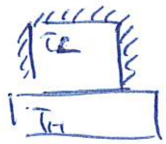
On Reversible and Irreversible Process

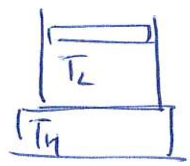
- Any reversible process is necessarily quasistatic. The converse is not true.

Isochoric is not reversible though. $\oint dU = \frac{3}{2} N k_B (T_i - T_i) = 0$



b/c time reverse shows heat flow from T_L to T_H violation of 2^{nd} Law.

Isobaric irreversible



$\oint dU = N k_B (\overset{\to T_H}{T_H - T_L}) = 0$ but then again heat flow from T_L to T_H when reverse.

ex. compression of piston against system subject to friction — irreversible due to generation of dissipative entropy.

ex heat exchange between 2 bodies at two finite different temperature. b/c no matter how slow the process, two bodies never infinitesimally close to equilibrium. (note thermal equilibrium requires two bodies at same temperature.)

Summary

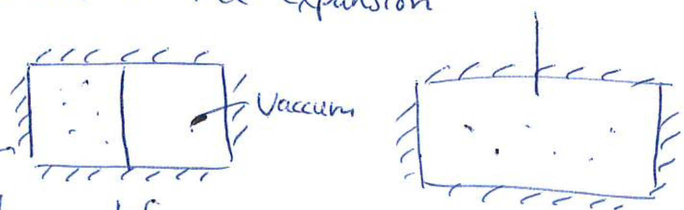
PV-work in quasi-static process:

1. Isobaric process $\Delta W = \int_1^2 P dV = P(V_2 - V_1)$
2. Isochoric process $\Delta W = \int_1^2 P dV = 0$
3. Isothermal process $\Delta W = \int_1^2 P dV = nRT \ln \frac{V_2}{V_1}$ (ideal gas)

reversible process : • a process can be reversed by infinitesimal change
• reversible process doesn't increases entropy (of sys and surr.)
• quasistatic $\not\Rightarrow$ thermal equilibrium.

quasi-static : at each instant, system departs only infinitesimally from equilibrium state, changes of state are describe in term of differentials.

Joule or free expansion



thermally isolated

bf

af

<u>Properties</u>. $dQ = 0$ · irreversible   sys. expand into vaccum

· $dW = 0$

$\Rightarrow dU(T,V) = 0$ $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

maxwell relation.

<u>observed</u>: $\boxed{\text{there is temperature change}}$

reciprical law: $\left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial U}{\partial T}\right)_V = -1 \Rightarrow \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]$

$$\Delta T = -\int_{V_1}^{V_2} \frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV$$

intermolecular interaction. but ideal gas $\left(\frac{\partial p}{\partial T}\right)_V = \frac{p}{T} \Rightarrow \Delta T = 0$

$\hookrightarrow$ attraction force btw atom has ~~negativ~~ negative potential, as expand, potential becomes less negative $\Rightarrow$ K.E decrease $\Rightarrow$ cooling effect.

Quantum State in k-space

$\Gamma(k)$ # of microstate

$g(k)$ density of state

$\gamma_s = \begin{cases} 2 & \text{fermion} \\ 1 & \text{boson} \end{cases}$

In square well, ∂ : $dN = \gamma_s \dfrac{\frac{1}{8}(4\pi k^2)dk}{\underset{\smile}{\pi^3}} = \gamma_s g(k) dk \qquad g(k) = \dfrac{Vk^2}{2\pi^2}\gamma_s$

V : $N_q = \gamma_s \dfrac{\frac{1}{8}(\frac{4}{3}\pi k^3)}{\underset{\smile}{\pi^3}} = \gamma_s \dfrac{Vk^3}{6\pi^2} \qquad \Gamma(k) = \dfrac{Vk^3}{6\pi^2}\gamma_s$

obs.

$$g(k) = \frac{d\Gamma(k)}{dk}$$

$$dN \text{ or } d\Gamma = g(k)dk$$

$$dE = \varepsilon(k) n(k) dN(k) \quad \text{or} \quad \varepsilon(k) n(k) g(k) dk$$

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ex Square potential well containing electrons.

$$\Gamma(k) = \frac{Vk^3}{3\pi^2} \qquad g(k) = \frac{Vk^2}{\pi^2} \qquad E = \frac{\hbar^2 k^2}{2m}$$

$$dE = \frac{\hbar^2 k^2}{2m}\frac{Vk^2}{\pi^2}dk \qquad E_{tot} = \frac{\hbar^2 k^5 V}{10m\pi^2}$$

ex photon $E = \hbar\omega \quad \omega = kc$

$$\Gamma(k) = \frac{Vk^3}{3\pi^2} \qquad g(k) = \frac{Vk^2}{\pi^2} \qquad n(k) = \frac{1}{e^{\frac{\hbar kc}{k_BT}} - 1}$$

$$dE = \hbar kc \frac{1}{e^{\frac{\hbar kc}{k_BT}} - 1}\frac{Vk^2}{\pi^2}dk$$ ~~since~~

$k = \dfrac{2\pi}{\lambda} \qquad |dk| = \left|-\dfrac{2\pi}{\lambda^2}d\lambda\right|$

thus $\rho(\lambda) = \dfrac{dE(\lambda)}{V} = \dfrac{16\pi^2\hbar c}{\lambda^5}\dfrac{1}{e^{\frac{2\pi\hbar c}{\lambda k_BT}} - 1}$