THERMODYNAMICS & ENERGETICS - II

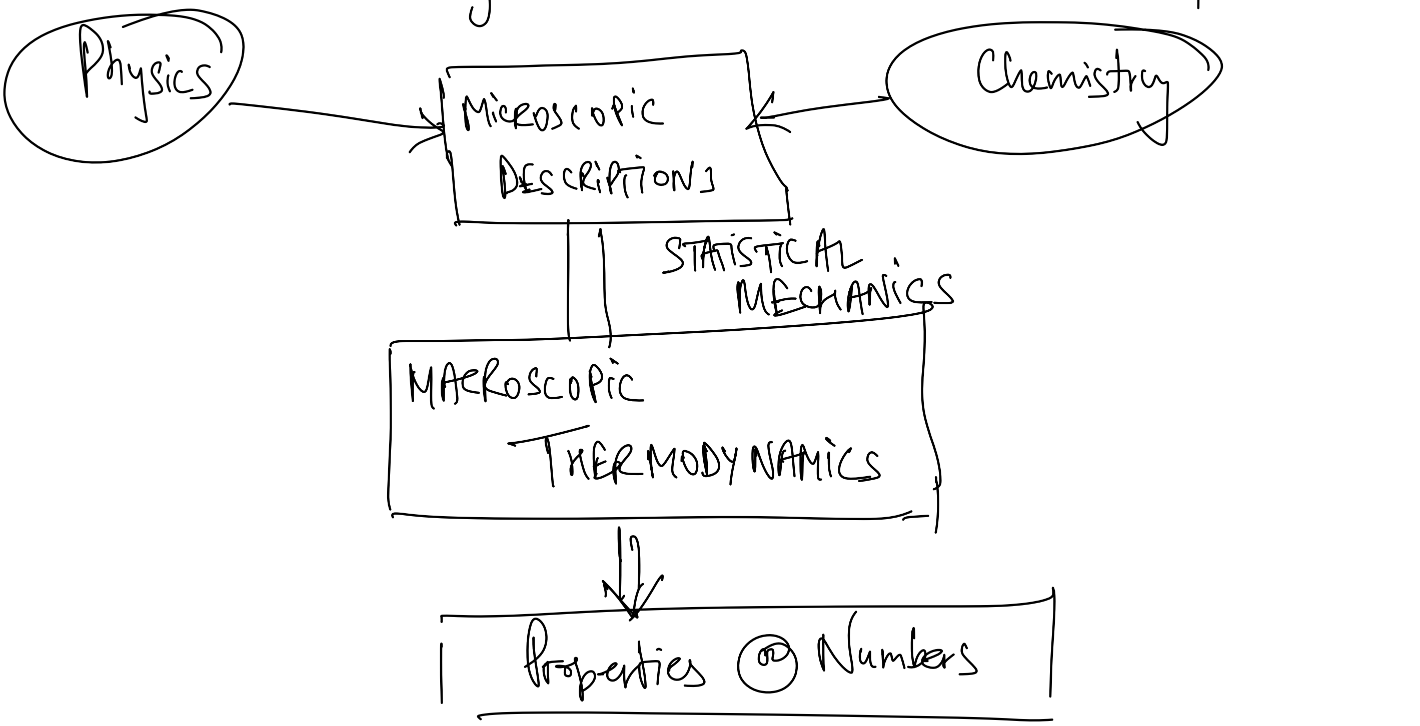
What is thermodynamics ?

Macroscopic framework of energy flows, and how they affect the properties of the system

- Macroscopic Theory → no atomic scale information
- deals only with macroscopic variables
  (eg) Volume (V)
  pressure (p)
  temperature (T) . . .
- Completely general framework that does not rely on atomic details.
- Thermodynamics is a "processor" or "accountant"
  ⇒ You have to put some information | physics into the framework to get other properties out

RELATION TO OTHER FIELDS :

Can derive thermodynamic relations from atomic | electronic



THERMO & ITS RELATIONSHIP TO OTHER FIELDS

Field	Key equation	Important variables
Mechanics	Newton (1643 – 1727)	(m), $\vec{v}$, $\vec{F}$, $\vec{x}$
Elasticity	Hooke's law (eqns. of elasticity) (1635 – 1703)	$\underline{\sigma}$, $\underline{\underline{\varepsilon}}$, $(\underline{\underline{E}}, \underline{\underline{C}})$
Electricity & Magnetism	Maxwells equations (1831 – 1879)	$\vec{E}$, $\vec{P}$, $\vec{M}$, $\vec{H}$ (χ, ε)
Thermal sciences	Fourier Law (1768 – 1830)	T, $\vec{J}$, (C_p, C_v)

all different ways of storing energy in a system

THERMO COUPLES THESE DISCIPLINES INTO ONE FRAMEWORK

- treating energy flows leads to the emergence of couplings between fields!

(eg) elasticity + EM $\Rightarrow$ piezoelectricity.

Thermo needs subdisciplines to provide data & constitutive relations on materials behavior (eg) elasticity $\underline{\underline{\varepsilon}} = C\, \underline{\underline{\sigma}}$ — C → tensor

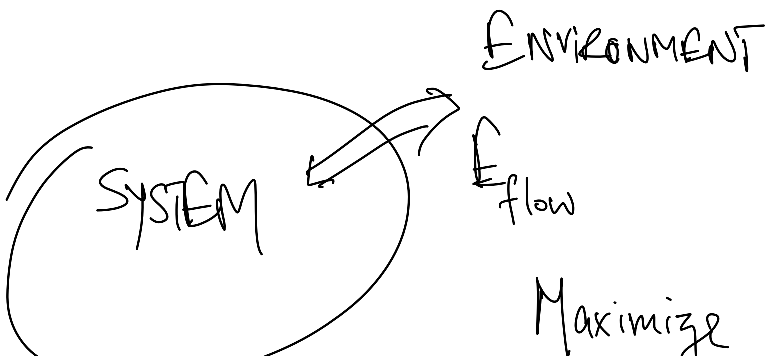
magnetism $M = \chi H$ — χ → susceptibility.

} Materials specific properties.

DEFINITIONS:

* **SYSTEM**: Any collection of matter that can be uniquely specified (and over which macroscopic averages can be specified)
* **SURROUNDING / ENVIRONMENT**: Universe − System
* **VARIABLES**:
  - extensive: scale with the size of the system
    $(V, N_i, U, \dots)$ ⟹ normalized extensive variables: $\frac{N_i}{V} = x_i$ → "densities"
  - intensive: do not scale with the size of the system
    $(T, p, \underline{\underline{\sigma}}, \dots)$

Thermo summarized



E = conserved

Maximize $S_{system} + S_{environment}$

<u>Solve</u> $dS_{system}(dE_{system}) + dS_{environment}(-dE_{system})$

STEPS TO <u>SOLVING A</u> THERMO PROBLEM

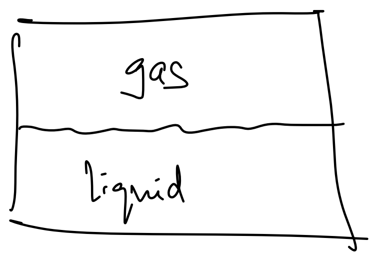
1. Carefully define system
2. Quantify the energy flows
3. Relate entropy to energy flows
4. Relate to properties

* <u>BOUNDARIES</u>

- permeable $\longrightarrow$ open system N_i is allowed to change $\hookrightarrow$ open system
- non-permeable $\longrightarrow$ N_i is constant $\to$ closed
- Deformable $\longrightarrow$ V can change
- Adiabatic or Insulated $\longrightarrow$ no heat flow
- Diathermic $\longrightarrow$ perfect heat flow (system is at same temperature as environment)
- Rigid $\to$ $V =$ constant

THERMODYNAMICS DEALS WITH EQUILIBRIUM STATES:

* HOMOGENEOUS EQUILIBRIUM: All bulk physical properties of the system are uniform throughout and do not change with time
* HETEROGENOUS EQUILIBRIUM: Collection of equilibrium phases coexisting



The beaker contains "distinct portions" whose properties markedly differ from one another

(eg) x_{NaCl} in the liquid v/s x_{NaCl} in the solid

ρ_{liquid} v/s ρ_{solid}

Each "distinct portion" ⟶ PHASE

IN EQUILIBRIUM: system has well-defined extensive & intensive variables eg $(T, V, p, \mu, \ldots)$ that uniquely characterize the STATE of the system

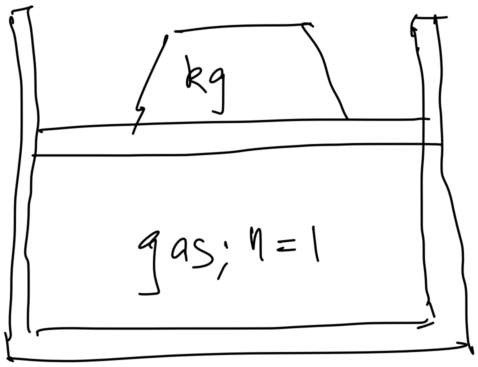
⟶ These variables are called STATE VARIABLES

State variables are independent of how equilibrium is reached.

EXAMPLE: ideal gas: Equation of state $\longrightarrow$ thermo does not predict this

Must be derived from

- experiment
- physics $\Rightarrow$ STAT. MECH



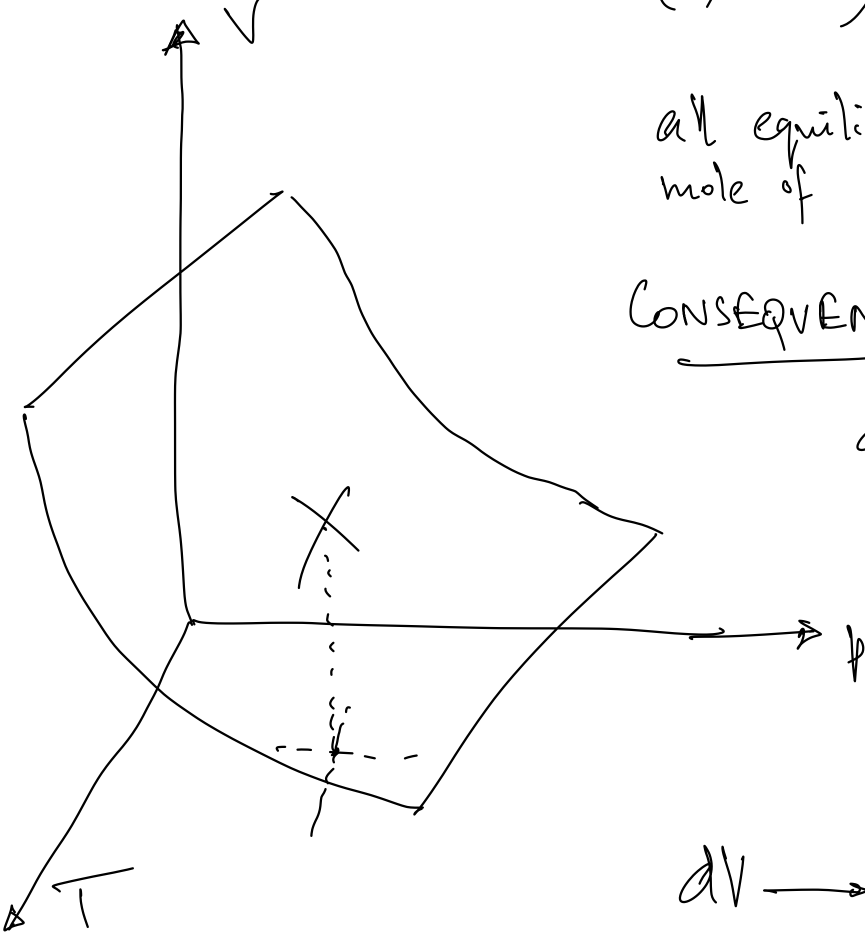
$$\boxed{pV = nRT}$$

fix $p, T \longrightarrow V$ is automatically determined in equilibrium

- does not depend on how the state was obtained
- fix 2-variables $\longrightarrow$ third is fixed by equilibrium

V = state function ; $V = f(T, p)$ [1 mole of gas]

or $f(V, p, T) = 0$



all equilibrium states for one mole of gas lie on this surface

CONSEQUENCE (Recall from calculus)

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT$$

slope @ constant T

slope @ const. p

$dV \longrightarrow$ total differential

exact differential

Measuring the equation of state

1. Directly measure $V(T, p)$ → several experiments @ $(T_1, p_1), (T_2, p_2), \ldots$

2. Measure derived quantities:

   * compressibility: $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

   * thermal volumetric expansion: $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

$$\Rightarrow \boxed{dV = -V\kappa\, dp + V\beta\, dT}$$

NOTE: can do the same thing for $p(V,T)$ or $T(V,p)$

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* State variables are determined by the allowed changes of the system

CHANGE OF STATE (process) – between stable and/or metastable states

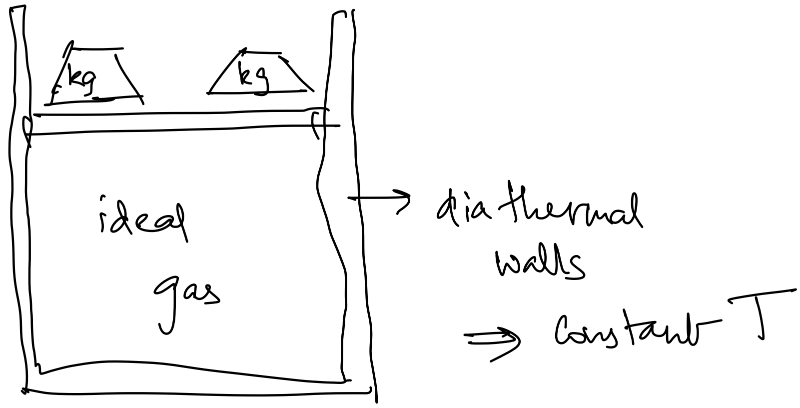
– describe in terms of state variables

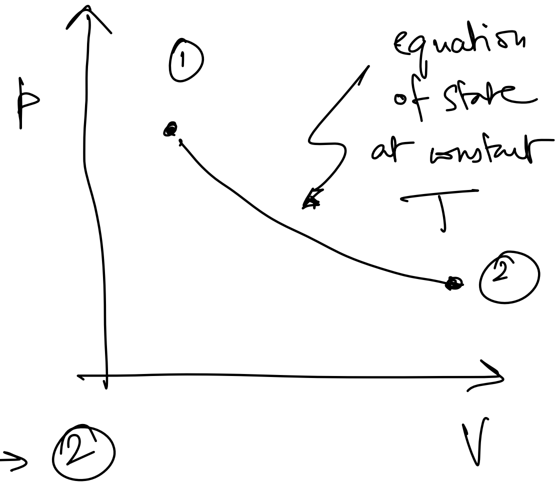
$$\begin{cases} X \longrightarrow \text{extensive } (V, N_i, \ldots) \\ Y \longrightarrow \text{intensive } (T, p, \mu, \ldots) \end{cases}$$

Two ways of changing the state of a system:

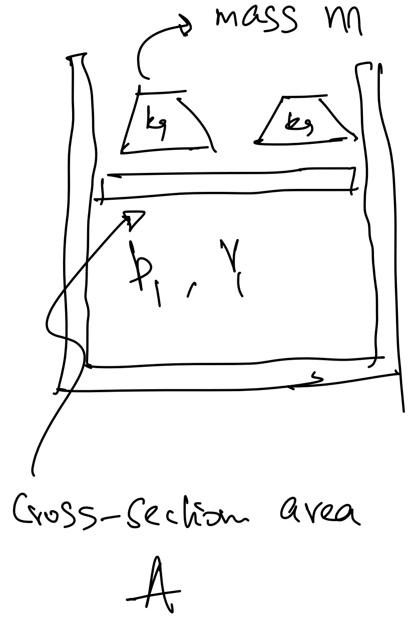
* perform work W — $W > 0$ if work is performed on the system
* exchange heat Q — $Q > 0$ if heat is supplied to the system.

Work

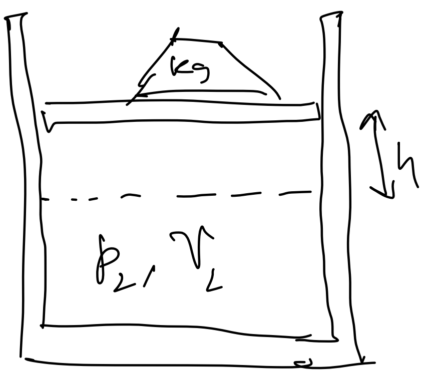




Change state from (1) ⟶ (2)



$$p_1 = \frac{2mg}{A}$$



$$\Delta V = V_2 - V_1 = A \cdot h$$

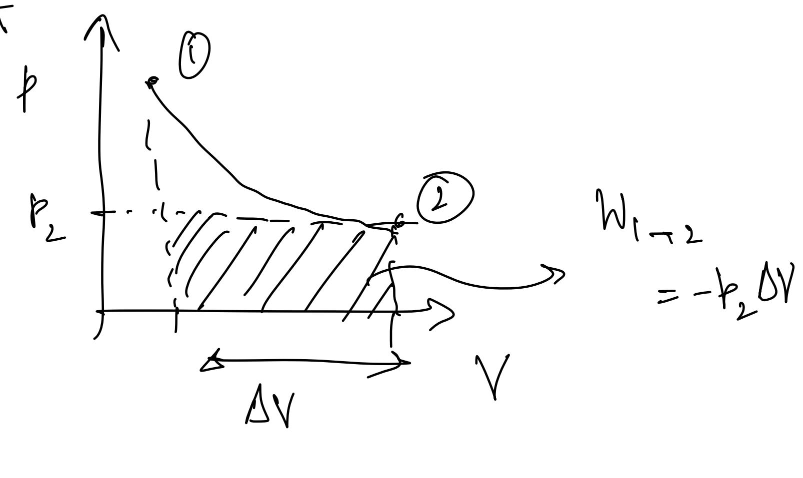
$$p_2 = \frac{mg}{A}$$

Work performed by the system to the environment

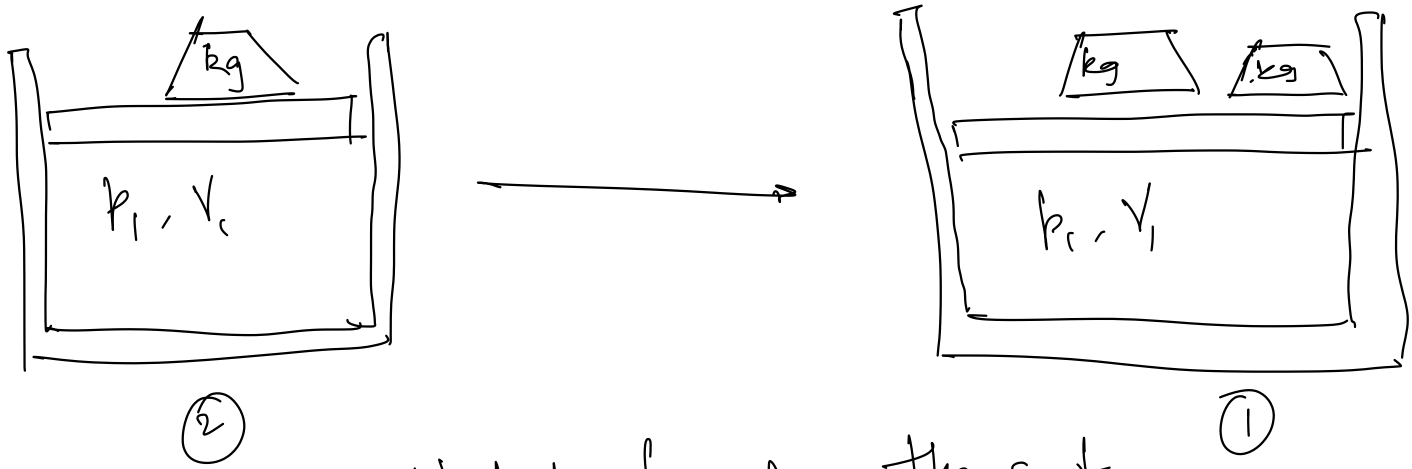
⟶ System lifted on weight of mass m by a height h

$$W = -mg \cdot h = -\frac{mg}{A} \cdot hA$$

$$\boxed{W = -p_2 \cdot \Delta V}$$



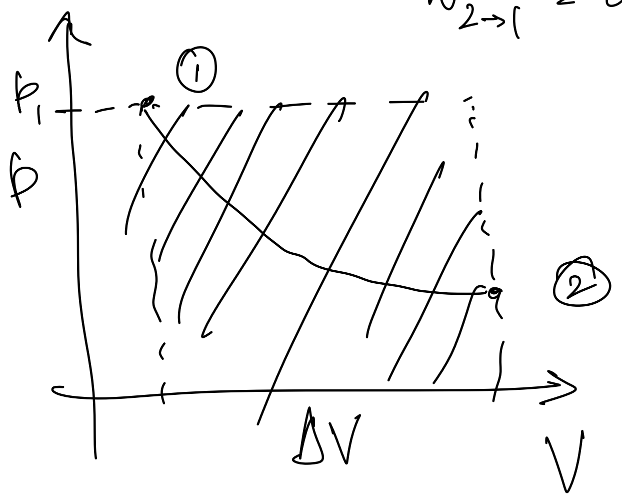
Go from ② $\longrightarrow$ ①:



Work performed on the system

$\longrightarrow$ two weights of mass m were dropped a height h

$$W_{2\to1} = 2mg\cdot h = \frac{2mg}{A}\cdot hA = p_1 \Delta V$$



To achieve a change of state in reality we need either an overpressure or an underpressure

$\longrightarrow$ for a real change of state

$$p_{system} \neq p_{environment}$$

$\longrightarrow$ Work is different when reversing the process

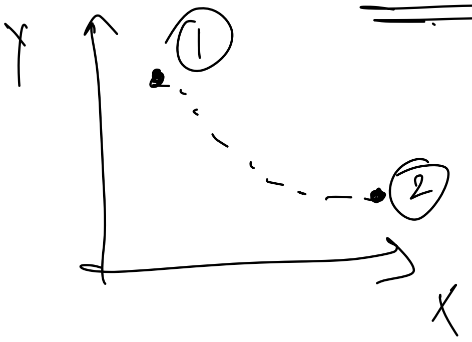
REAL PROCESSES ARE IRREVERSIBLE

When is $|W_{1\to2}| = |W_{2\to1}|$?

when $p_{system} = p_{env}$ at all stages – Idealized REVERSIBLE change of state

THREE TYPES OF PROCESSES

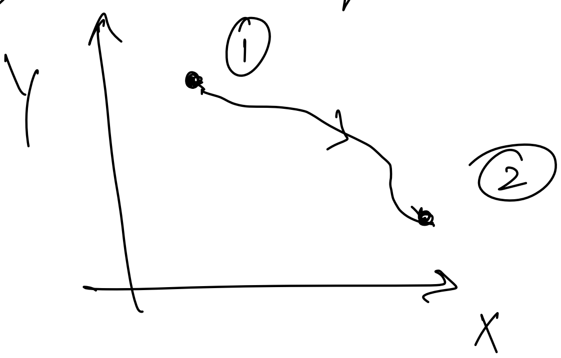
I Discontinuous IRREVERSIBLE



- X, Y cannot be measured along path
- change is fast & turbulent

(eg) H_2, O_2 combustion

II Continuous quasi-static IRREVERSIBLE

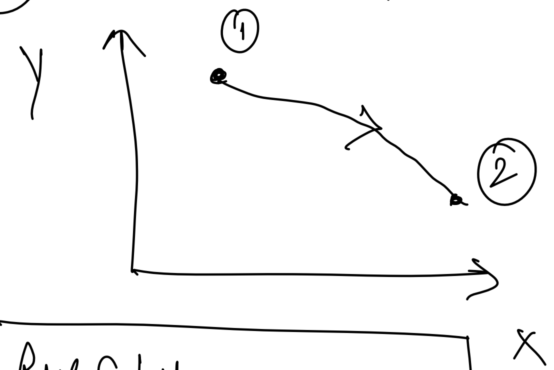


- process is slow enough that X & Y can be specified along path
- System & environment are not in equilibrium

- make small changes to X & Y and allow to equilibrate

(eg) expansion of a gas $P_{env} < P_{sys}$

III Continuous quasi-static REVERSIBLE



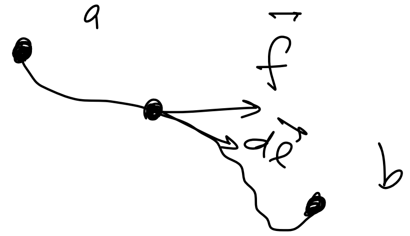
- same as II but the system is always in equilibrium with the surroundings
- Can retrace steps restoring both system & environment to its original state

$\boxed{\text{PURELY MATHEMATICAL}}$

Change of state (process) through exchange of **work** and **heat** between system & environment

WORK: energy transfer from "displacement" under a "force"

* classical mechanics



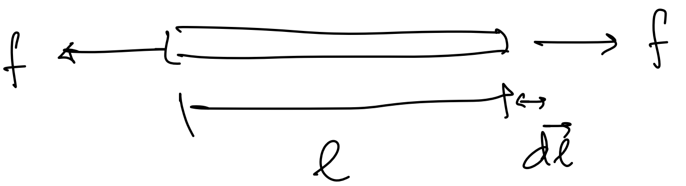
$$\delta W = \vec{f} \cdot \vec{dl}$$

$$\Delta W = \int_a^b \vec{f} \cdot \vec{dl}$$

$\boxed{\text{path dependent}}$

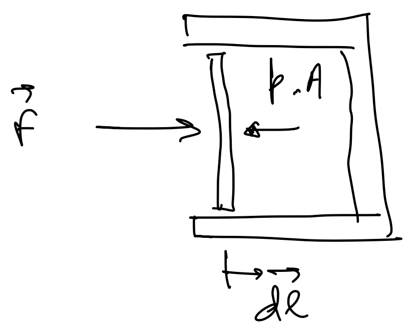
$\delta W > 0$ if work is done on the system

elongation of a rod



$$\boxed{\delta W = \vec{f} \cdot \vec{dl}}$$

piston work



$$\delta W = \vec{f} \cdot \vec{dl}$$

Assume mechanical equilibrium

$\Rightarrow f = pA$

$$\boxed{\delta W = p\underbrace{A\,dl}_{-dV} = -p\,dV}$$

ONLY TRUE IF IN MECHANICAL EQUILIBRIUM

$\Longrightarrow$ ONLY FOR REVERSIBLE PROCESSES

* Work is expressed in terms of state variables of the system

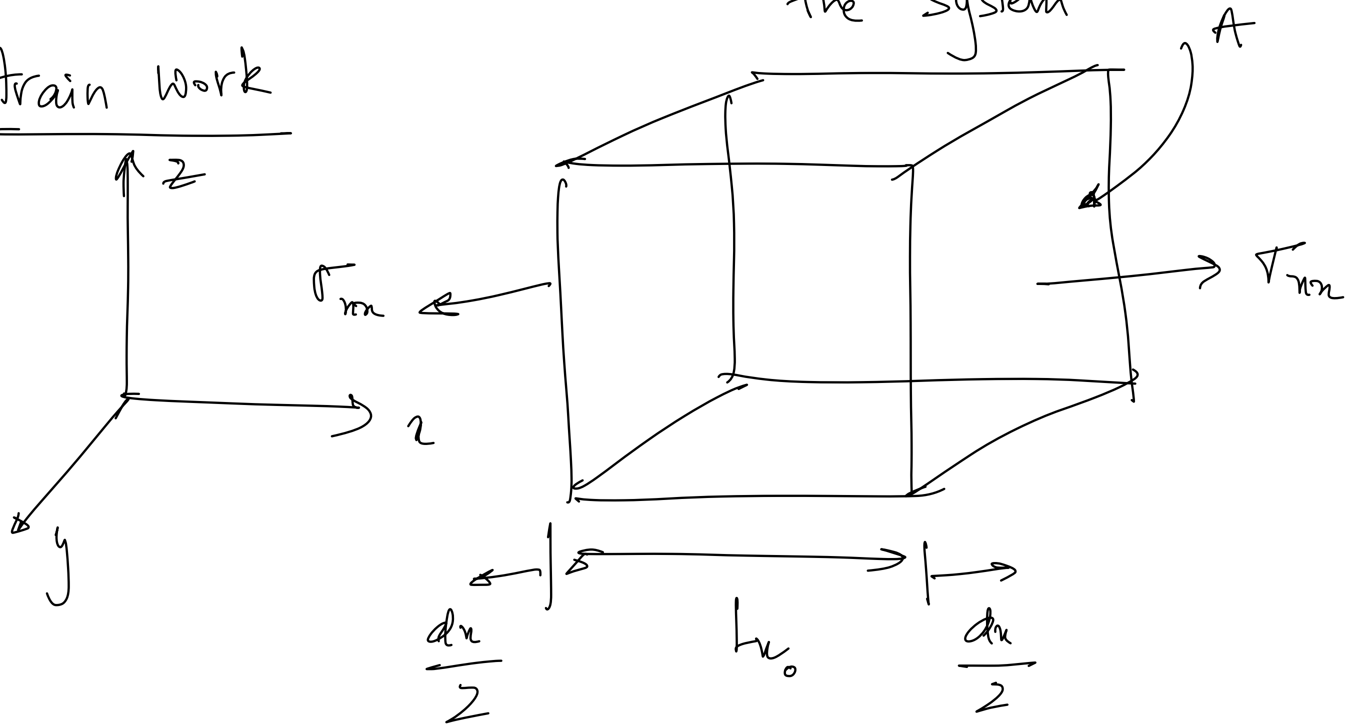
NOTE: ① quasi-static irreversible compression

$f > p \cdot A \longrightarrow$ perform more work than the reversible case

② quasi-static irreversible expansion

$f < p \cdot A \longrightarrow$ get less work out of the system

Strain work



$$\delta W = 2\, \sigma_{xx} A_0 \frac{dx}{2} = \sigma_{xx} \underbrace{A_0 L_{x_0}}_{V_0} \frac{dx}{L_{x_0}}$$

$$= V_0\, \sigma_{xx}\, d\varepsilon_{xx}$$

In general: $\boxed{\delta W = \sum_i \sum_j V_0\, \sigma_{ij}\, d\varepsilon_{ij}}$

Special case:

hydrostatic pressure

$$\left.\begin{aligned} \sigma_{xx} &= \sigma_{yy} = \sigma_{zz} = -p \\ \sigma_{xy} &= \sigma_{yz} = \sigma_{xz} = 0 \end{aligned}\right] \longrightarrow$$

$V = V_0 (1 + \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$

(Assuming infinitesimal strains

$\delta W = -V_0 p\, d(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$

$\boxed{\delta W = -p\,dV} \longleftarrow dV = V_0\, d(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})$