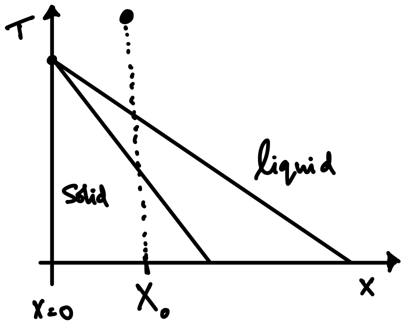
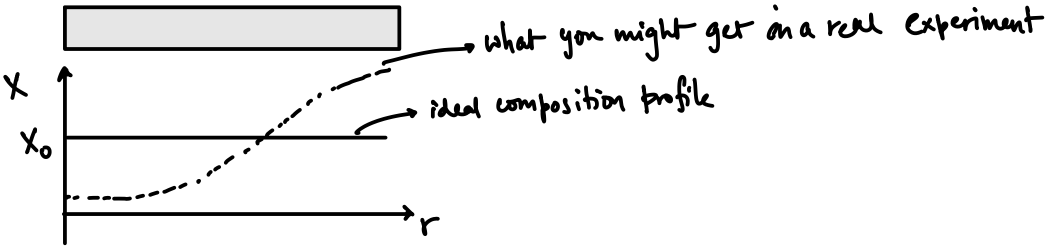
SCHEIL ANALYSIS OF SOLIDIFICATION



During solidification from a melt, there will be segregation due to slow diffusion in the solid & fast diffusion in the liquid.



ASSUME①: Phase boundaries are straight lines.

$$\text{(ie)}\ \left.\frac{T-T_{melt}}{X_s-0} = m_1 \ \&\ \frac{T-T_{melt}}{X_\ell-0} = m_2\right] \Rightarrow X_\ell = \frac{T-T_{melt}}{m_2} \text{ and } X_s = \frac{T-T_{melt}}{m_1} \Bigg] \Rightarrow \frac{X_s}{X_\ell} = \frac{m_2}{m_1} = k$$

partition coefficient

② No diffusion in the solid, infinitely quick diffusion in the liquid.

We want to derive a relationship b/w the phase fraction of S/L and the composition of the S/L

Lever Rule:

$$f_s = \frac{X_L - X_0}{X_L - X_s} \ ; \ f_L = \frac{X_0 - X_s}{X_L - X_s}$$

$$\frac{f_s}{f_L} = \frac{X_L - X_0}{X_0 - X_s} \Rightarrow f_s(X_0 - X_s) = f_L(X_L - X_0)$$

Eliminating X_2 with $X_L = \frac{X_s}{k}$

$$f_s(X_0 - X_s) = f_L\left(\frac{X_s}{k} - X_0\right) \text{ —— ①}$$

Differentiate ① wrt T:

$$\frac{df_s}{dT}(X_0 - X_s) - f_s\frac{dX_s}{dT} = \frac{df_L}{dT}\left(\frac{X_s}{k} - X_0\right) + \frac{f_L}{k}\frac{dX_s}{dT}$$

Since $f_L + f_s = 1 \Rightarrow df_L = -df_s$

$$\frac{df_s}{dT}(X_0 - X_s) - f_s\frac{dX_s}{dT} = -\frac{df_s}{dT}\left(\frac{X_s}{k} - X_0\right) + \frac{f_L}{k}\frac{dX_s}{dT}$$

$$\boxed{\frac{df_s}{dT}\left(\frac{X_s}{k} - X_s\right) = \frac{dX_s}{dT}\left(f_s + \frac{1-f_s}{k}\right)}$$

ASSUME: $f_s\frac{dX_s}{dT} \simeq 0$ [(ie) we are considering the early stages of solidification when $f_s \simeq 0$]

$$\frac{df_s}{dT}\frac{X_s(1-k)}{k} = \frac{dX_s}{dT}\frac{(1-f_s)}{k}$$

Rearranging: $$\frac{df_s}{1-f_s} = \frac{1}{1-k}\frac{1}{x_s}dx_s$$

or $$\frac{-df_L}{f_L} = \frac{1}{1-k}\frac{dx_s}{x_s}$$

$$-\int_{1}^{1-f_s}\frac{df_L}{f_L} = \left(\int_{kx_0}^{x_s}\frac{dx_s'}{x_s'}\right)\frac{1}{1-k}$$

$$-\left[\log f_L\right]_{1}^{1-f_s} = \frac{1}{1-k}\left[\log x_s'\right]_{kx_0}^{x_s}$$

$$-\log(1-f_s) = \frac{1}{1-k}\log\frac{x_s}{kx_0}$$

$$\Rightarrow \boxed{x_s = kx_0(1-f_s)^{k-1}}$$

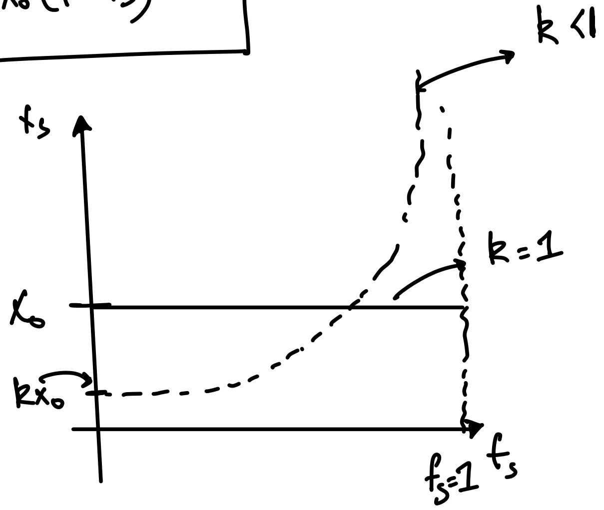
or $$\boxed{x_l = x_0(1-f_s)^{k-1}}$$

$k \le 1$, $x_s, x_l, f_s \le 1$

when $k = 1 \Rightarrow x_l = x_s = x_0 \Rightarrow$

when $k < 1$

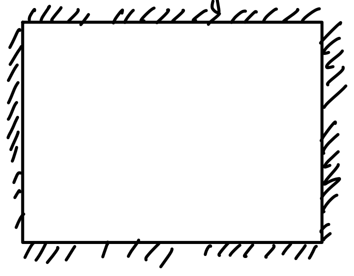
$$\Rightarrow x_s = \frac{kx_0}{(1-f_s)^{1-k}}$$



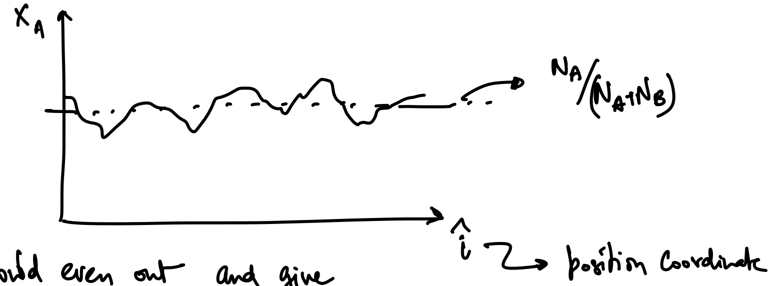
Analysis is not quite right as $f_s \to 1$, however provides a qualitative model of the solid composition.

PHENOMENOLOGICAL TREATMENT OF NON-EQUILIBRIUM PROCESSES:

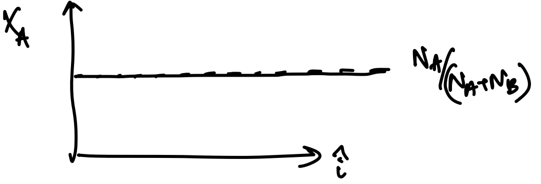
Let us consider an isolated system that is out of eq^m



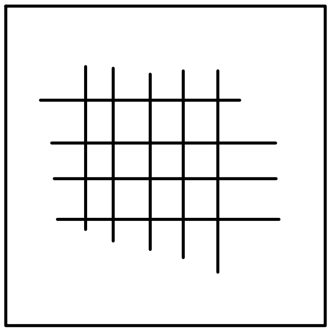
Say it contains N_A, N_B atoms with a total internal energy of $U(N_A, N_B)$



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 eq^m approximation holds as long as extensive variables vary slowly from sub region to sub region.

$$\frac{U}{V_0} = \underbrace{u(\vec{r})}_{\text{location of the sub-region}} \qquad \frac{N_i}{V_0} = c_i(\vec{r}) \qquad \frac{S}{V_0} = s(\vec{r}) \qquad \frac{N_i}{N} = X_i(\vec{r}) \rightarrow \text{mole fraction.}$$

Consider a sub-region within the larger system.

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

$\Rightarrow$ Start from the fundamental equation of thermodynamics:

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

neglect volume change for simplicity $dV = 0$

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

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

the system is overall out of $eq^m \Rightarrow$ heat and matter will flow in and out of each element

ALL LOCAL THERMODYNAMIC STATE VARIABLES WILL EVOLVE OVER TIME

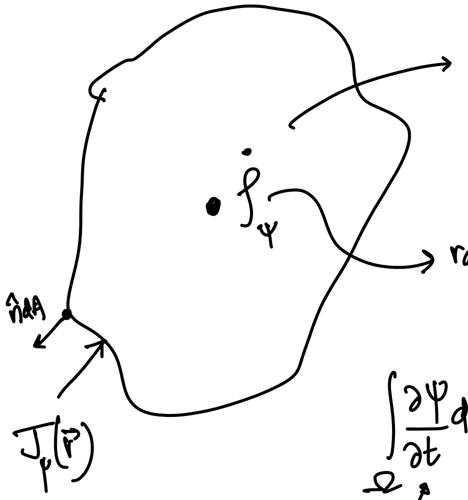
Take the time derivative of ①

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

* A BRIEF DESCRIPTION OF FLUXES, AND CONSERVATION LAWS:

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

$\psi \rightarrow$ extensive variable such as $V, c, x, \ldots, u, \ldots$



$\rightarrow$ sub-region of material.

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

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

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

Ω: the entire volume of the element

Divergence theorem:

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

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

Conserved quantities such as u, c_i ... do not have sources or sinks

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

$$\boxed{\left(\frac{\partial c_i}{\partial t}\right) = -\vec{\nabla}\cdot J_{c_i}} \rightarrow \text{"FICKS SECOND LAW"}$$

IS ENTROPY CONSERVED? NO

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

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

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

Coming back to equation ②:

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

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

Recall from calculus:

$$\vec{\nabla}\cdot(\underset{\text{Scalar}}{A}\underset{\text{vector}}{\vec{B}}) = (\vec{\nabla}A)\cdot\vec{B} + A\,\vec{\nabla}\cdot\vec{B}$$

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

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

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

Substituting into ③

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

$$-\vec{\nabla}\cdot\vec{J}_s + \dot{\sigma} = -\vec{\nabla}\cdot\underbrace{\left(\frac{J_u - \sum_i \mu_i J_{c_i}}{T}\right)}_{\vec{J}_s\ \left(\text{from the fundamental eq}^n\text{ of thermo}\right)} + \underbrace{\vec{J}_u\cdot\nabla\left(\frac{1}{T}\right) - \vec{J}_{c_i}\cdot\vec{\nabla}\left(\frac{\mu_i}{T}\right)}_{\dot{\sigma}}$$

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

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

analogous with the II Law of thermodynamics.

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

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

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

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

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

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

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

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

★ ENTROPY PRODUCTION : Conjugate forces and fluxes

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

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

@ 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.

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

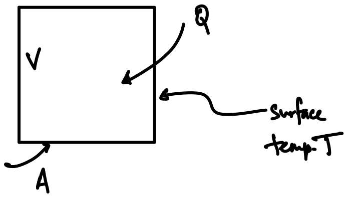
Extensive quantity	Flux	Conjugate force
Heat	$\vec{J}_q$	$-(\vec{\nabla}T)/T$
Component i	$\vec{J}_{c_i}$	$-\vec{\nabla}\mu$

★ POSTULATE OF IRREVERSIBLE THERMODYNAMICS:

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

entropy production rate is positive.

Example:



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

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

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

from the divergence theorem.

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

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

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

* ANOTHER POSTULATE OF IRREVERSIBLE THERMO:

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

$$\vdots$$

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

$$\vdots$$

→ we need gradients in intensive variables for entropy production

→ we need fluxes for there to be dynamic evolution

No gradients ⇒ No entropy production

⇒ local eq^{m}

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

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

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

or in matrix form:

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

→ 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: $J_Q = -\underline{K}\,\nabla T$

thermal conductivity.

$$\boxed{\underline{K} = \frac{L_{QQ}}{T}}$$

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

→ mass diffusion can be driven by thermal gradients.

② Assume both thermal & chemical potential gradients:

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

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