

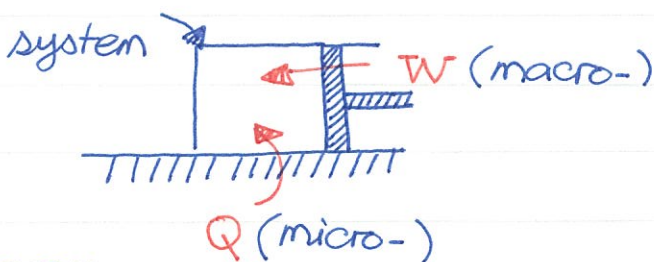
HH0011 Thermal Processes for Ideal Gas

We derive the thermal identity before: $\tau d\sigma = dU + pdV$

This is the infinitesimal form for the 1st law.

$$\Delta U = Q + W$$

$$dU = \tau d\sigma - pdV$$



The 1st law is nothing but energy

conservation. The work done with macroscopic change is W ;

while the work done without any macroscopic change is referred as Q . Loosely speaking, internal energy U depends on (1) dist. of particle occupation (2) energy levels.



E_n remains the same
but $f(E_n)$ is diff!

$\tau d\sigma \neq 0$
entropy changes



$f(E_n)$ is the same
but E_n changes!

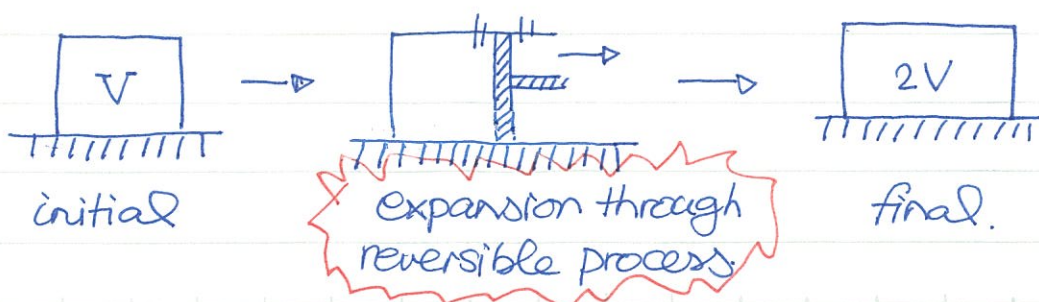
$pdV \neq 0$
external work

$$U = \sum_n E_n f(E_n)$$

$$dU = \sum_n f(E_n) dE_n + \sum_n E_n df(E_n)$$

Energy change can be separated into two parts.

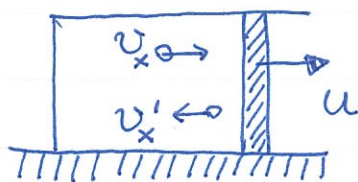
① reversible isothermal expansion



$$W = -\int p dV = \underline{-N\tau \log 2}$$

$$U = \frac{3}{2}N\tau \rightarrow \underline{\Delta U = 0}$$

$$\left. \begin{array}{l} W = -\int p dV = \underline{-N\tau \log 2} \\ U = \frac{3}{2}N\tau \rightarrow \underline{\Delta U = 0} \end{array} \right\} Q = \Delta U - W = \underline{N\tau \log 2}$$



Collisions occur only if $v_x > u$.

$$\Delta \mathcal{E} = \frac{1}{2}m v_x'^2 - \frac{1}{2}m v_x^2$$

$$v_x' = -v + 2u$$

$$= -2mu(v_x - u) < 0$$

— Energy change $\Delta \mathcal{E}$ is always negative! We can estimate the energy changing rate

$$\frac{\Delta \mathcal{E}}{\Delta t} = \langle f \Delta \mathcal{E} \rangle \approx \left\langle \frac{N v_x}{2L} \cdot (-2mu v_x) \right\rangle$$

← assuming $u \ll v_x$.

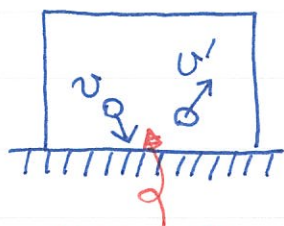
$$= -\frac{Nu}{L} \langle m v_x^2 \rangle$$

From equipartition theorem,
 $\langle \frac{1}{2}m v_x^2 \rangle = \frac{1}{2}\tau = \frac{1}{2}PV/N$

$$\rightarrow \frac{\Delta \mathcal{E}}{\Delta t} = -\frac{Nu}{L} \cdot \frac{P \times A}{N} = -PAu = -P \frac{\Delta V}{\Delta t}$$

— That is to say, $\Delta \mathcal{E} = -P \Delta V$ as expected ☺ Thus, collisions with the macroscopic piston give rise to energy change equal to $W = -\int p dV$.

— Microscopic collisions with thermal reservoir:



$\Delta \mathcal{E} > 0$ to keep τ const.

In general, it is hard to calculate the energy transfer rate. But since the temp τ remains constant, it means $\Delta \mathcal{E} > 0$ to compensate the energy loss ($W < 0$) so that the average kinetic energy is the same.

i.e.

$$Q + W = 0 \text{ to keep } \tau \text{ constant for ideal gas}$$

① reversible expansion at const entropy.



no reservoir.

$$\sigma = N \log \left(\frac{n_Q}{n} \right) + \frac{5}{2} N$$

$Q = 0$ + reversible process

$$\rightarrow dQ = 0, \text{ i.e. } d\sigma = 0$$

From Sackur-Tetrode equation,

$$\rightarrow \sigma = N \log \tau^{\frac{3}{2}} + N \log V + \text{other terms.}$$

$$d\sigma = 0 \rightarrow \tau^{\frac{3}{2}} V = \text{const for ideal gas.}$$

Making use of $PV = N\tau$, $p^{\frac{3}{2}} V^{\frac{5}{2}} = \text{const} \rightarrow PV^\gamma = \text{const}$

The exponent $\gamma = \frac{5}{3} = C_p/C_v$. One can also rewrite the relation for τ and V .

$$\tau_1 V_1^{\gamma-1} = \tau_2 V_2^{\gamma-1}$$

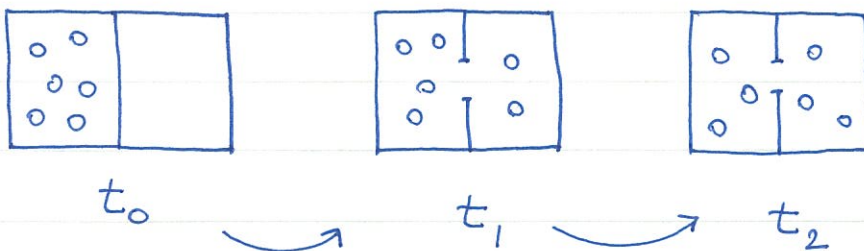
$$\begin{aligned} \rightarrow \Delta U &= \frac{3}{2} N (\tau_2 - \tau_1) \\ &= \frac{3}{2} N \tau_1 \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] < 0 \end{aligned}$$

Similarly, one can compute \bar{W} .

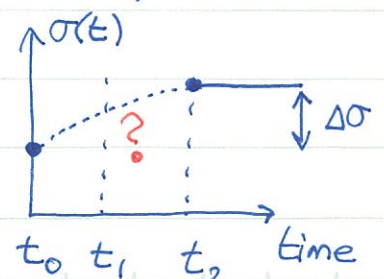
$$\begin{aligned} W &= - \int p dV = - P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = - P_1 V_1^\gamma \cdot \frac{1}{(-\gamma+1)} (V_2^{-\gamma+1} - V_1^{-\gamma+1}) \\ &= \frac{P_1 V_1}{(\gamma-1)} \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] = \frac{3}{2} N \tau_1 \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] < 0 \end{aligned}$$

It's clear that $\Delta U = W$ because $Q = 0$ here \ddot{o} .

① sudden expansion into vacuum.



entropy increases



No work is done $W=0$ and no heat is added $Q=0$

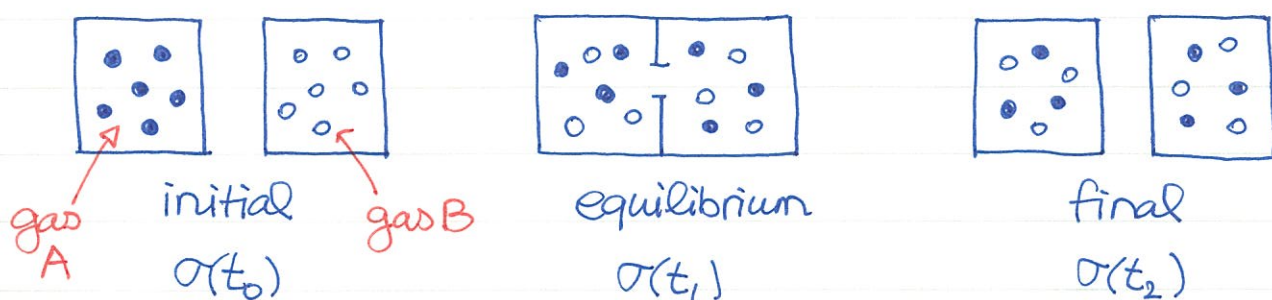
→ $\Delta U = Q + W = 0$, The temperature for the ideal gas is the same!! *a bit strange*

The tricky part is $W=0$ $\ddot{\circ}$ ($Q=0$ is quite trivial, ha!)

$$\Delta\sigma = N \log(V_2/V_1) = \underline{N \log 2} \text{ assuming } V_2 = 2V_1.$$

Note that $\sigma(t)$ is not well defined $t_0 < t < t_2$ because the system may not be close to the most probable configuration.

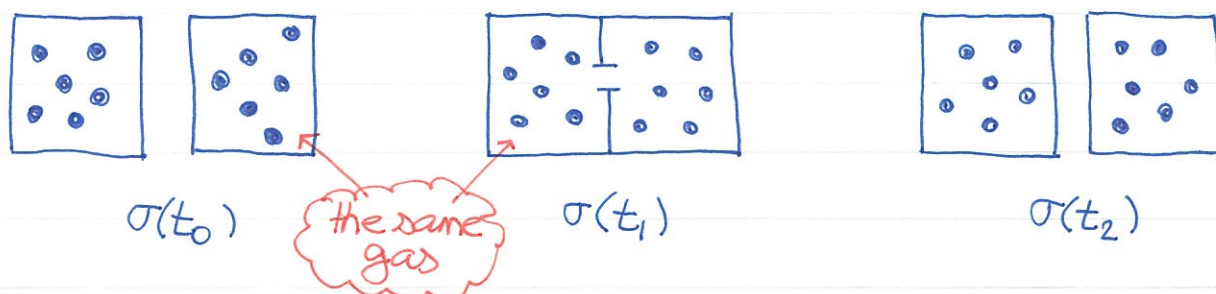
⊗ Gibbs paradox.



What are the relations between $\sigma(t_0), \sigma(t_1), \sigma(t_2)$? The answer is quite simple

$$\sigma(t_0) < \sigma(t_1) = \sigma(t_2)$$

$$\begin{aligned} \sigma(t_1) - \sigma(t_0) &= \Delta\sigma_A + \Delta\sigma_B = N \log 2 + N \log 2 \\ &= \underline{2N \log 2} \text{ entropy of mixing } \ddot{\circ} \end{aligned}$$



What are the relations between $\sigma(t_0), \sigma(t_1), \sigma(t_2)$?

→ $\sigma(t_0) = \sigma(t_1) = \sigma(t_2)$

Let us go back to the Gibbs factor,

$$Z = \underbrace{Z_1 \cdot Z_1 \cdots Z_1}_N = (n_q V)^N \quad \rightarrow \quad F = -\tau \log Z \\ = -N\tau \log(n_q V)$$

From the thermal identity $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{N,V}$

$$\sigma = N \log(n_q V) + \frac{3}{2} N \quad \text{Let's compute } \sigma(t_0) \text{ and } \sigma(t_1)$$

$$\sigma(t_0) = \sigma_1 + \sigma_2 = \left[N \log(n_q V) + \frac{3}{2} N \right] + \left[N \log(n_q V) + \frac{3}{2} N \right] \\ = \underline{2N \log(n_q V) + 3N}$$

$$\sigma(t_1) = (2N) \cdot \log(2n_q V) + \frac{3}{2}(2N) = \sigma(t_0) + 2N \log 2$$

$$\rightarrow \Delta\sigma \equiv \sigma(t_1) - \sigma(t_0) = 2N \log 2 \neq 0$$

But this cannot be true since $\sigma(t_0) = \sigma(t_1) = \sigma(t_2) !!$ Therefore, Gibbs come up with the smart solution $\ddot{\circ}$

$$Z = \frac{\sum_1^N}{N!} \quad \rightarrow \quad \Delta F = N\tau \log N - N\tau \quad \text{giving rise} \\ \text{an entropy correction}$$

Gibbs factor:

$$\Delta\sigma = -N \log N + N$$

- That is to say, the notion of "identical particle" reduces the entropy by the amount

- This $N!$ factor resolves Gibbs paradox (although not being completely correct in the quantum regime).



20111218

東院19號