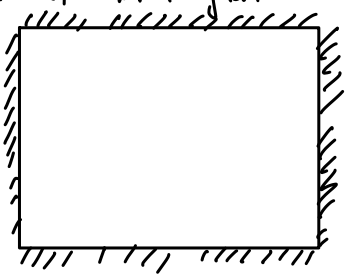
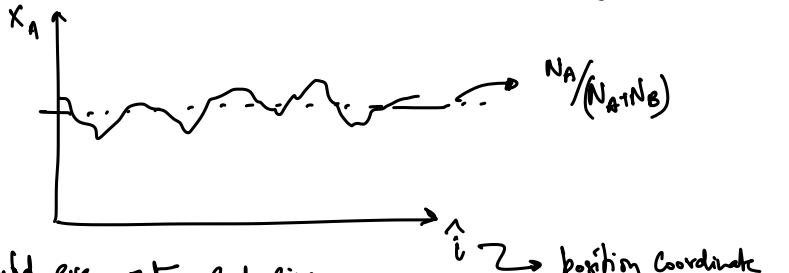
PHENOMENOLOGICAL TREATMENT OF NON-EQUILIBRIUM PROCESSES:

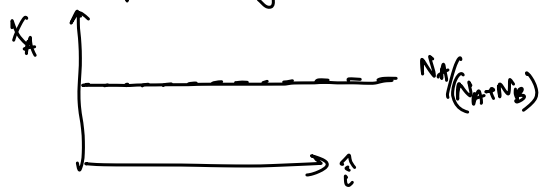
Let us consider an isolated system that is out of eqm



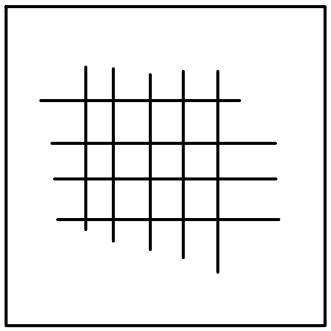
Say it contains N_A, N_B atoms with a total internal energy of $U(N_A, N_B)$



After a long-time composition fluctuations should even out and give a constant composition profile everywhere.



To study the evolution of the system we will begin by making the "local equilibrium" approximation:



divide the system into smaller sub-systems

- small enough such that local variations in extensive variables are minimal within a sub-system
- not so small that statistical mechanics breaks down. (ie) not atomic scale.

Local eqm approximation holds as long as extensive variables vary slowly from sub region to sub region.

$$\frac{U}{V_0} = u(\vec{r}) \qquad \frac{N_i}{V_0} = c_i(\vec{r}) \qquad \frac{S}{V_0} = s(\vec{r}) \qquad \frac{N_i}{N} = x_i(\vec{r})$$

$\vec{r}$ → location of the sub-region

→ mole fraction.

Consider a sub-region within the larger system.

$(u, s, c_i, x_i, T, \mu_i, p, \cdots)$ → a set of well-defined state variables for the sub-region.

⇒ Start from the fundamental equation of thermodynamics:

$$\boxed{du = Tds - pdV + \sum_i \mu_i dc_i}$$

neglect volume change for simplicity $dV = 0$

$$du = Tds + \sum_i \mu_i dc_i$$

$$\Rightarrow \boxed{ds = \left(\frac{1}{T}\right) du - \sum_i \left(\frac{\mu_i}{T}\right) dc_i} \quad \text{——— (1)}$$

the system is overall out of eqm ⇒ heat and matter will flow in and out of each element

ALL LOCAL THERMODYNAMIC STATE VARIABLES WILL EVOLVE OVER TIME

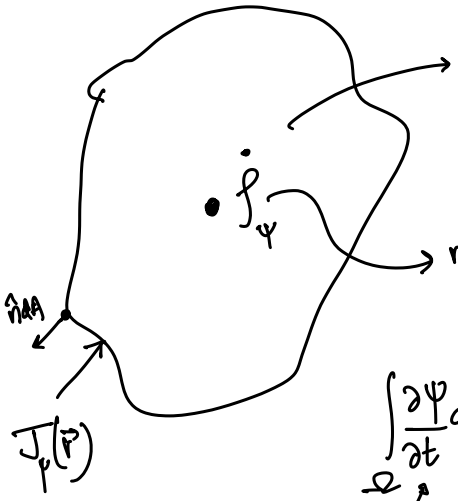
Take the time derivative of (1)

$$\left(\frac{\partial s}{\partial t}\right) = \left(\frac{1}{T}\right)\left(\frac{\partial u}{\partial t}\right) - \sum_i \left(\frac{\mu_i}{T}\right)\left(\frac{\partial c_i}{\partial t}\right) \quad \text{---------- (2)}$$

* A BRIEF DESCRIPTION OF FLUXES, AND CONSERVATION LAWS:

$\vec{J}_\psi(\vec{r})$ → amount of "extensive" ψ flowing through at location $\vec{r}$ in the system:

→ extensive variable such as $T, c, x, \cdots, u, \cdots$



$\dot{\rho}_\psi$ → rate of production of ψ within the volume element

$$\int_\Omega \frac{\partial \psi}{\partial t} dV = \underbrace{-\oint_S \vec{J}_\psi \cdot \hat{n} dA}_{\text{Amount of } \psi \text{ coming in or leaving at the boundary.}} + \underbrace{\int_\Omega \dot{\rho}_\psi dV}_{\text{amount of } \psi \text{ being produced within the boundary.}}$$

$\int_\Omega \frac{\partial \psi}{\partial t} dV$: change in ψ throughout the entire volume.

$\int_\Omega$: the entire volume of the element

Divergence theorem:

$$\oint_S \vec{J}_\psi \cdot \hat{n} dA = \int_\Omega \vec{\nabla} \cdot \vec{J}_\psi \, dV$$

$$\Rightarrow \int_\Omega \left(\frac{\partial \psi}{\partial t}\right) dV = \int_\Omega \left(-\vec{\nabla} \cdot \vec{J}_\psi + \dot{\rho}_\psi\right) dV$$

Conserved quantities such as $u, c_i \cdots$ do not have sources or sinks

$$\boxed{\left(\frac{\partial u}{\partial t}\right) = -\vec{\nabla} \cdot \vec{J}_u}$$

$$\boxed{\left(\frac{\partial c_i}{\partial t}\right) = -\vec{\nabla} \cdot \vec{J}_{c_i}}$$ → "FICKS SECOND LAW"

IS ENTROPY CONSERVED? NO

$$\boxed{\left(\frac{\partial s}{\partial t}\right) = -\vec{\nabla} \cdot \vec{J}_s + \dot{\sigma}}$$

$\vec{J}_s$: entropy flowing into or out of the volume element

$\dot{\sigma}$: entropy production within a volume element.

Coming back to equation (2):

$$\left(\frac{\partial s}{\partial t}\right) = \left(\frac{1}{T}\frac{\partial u}{\partial t}\right) - \sum_i \left(\frac{\mu_i}{T}\right)\frac{\partial c_i}{\partial t}$$

$$\left(\frac{\partial s}{\partial t}\right) = -\vec{\nabla}\cdot\vec{J}_s + \dot{\sigma} = \frac{1}{T}\left(-\vec{\nabla}\cdot\vec{J}_u\right) - \sum_i \left(\frac{\mu_i}{T}\right)\left(-\vec{\nabla}\cdot\vec{J}_{c_i}\right) \quad \text{— (3)}$$

Recall from calculus:

$$\vec{\nabla}\cdot(A\vec{B}) = (\vec{\nabla}A)\cdot\vec{B} + A\vec{\nabla}\cdot\vec{B}$$

(A: scalar, $\vec{B}$: vector)

$$A\,\vec{\nabla}\cdot\vec{B} = \vec{\nabla}\cdot(A\vec{B}) - (\vec{\nabla}A)\cdot\vec{B}$$ Rearranging

$$A = \frac{1}{T} \;\&\; \vec{B} = \vec{J}_u$$

$$\Rightarrow \frac{1}{T}\vec{\nabla}\cdot\vec{J}_u = \vec{\nabla}\cdot\left(\frac{J_u}{T}\right) - \vec{\nabla}\left(\frac{1}{T}\right)\cdot\vec{J}_u \;;\; \text{Similarly for } \left(\mu_i/T\right) \& \vec{J}_{c_i}$$

Substituting into (3)

$$-\vec{\nabla}\cdot\vec{J}_s + \dot{\sigma} = -\vec{\nabla}\cdot\frac{\vec{J}_u}{T} + \vec{\nabla}\left(\frac{1}{T}\right)\cdot\vec{J}_u + \sum_i \vec{\nabla}\cdot\left(\frac{\mu_i\vec{J}_{c_i}}{T}\right) - \vec{\nabla}\left(\frac{\mu_i}{T}\right)\cdot\vec{J}_{c_i}$$

$$-\vec{\nabla}\cdot\vec{J}_s + \dot{\sigma} = -\vec{\nabla}\cdot\left(\frac{J_u - \sum_i \mu_i J_{c_i}}{T}\right) + \vec{J}_u\cdot\nabla\left(\frac{1}{T}\right) - \vec{J}_{c_i}\cdot\vec{\nabla}\left(\frac{\mu_i}{T}\right)$$

$\vec{J}_s$ (from the fundamental eq^n of thermo) — $\dot{\sigma}$

$$\vec{J}_u - \sum_i \mu_i\vec{J}_{c_i} = \vec{J}_s$$

$$\left(\vec{J}_s\right) = \frac{\vec{J}_q}{T}$$ → heat flux

analogous with the II Law of thermodynamics.

$$dS = \frac{dq}{T}$$

$\dot{\sigma}$ = rate of entropy production

$$= \vec{J}_u\cdot\vec{\nabla}\left(\frac{1}{T}\right) + \sum_i \vec{J}_{c_i}\cdot\vec{\nabla}\left(\frac{\mu_i}{T}\right)$$

$$du = \frac{dq}{V_0} + \sum_i \mu_i dc_i$$

$$\vec{J}_u = \vec{J}_q + \sum_i \mu_i\vec{J}_{c_i}$$

$$\dot{\sigma} = \vec{J}_q\cdot\vec{\nabla}\left(\frac{1}{T}\right) + \sum_i \mu_i\vec{J}_{c_i}\cdot\nabla\left(\frac{1}{T}\right) - \sum_i \vec{J}_{c_i}\mu_i\vec{\nabla}\left(\frac{1}{T}\right) - \sum_i \frac{\vec{J}_{c_i}}{T}\nabla\mu_i$$

$$\dot{\sigma} = \vec{J}_q \cdot \vec{\nabla}\left(\frac{1}{T}\right) - \sum_i \frac{\vec{J}_{c_i}}{T} \cdot \vec{\nabla}\mu_i \quad (*)$$

* entropy flux is associated with the heat flux
* entropy production is associated with gradients in intensive variables.

★ ENTROPY PRODUCTION : Conjugate forces and fluxes

$$\dot{\sigma} = \vec{J}_q \cdot \underbrace{\vec{\nabla}\left(\frac{1}{T}\right)}_{= -\frac{1}{T^2}\vec{\nabla}(T)} - \sum_i \frac{\vec{J}_{c_i}}{T} \vec{\nabla}\mu_i$$

$$T\dot{\sigma} = -\frac{\vec{J}_q}{T} \cdot \vec{\nabla}T - \sum_i \vec{J}_{c_i} \cdot \vec{\nabla}\mu_{c_i}$$

units of each term: $J/m^3/s$ ⟶ "energy dissipation density".

@ more generally $T\dot{\sigma} = -\frac{\vec{J}_Q}{T} \cdot \vec{\nabla}T - \sum_i \vec{J}_{X_i} \cdot \vec{\nabla} Y_i$ (conjugate pairs.)

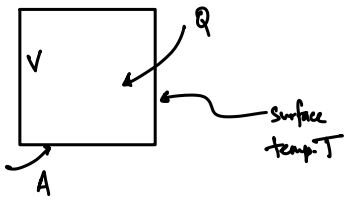
Extensive quantity	Flux	Conjugate force
Heat	$\vec{J}_q$	$-(\vec{\nabla}T)\,1/T$
Component i	$\vec{J}_{c_i}$	$-\vec{\nabla}\mu$

★ POSTULATE OF IRREVERSIBLE THERMODYNAMICS:

$$\dot{\sigma} = \frac{\partial s}{\partial t} + \vec{\nabla}\cdot\vec{J}_s \geq 0$$

entropy production rate is positive.

Example:



$$\Delta S = \int_V \int_t \frac{\partial s}{\partial t}\, dt\, dV$$

$$= \int_V \int_t \left(\dot{\sigma} - \vec{\nabla}\cdot\vec{J}_s\right) dt\, dV$$

$$= \int_V \int_t \left(-\vec{\nabla}\cdot\vec{J}_s\right) dt\, dV \Big] + \int_V \int_t \dot{\sigma}\, dt\, dV$$

from the divergence theorem.

$$\int_A \int_t -\vec{J}_s \cdot \hat{n}\, dA\, dt = \int_A \int_t -\frac{\vec{J}_Q}{T} \cdot \hat{n}\, dA\, dt = \frac{Q}{T}$$

$$\Delta S = \frac{Q}{T} + \underbrace{\int_V \int_t \dot{\sigma}\, dV\, dt}_{\geq 0 \; [\because \dot{\sigma} \geq 0]}$$

$$\Rightarrow \Delta S - Q/T \geq 0 \Rightarrow \boxed{\Delta S \geq Q/T}$$ ⟶ II Law of thermo.

★ ANOTHER POSTULATE OF IRREVERSIBLE THERMO:

$$J_Q = J_Q\left(-\frac{\nabla T}{T}, -\nabla\mu_1, -\nabla\mu_2, \cdots, -\nabla\mu_N\right)$$

$$\vdots$$

$$J_{C_i} = J_{C_i}\left(-\frac{\nabla T}{T}, -\nabla\mu_1, -\nabla\mu_2, \cdots, -\nabla\mu_N\right)$$

$$\vdots$$

→ we need gradients in intensive variables for entropy production

→ we need fluxes for there to be dynamic evolution

No gradients ⇒ No entropy production

⇒ local eqm

Taylor expand fluxes as a function of the gradients of intensive variables:

$$J_Q = -L_{QQ}\frac{\nabla T}{T} - \sum_j L_{Qj}\nabla\mu_j$$

$$J_{C_i} = -L_{iQ}\frac{\nabla T}{T} - \sum_j L_{ij}\nabla\mu_j$$

(N) in matrix form:

$$\begin{bmatrix} L_{QQ} & L_{Q1} & L_{Q2} & \cdots & L_{QN} \\ L_{1Q} & L_{11} & \cdots & & \\ \vdots & & \ddots & & \\ & & & L_{ii} & \\ & & & & L_{NN} \end{bmatrix} \begin{bmatrix} -\nabla T/T \\ -\nabla\mu_1 \\ -\nabla\mu_2 \\ \vdots \\ -\nabla\mu_N \end{bmatrix} = \begin{bmatrix} J_Q \\ J_{C_1} \\ \vdots \\ J_{C_N} \end{bmatrix}$$

→ ONSAGER RELATIONS + POSITIVE DEFINITESS OF THE MATRIX

① Assume no gradients in chemical potential:

$$J_Q = -L_{QQ}\frac{\nabla T}{T} = -\left(\frac{L_{QQ}}{T}\right)\nabla T$$

Fourier's Law: $J_Q = -\underbrace{K}_{\text{thermal conductivity}}\nabla T$ $\qquad \boxed{K = \frac{L_{QQ}}{T}}$

$$J_{C_i} = -L_{iQ}\frac{\nabla T}{T}$$

mass diffusion can be driven by thermal gradients.

② Assume both thermal & chemical potential gradients:

$$J_Q = -L_{QQ}\frac{\nabla T}{T} - \sum_j L_{Qj}\nabla\mu_j$$

→ atomic diffusion / chemical potential gradients can result in heat fluxes.