0$$

$$\Rightarrow \frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E} = \frac{\partial \ln \Omega(E)}{\partial E} - \frac{\partial \ln \Omega'(E')}{\partial E'} = 0.$$

(*)

$$\beta(E) \equiv \left.\frac{\partial \ln \Omega}{\partial E}\right|_{\tilde{E}}, \qquad \boxed{\beta(\tilde{E}) = \beta'(\tilde{E}')} \text{ at equilibrium.}$$

$$S \equiv k \ln \Omega \qquad\qquad \equiv \quad S + S' = \text{maximum}$$

$$kT \equiv \frac{1}{\beta} \qquad\qquad \equiv \quad T = T'$$

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

$\Delta S + \Delta S' \geq 0 \Rightarrow (\beta_i - \beta_i')Q \geq 0 \Rightarrow \boxed{T_i < T_i' \to Q > 0}$

※ $Q \equiv \bar{E}_f - \bar{E}_i$ $\qquad$ (~~...~~) $Q + Q' = 0$ during the relaxation process.

$\equiv$

※ $\bar{E} \approx \tilde{E}$ due to the sharpness of $P(E)$ $\qquad$ $\bar{E}_i + \bar{E}_i' = \bar{E}_f + \bar{E}_f'$: energy conservation

※ β ~ can be used as a thermometric parameter

$\because$ $\beta = \beta'$ at equilibrium.

$\Rightarrow T \equiv (k\beta)^{-1}$ ~ absolute temperature

※ T ~ a rough measure of the mean energy above the ground energy per degrees of freedom.

$$\Omega(E) \propto E^f \Rightarrow kT \simeq \frac{\bar{E}}{f}$$

⊙ Thermal reservoir A' $(f' \gg f)$

$$\Rightarrow \left|\frac{\partial \beta'}{\partial E'} Q'\right| \ll \beta' \Rightarrow \beta' \text{ does not change, irrespective of any amount of heat } Q' \text{ absorbed from the smaller system } A.$$

$$\Delta S' = k\left(\ln \Omega'(E' + Q') - \ln \Omega'(E')\right) \simeq k\beta' Q' \Rightarrow \Delta S' = \frac{Q'}{T'}$$

① Thermal reservoir A' (= heat bath)

The temperature parameter A' does not change irrespective of any amount of heat Q' from A

$$\Leftrightarrow \quad \underbrace{\left|\frac{\partial\beta'}{\partial E'} Q'\right|}_{\lesssim \frac{\beta' \bar{E}}{\bar{E}'}} \ll \beta'$$

$$\frac{\beta' \bar{E}}{\bar{E}'} \ll \beta' \Rightarrow \boxed{\bar{E} \ll \bar{E}'}$$

※ Entropy change of heat bath due to Q' from A

$$\Delta S' = k\left(\ln \Omega'(E' + Q') - \ln\Omega'(E')\right)$$

$$= k\left(\beta' Q' + \frac{1}{2}\frac{\partial\beta'}{\partial E'} Q'^2 + \cdots\right)$$

$$= \frac{Q'}{T'}$$

Similarly,

$$dS = \frac{dQ}{T}, \quad dQ \sim \text{infinitesimal}$$

※ An argument by using $T \sim \frac{\bar{E}}{f}$

$$T'(\bar{E}' + Q) \simeq \frac{\bar{E}' + Q}{f'} \lesssim \frac{\bar{E}' + \bar{E}}{f'} = \frac{\bar{E}'}{f'}\left(1 + \frac{\bar{E}}{\bar{E}'}\right)$$

$$= T'\left(1 + \frac{\bar{E}}{\bar{E}'}\right) \simeq T', \quad \text{if } \bar{E} \ll \bar{E}'$$

Q. Do we need the condition of $f \ll f'$?

$$\bar{E}' \gg \bar{E} \neq f' \gg f.$$

if $T' \simeq T$ & $f' \gg f \Rightarrow \bar{E}' \gg \bar{E}$

⊙ mechanical interaction : $\dfrac{\partial \ln \Omega}{\partial x_\alpha} = \beta \bar{X}_\alpha$, $\bar{X}_\alpha$ ~ generalized force

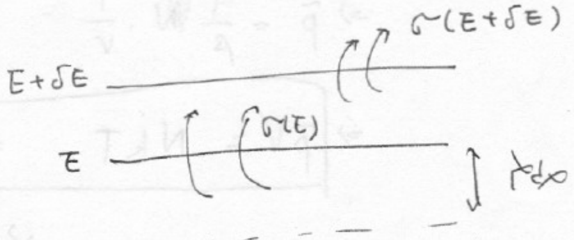
$\boxed{\text{Q.}}$ A single external parameter x_α is free to vary. How does Ω depend on x_α ?

(cf $\dfrac{\partial \ln \Omega}{\partial E} = \beta$)

$$x_\alpha \to x_\alpha + dx_\alpha \quad \Rightarrow \quad E_r \to E_r + \underbrace{\frac{\partial E_r}{\partial x_\alpha}}_{=Y} dx_\alpha .$$

$\Omega(E, x_\alpha) = \sum_Y \Omega_Y(E, x_\alpha)$ $\qquad$ $\Omega_Y(E, x_\alpha)$: $E \in [E, E+\delta E)$, $Y \in [Y, Y+\delta Y]$

$\sigma_Y(E)$: # of states whose energy ~~behaves as~~ is changed from a value less than E to that larger than E as $x_\alpha \to x_\alpha + dx_\alpha$.



$$\sigma_Y(E) = \frac{\Omega_Y(E, x_\alpha)}{\delta E} \cdot Y dx_\alpha$$

$$\sigma(E) = \sum_Y \frac{\Omega_Y}{\delta E} Y dx_\alpha = \frac{\Omega(E, x_\alpha)}{\delta E} \bar{Y} dx_\alpha$$

$$\left(\bar{Y} = \frac{1}{\Omega} \sum \Omega_Y Y \right)$$

$$\bar{Y} = \overline{\frac{\partial E_r}{\partial x_\alpha}} \equiv -\bar{X}_\alpha$$

$$\frac{\partial \Omega}{\partial x_\alpha} dx_\alpha = \sigma(E) - \sigma(E+\delta E) = -\frac{\partial \sigma}{\partial E} \delta E$$

$$\Rightarrow \frac{\partial \Omega}{\partial x_\alpha} = -\frac{\partial}{\partial E}(\Omega \bar{Y}) = -\frac{\partial \Omega}{\partial E} \bar{Y} - \Omega \frac{\partial \bar{Y}}{\partial E}$$

$$\Rightarrow \frac{\partial \ln \Omega}{\partial x_\alpha} = -\frac{\partial \ln \Omega}{\partial E} \bar{Y} - \cancel{\frac{\partial \bar{Y}}{\partial E}} \qquad \left(\because \frac{\partial \ln \Omega}{\partial E} \bar{Y} \sim f \frac{\bar{Y}}{E} \right)$$

$$= \frac{\partial \ln \Omega}{\partial E} \bar{X}_\alpha = \beta \bar{X}_\alpha$$

Example: $\bar{p} = \dfrac{1}{\beta} \dfrac{\partial \ln \Omega}{\partial V}$ (see the back.)

(eg)

$x_\alpha = V$ volume.

$\rightarrow$ generalized force $\overline{X_\alpha} = p$ - pressure

mean pressure $\bar{p} = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V}$

An ideal gas of N molecules in a volume V

$$\Omega \propto V^N \underbrace{\chi(E)}_{\leftarrow \text{ independent of } V}$$

$$\ln \Omega = N \ln V + \ln \chi + \text{constant}$$

(for the detailed form of $\chi(E)$, see p. 6x - chap. 2.5)

$$\Rightarrow \bar{p} = \frac{1}{\beta} N \cdot \frac{1}{V}$$

$$\Rightarrow \boxed{\bar{p}V = NkT = \nu RT}, \text{ eq. of state}$$

($\nu = N/N_a$, N_a: 1 mole (Avogadro's #)
$R = N_a k$, gas constant

$$\beta = \left.\frac{\partial \ln \chi(E)}{\partial E}\right|_{\bar{E}}$$

$$\Rightarrow \bar{E} = \bar{E}(T)$$

General case

$$A^{(0)} = A \oplus A'$$
$$E^{(0)} = E + E'$$
$$\Omega^{(0)} = \Omega \times \Omega'$$
$$\{x_\alpha\} \qquad \{x_\alpha'\}$$

$\Rightarrow$ $\Omega^{(0)}(E;\{x_\alpha\})$ ~ very sharp maximum at $\tilde{E}$ and $\tilde{x}_\alpha$

$\Rightarrow$ At equilibrium, $\bar{E} \simeq \tilde{E}$, $\bar{x}_\alpha \simeq \tilde{x}_\alpha$

general statement?

(eg. Ideal gas. $\Omega(E) \sim E^f$, $\Omega(V) \sim V^N$)

Equilibrium condition:

(ex) external parameter: Volume. $V + V' = V^{(0)}$

$$\Omega^{(0)}(E, V) = \Omega(E, V)\ \Omega'(E', V')$$

$$\Rightarrow \quad d\ln\Omega^{(0)} = d\ln\Omega + d\ln\Omega' = 0$$

$$d\ln\Omega = \beta\, dE + \beta\bar{p}\, dV \qquad \left(\beta = \frac{\partial\ln\Omega}{\partial E},\ \beta\bar{p} = \frac{\partial\ln\Omega}{\partial V}\right)$$

$$d\ln\Omega' = \beta'\, dE' + \beta'\bar{p}'\, dV'$$

$$dE' = -dE,\ dV' = -dV$$

$$\Rightarrow \quad \beta = \beta', \quad \bar{p} = \bar{p}'$$

thermal equilibrium

mechanical equilibrium

Entropy

a. Infinitesimal quasi-static process

$$(\bar{E}, \bar{x}_\alpha) \longrightarrow (\bar{E} + d\bar{E}, \bar{x}_\alpha + d\bar{x}_\alpha)$$

change of equilibrium due to the interaction with environment

$$d\ln\Omega = \frac{\partial \ln\Omega}{\partial E} d\bar{E} + \sum \frac{\partial \ln\Omega}{\partial x_\alpha} d\bar{x}_\alpha$$

$$= \beta \left(d\bar{E} + \underbrace{\sum_\alpha \bar{X}_\alpha d\bar{x}_\alpha}_{= đW \text{ in quasi-static process}} \right)$$

$$= \beta (d\bar{E} + đW)$$

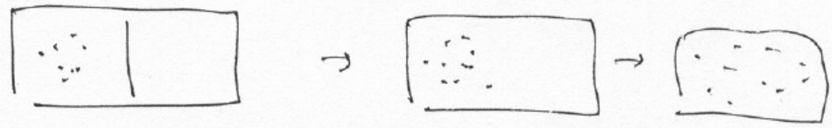
$$= \beta\, đQ$$

$\Rightarrow$ $T dS = đQ$ (cf. infinitesimal pure thermal interaction $\sim dS = \frac{đQ}{T}$)

$\rightarrow$ $\boxed{\text{quasi-static} \oplus đQ = 0} \rightarrow dS = 0$

※ not quasi-static $\oplus$ $đQ = 0$ $\not\longrightarrow$

(ex)

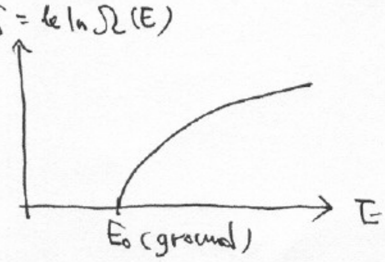


Entropy increases as the system approaches to equilibrium.

b. dS ~ exact differential

$\Rightarrow$ $\frac{đQ}{T}$ ~ exact differential for quasi-static processes.

c. $S = k \ln\Omega(E)$



$\Omega \propto (E - E_0)^f$

$T \rightarrow 0$ $\Rightarrow$ system $\rightarrow$ ground state.

$\Rightarrow$ $S \rightarrow S_0 = k \ln\Omega_s$ $\quad$ Ω_s ~ ground state degeneracy.