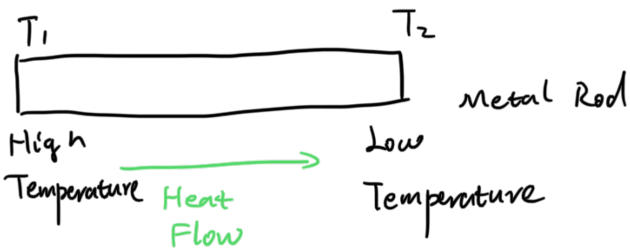
1_Irreversible Thermodynamics & Non-equilibrium Thermodynamics

Link: https://www.youtube.com/watch?v=yBcz5ZaIdus&list=PLdBDmcnzLC_ZMUWMdy7SmcTgnnzyiRpqI

Example (Irreversible Transport/process

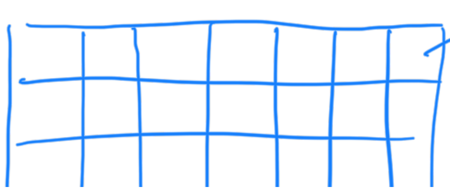


Irreversible Thermodynamics <=> Non-equilibrium Thermodynamics

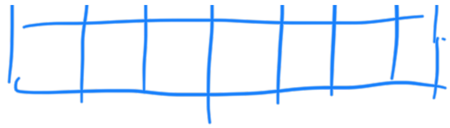
Some Postulates which are applicable to some systems that are NOT FAR from the equilibrium : (very near to equibrium)

(I) Postulate of Local equilibrium

Consider a system at equilibrium that can be divided into many small elements. (or cell)



-> for each elements. (cell)
it has volume V.
internal energy U, and mass



m_i: (mass unit of the molecular species)

$$\boxed{T,\ P,\ \mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,P},\ S}$$

They are dependent on v, U, and m_i.

For non-equilibrium system,

T, P, $\mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T,P}$, S are also dependent on v, U, m_i.

For each cell in the "local equilirium state", we treat them as if they are in the real equilirium state.

(II) Phenomenological laws & Onsager's Reciprocal Relation

In non-equilibrium processes, they usually involve transport phenomenon.

$\underline{\text{Flux}}$
- heat ← Temperature gradient
- mass ← Concentration gradient
- electricity ← Potential gradient

Driving force for thess flux → X (driving force)

We can see that the Flux is always proportional to these driving force.

$$J \propto X \implies J = LX$$

X: driving force

J: Flux

L: Transport Coefficient

Then we got

1) Heat transfer

$$J_Q = -k\frac{dT}{dx} \quad \text{(Fourier Law)}$$

2) Mass transfer

$$J_m = -D\frac{dc}{dx} \quad \text{(Fick's Law)}$$

3) Momentum transfer

$$J_\mu = -\mu\frac{du}{dx} \quad \text{(Newton's Law)}$$

4) Flow of electricity

$$J_e = -\alpha\frac{dE}{dx} \quad \text{(Ohm's Law)}$$

All these expressions (Flux $\propto$ Driving Force) are called Phenomelogical Laws. $(F = LX)$

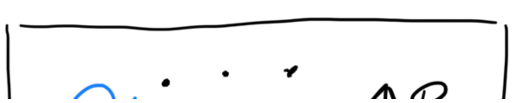
Take Fick's Law as an example.

$$J_m = -D\frac{dc}{dx}$$

不太严谨的变换: $\dfrac{dm}{dt} = D\left(\dfrac{dc}{dx}\right)$

$\dfrac{dm}{dt}$: rate of change of solute of solute across the surface

we need to modify this expression so that it can explain the effect of change of temperature on the system.



semi-permeable

$J_1: \frac{dm_1}{dt} = D\frac{dc_1}{dx} + E\frac{dc_2}{dx}$

For the 1st system

$\frac{dc_1}{dx} \to X_1$, $\frac{dc_2}{dx} \to X_2$

X_i (Driving Force)

This 2 flows are dependent on each other!

⇓

Coupled Flow

$J_2: \frac{dm_2}{dt} = F\frac{dc_2}{dx} + G\frac{dc_1}{dx}$

For the 2nd system:

In order to simplify the notation:
(Coefficient is written as L)

$J_i \quad J \qquad D = L_{11}\ ;\ E = L_{12}$

$F = L_{22}\ ;\ G = L_{21}$

L_{11}

2nd subscript refers to the component whose gradient is being considered

First subscript refers to the component that moves.

Thus. $J_i = L_{i1}X_1 + L_{i2}X_2 + \cdots + L_{in}X_n$

Linear Phenomenological Relation (LPR)

The coefficient L_{ii}: known as Primary Phenomenological Coefficients (PPC)
$(L_{11}, L_{22}, L_{33}, \ldots)$

The coefficient L_{ij}: known as Onsager Phenomenological Coefficients (OPC)
$(L_{12}, L_{13}, L_{14}, \ldots)$

Onsager shows that $L_{ij} = L_{ji}$
(Theoretically)

(known as Onsager Reciprocal Relations (OPR))

⇓

This relationship exists only for a selected pair of flows known as conjugate flows

Example of conjugate flows.

——————— ← conducting wire.

ΔE , ΔT ⟹ driving force

↑

potential difference

$\Delta E \rightarrow$ $J_e = I$

$\Delta T \rightarrow$ Entropy flow J_s

Heat flux J_Q

They are considered as conjugate flow (I & J_s)

Applying Onsager Relation:

conjugate flow

$$\begin{cases} I = L_{11}\Delta E + L_{12}\Delta T \\ J_s = L_{21}\Delta E + L_{22}\Delta T \end{cases}$$

$$\boxed{L_{12} = L_{21}}$$

Influence of 1 on 2 is same as the influence of 2 on 1.