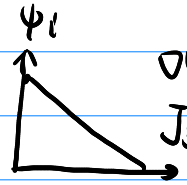
MATE664 L04

Jan-14 2026

1 Recap : driving forces in irreversible thermodyn.

$$\begin{cases} \frac{dS}{dt} = -\nabla \cdot \vec{J}_S + \dot{\sigma} & \text{entropy not conserved} \\ \frac{d\xi_i}{dt} = -\nabla \cdot \vec{J}_{\xi_i} & \xi_i \text{ conserved} \end{cases}$$

$$\begin{cases} \vec{J}_S = -\sum_i \frac{\psi_i}{T} \vec{J}_{\xi_i} \\ T\dot{\sigma} = -\sum_i \vec{J}_{\xi_i} \cdot \nabla \psi_i \end{cases}$$



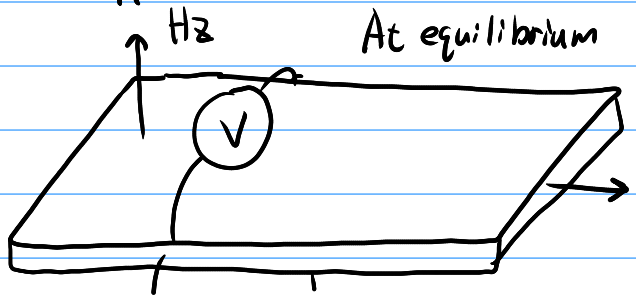
$-\vec{J}_{\xi_i} \cdot \nabla\psi \geq 0$

We have the relation between $-\nabla\psi_i$ (driving force) & flow $\vec{J}_{\xi_i}$

$$\vec{J}_{\xi_i} = \sum_j L_{ij} F_j$$

Example of orthogonal driving force & flux

Hall effect



At equilibrium $\vec{J}_y = 0$ But $\nabla\phi_y \neq 0$

Current $\vec{J}_{qx}$

(see Callen Phys Rev 1948, 73, 1349)

Current $\vec{J}_{qx}$ applied, Magneticfied $\vec{B}_z$ $\Rightarrow$ measured potential across y

$\dot{\sigma}$ for $\boxed{\vec{J}_{qx}}^{>0} \cdot \boxed{\nabla\phi_y}^{>0} = 0$ Because orthogonality

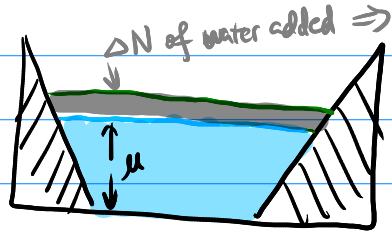
Fick's law of diffusion

chemical potential ↓

Consider 1 chemical species with μ

(chemical potential $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

Riverbank analog:)



U as total gravitational energy

$\Delta U = \Delta N \cdot \frac{m_\omega}{N_A} \cdot g \cdot \mu$

↓ change of grav. pot. ; gravity ; height

↳ $\mu = \left(\frac{\partial U}{\partial N}\right)$ .... height analog

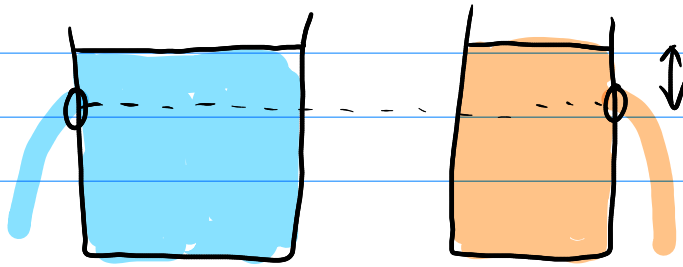
Entropy production w.r.t chemical potential

$$\begin{cases} T\dot{\sigma} = -\vec{J}_M \cdot \nabla\mu \\ \vec{J}_S = -\frac{\mu}{T} \cdot \vec{J}_M \\ \vec{J}_M = -L_{MM} \nabla\mu \end{cases} \Rightarrow T\dot{\sigma} = L_{MM} \|\nabla\mu\|^2$$

What is the coefficient L_{MM} ?

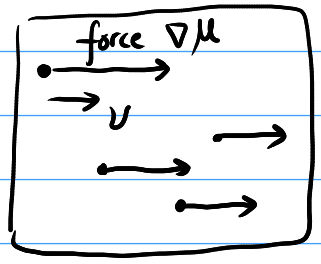
Use the tank analogy

Tank of water — tank of gasoline

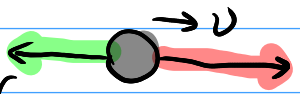


Similarly, as J_M has unit $\left[\frac{mol}{m^2 \cdot s}\right]$

we should consider the concentration of the species that is moved



Another analog:



f = friction $\propto v$

Balance $F = f \propto v$

We use mobility $\mathcal{M}$ to denote relation between $\nabla\mu$ and v

$$v = \mathcal{M} \cdot \nabla\mu$$

So diffusion eq is

$$J = -\mathcal{M} c \nabla\mu$$

L_{MM}

Where does Fick's term come from?

For <NPT> system (general chemistry) μ can be also expressed linked to Gibbs F.E G

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$ If in a mixture with molar fraction x_i

$$\Delta G(x_i) = \Delta G(x_i = 1) + T\Delta S_{mix}$$
$$= \underbrace{\Delta G^\circ}_{\text{Reference}} + T k_B \ln(\gamma_i x_i) \cdot N_i$$

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{x_i} = \mu^\circ + k_B T \ln(\gamma_i x_i)$$

γ_i: Counting for non-ideal case

For ideal solution $\gamma_i = 1$

$$\mu \simeq \mu^\circ + k_B T \ln x_i$$
$$= \mu^\circ + k_B T \ln \frac{c_i}{c}$$

So rewrite $J \Rightarrow J_i = -u_i c_i \nabla \mu_i$

$$= -u_i c_i \nabla\left(\mu^\circ + k_B T \ln \frac{c_i}{c}\right)$$
$$= -u_i c_i \cdot k_B T \cdot \frac{1}{c_i} \nabla c_i$$
$$= -\boxed{u_i k_B T} \nabla c_i$$

$\downarrow$ Fick's Diffusivity D

Consider:

① Do D depend on T ?

② Do D depend on c ?

③ Can D be spatially varied ?

Using conjugate relation between $\xi_i \longrightarrow \psi_i$

In diffusive mass transfer

$\begin{cases} \xi_i \rightarrow c_i \\ \psi_i \rightarrow \mu_i \end{cases}$

Fick's term ∇c_i is a special case of $\frac{1}{c_i} \nabla \mu_i$

Fick's second law

General flux eq. for concentration

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \vec{J}_i + \dot{C}_i$$

$\dot{C}_i$: production (e.g. chemical reaction)

If no $\dot{C}$ $\Rightarrow$ $\frac{\partial C_i}{\partial t} = -\nabla \cdot \vec{J}_i$

$$= -\nabla \cdot (-D \nabla C_i)$$

If D is spatially invariant ($D(x,y,z) = \text{const}$)

$$\frac{\partial C_i}{\partial t} = \nabla^2 C_i \cdot D$$

∇^2: Laplace operator

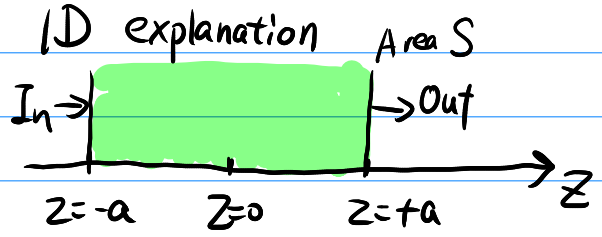
1D case

$$\frac{\partial C_i}{\partial t} = \frac{d^2 C_i}{dx^2} \cdot D$$

(Laplace operator

$$\nabla^2 u = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}$$)

1D explanation



In − Out = Accumulation

$$S(J_{z=-a} - J_{z=+a}) = \frac{\partial C_i}{\partial t} \cdot S \cdot 2a$$

$$-D \frac{dC_i}{dx_i}\Big|_{-a} - \left(-D \frac{dC_i}{dx_i}\right)\Big|_{+a} =$$

$$D\left(\frac{dC_i}{dx_i}\Big|_a - \frac{dC_i}{dx}\Big|_{-a}\right) = \frac{\partial C_i}{\partial t} \cdot 2a$$

$$D \cdot \frac{\Delta\left(\frac{dC_i}{dx_i}\right)}{\Delta x} \cdot 2a = \frac{\partial C_i}{\partial t} \cdot 2a$$

$$\frac{d^2 C_i}{dx^2}$$

Compare 1st & 2nd law of Fick

1st: $\vec{J}_i = -D_i \nabla C_i \Rightarrow$ (Coordinate only)

2nd $\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i) \Rightarrow$ (coordinat & time)

$= D_i \nabla^2 C$ (isotropic, spatially invariant)

① Steady state $\frac{\partial C_i}{\partial t} = 0 \Rightarrow \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) C_i = 0$

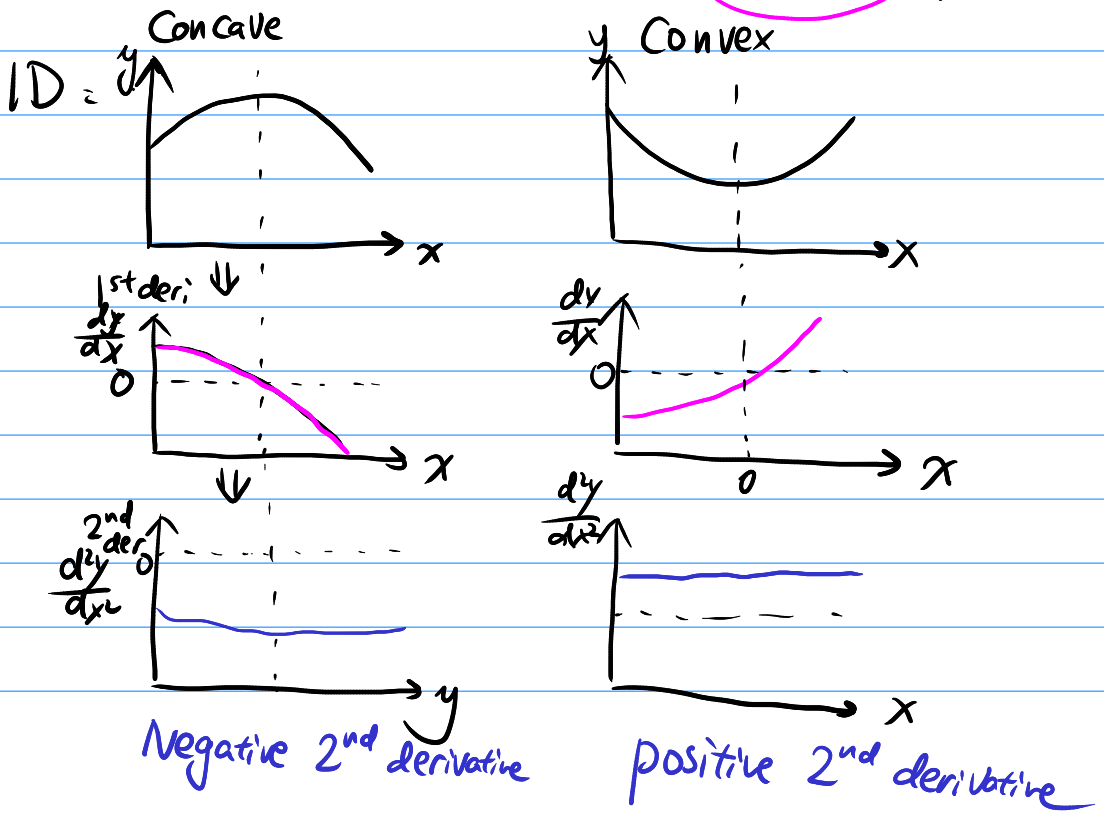
Each should have $\frac{\partial^2 C_i}{\partial x^2} = \frac{\partial^2 C_i}{\partial y^2} = \frac{\partial^2 C_i}{\partial z^2} = 0$

$\frac{\partial^2 C_i}{\partial x^2} = 0 \Rightarrow \frac{\partial C_i}{\partial x} = \text{const} \Rightarrow \nabla C_i = \left(\frac{\partial C_i}{\partial x}, \frac{\partial C_i}{\partial y}, \frac{\partial C_i}{\partial z}\right)$ is const.

⇓ Linear C profile in (x,y,z)
first law

② What do $\nabla^2 C_i$ actually mean?

Laplace operator is linked to curvature of smooth func



Negative 2nd derivative

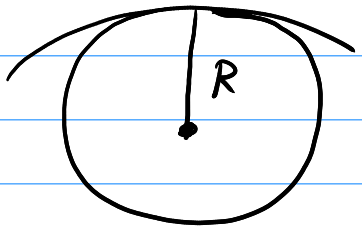
positive 2nd derivative

Tian's memorization for curve shape, 2nd derivative & Curvature

Curve shape		
Name	ConcAve	ConVex
2nd derivative $\frac{d^2y}{dx^2}$ (Left + Right − 2*center)	negative	positive
Curvature	negative	positive

direction of dragging to flat

Geometric explanation of curvature



In every principle direction

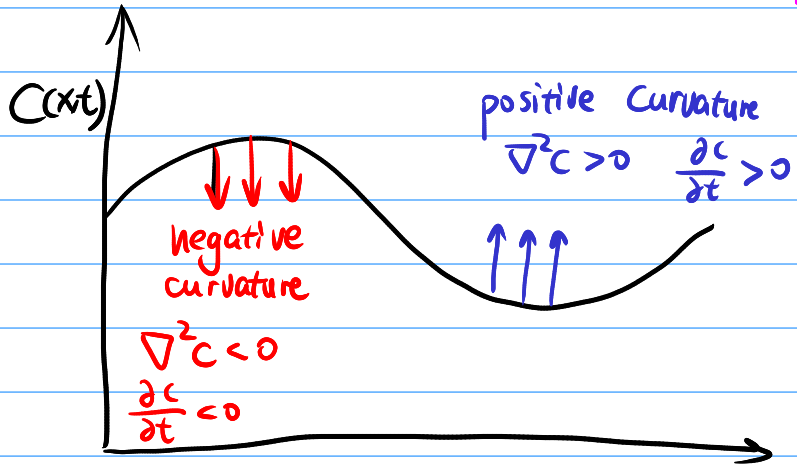
$$\|k\| = \frac{1}{R}$$

Sign of k

If we sit at center of circle

negative k → towards us

Balluffi fig 4.1



How large are D ?

Gas $\simeq 10^{-5}\ m^2/s$ Liquid $< 10^{-10}\ m^2/s$

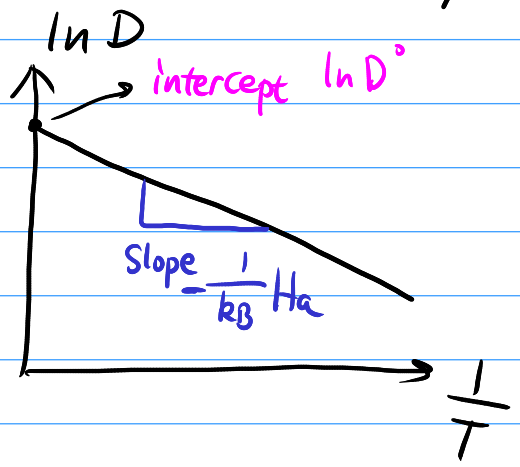
Solid $< 10^{-9}\ m^2/s$

Temperature factor !!

In solid & liquid diffusion, we may use Arrhenius-type rate equation

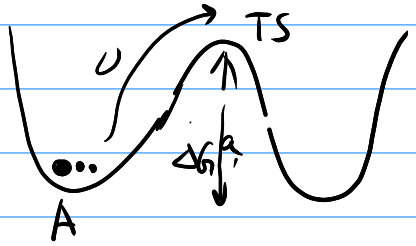
$$D = D^\circ \exp\left(-\frac{Ha}{k_B T}\right)$$

$$\ln D = \ln D^\circ - \frac{Ha}{k_B} \cdot \frac{1}{T}$$



Ha : activation enthalpy (why ?)

Physical Intepretation



Frequency at A & TS

A state "attempts" to jump with frequency υ over barrier ΔG^a

Frequency that A jumps over barrier

$$\Gamma = \upsilon e^{-\frac{\Delta G^a}{k_B T}}$$

Diffusivity model typically has relation

$$D_I \propto \Gamma \cdot \langle r \rangle^2$$

↑ average dist between jumped sites

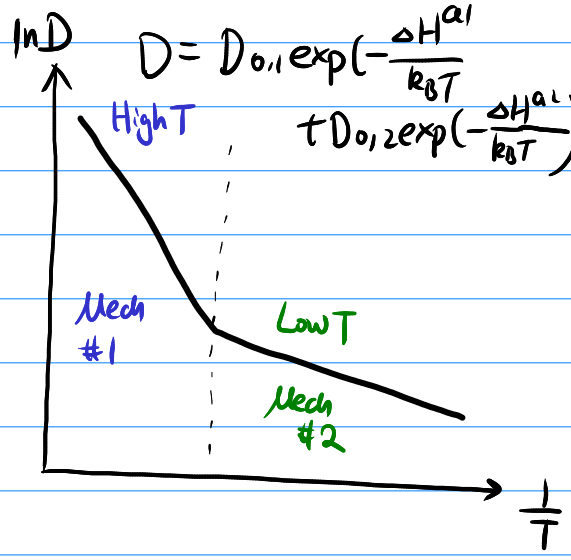
$$D \propto r^2 \nu \exp\left(-\frac{\Delta G^a}{k_B T}\right)$$

$$\propto r^2 \nu \exp\left(-\frac{\Delta H^a - T\Delta S^a}{k_B T}\right)$$

$$\propto r^2 \nu \exp\left(\frac{\Delta S^a}{k_B T}\right) \exp\left(-\frac{\Delta H^a}{k_B T}\right)$$

D° (with some factor)

$$D = D^\circ \exp\left(-\frac{\Delta H^a}{k_B T}\right)$$ Arrhenius-like equation (in other words ΔS^a is independent of T)



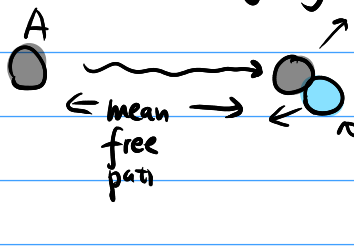
$D = D_{0,1} \exp\left(-\frac{\Delta H^{a1}}{k_B T}\right) + D_{0,2} \exp\left(-\frac{\Delta H^{a2}}{k_B T}\right)$ System with multiply kinetic ΔH^a

In general there may be multiply mechanisms / diffusion sites co-existing in the system !

Plotting Arrhenius-like curve always need to consider the mechism !

Mechanism / Atomistic Model for Diffusion

Gas molecules : usually by kinetic theories of gases



Movement of particle is disrupted by collision

Chapman-Enskog theory $D_{AB} \propto T^{1.5} \left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{\frac{1}{2}} \cdot \frac{1}{P} \cdot \frac{1}{\sigma_{AB}^2}$

D_{AB}: interdiffusivity A in B

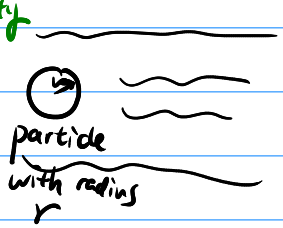
Liquid phase

Stokes-Einstein equation

$D = k_B T \cdot \mu$ (from revised Fick)

μ: mobility

$= k_B T \cdot \frac{1}{6\pi\eta r}$



η: dynamic viscosity

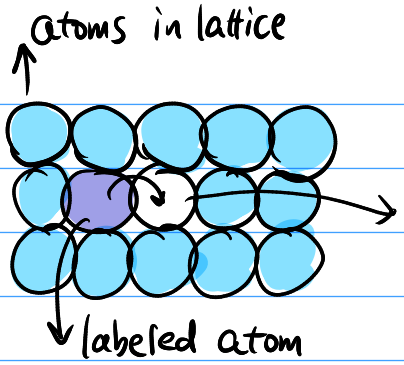
OR $D = \frac{\mu_q k_B T}{q}$

μ_q: electrical mobility in charged particles (salt solution semiconductor ?)

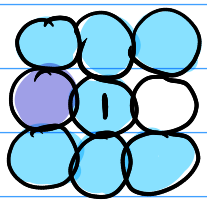
Diffusion in solid

Multiple mechanisms exist !

One example: vacancy mechanism



purple atom can jump to vacancy site only if they're adjacent !



⇒ purple atom cannot jump to vacancy !
Only after atom labeled 1 swap with vacancy

In vacancy mechanism, multiple "sources" { vacancies can be generated by
- Surface
- Grain boundary (GB)
- dislocation

We also need to distinguish different "Diffusivities"

Self-diffusivity $^*D$ = atoms diffuse through homogeneous medium

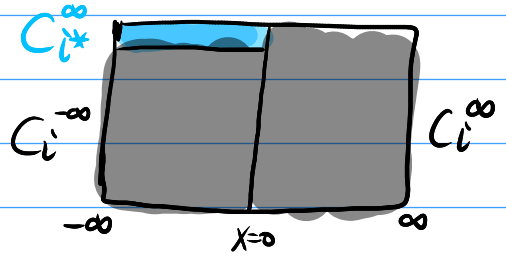
Intrinsic diffusivity D_i = diffusivity measured locally in chemically inhomogeneous medium (from local frame)

Inter diffusivity $\tilde{D}$ = diffusivity in inhomogeneous medium (from lab frame)

How to measure Self-diffusivity?

Use radioactive lable

Fluxes for { Normal species → i ; Isotope → i^* ; Vacancy → V



The lattice does not change during self diffusion.

① All sites must be occupied by either i, i^* or V

$$\Rightarrow \quad dC_i + dC_i^* + dC_V = 0 \qquad dC_V = -dC_i - dC_i^*$$

1st law becomes

$$Tds = du + dw - \mu_i dC_i - \mu_{i^*} dC_i^* - \mu_V dC_V$$

$$= \cdots \quad \cdots \quad \cdots \quad \cdots - \mu_V(-dC_i - dC_i^*)$$

$$= du + dw - (\mu_i - \mu_V) dC_i - (\mu_i^* - \mu_V) dC_{i^*}$$

In such **network-constrained** system, identify Flux, Driving Force

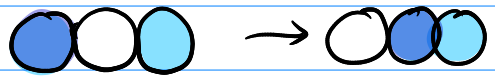
Flux	D.F.
$\vec{J}_i$	$-\nabla(\mu_i - \mu_V)$
$\vec{J}_{i^*}$	$-\nabla(\mu_{i^*} - \mu_V)$

Symmetry ⟹ 1D

$$J_i = -L_{ii} \frac{\partial(\mu_i - \mu_V)}{\partial x} - L_{ii^*} \frac{\partial(\mu_{i^*} - \mu_V)}{\partial x}$$

$$J_{i^*} = -L_{i^*i} \frac{\partial(\mu_i - \mu_V)}{\partial x} - L_{i^*i^*} \frac{\partial(\mu_{i^*} - \mu_V)}{\partial x}$$

Flux of vacancy?



$\leftarrow J_V$

$$J_i + J_{i^*} + J_V = 0$$

Assumptions: {
- Vacancies only account for negligible portion $x_V \approx 0$
- Vacancy chem potential $\mu_V = 0$ (equilibrium for V)
- i, i^* mixing follows $\gamma_i = \gamma_{i^*} = 1$ (Raoult's law)

We thus have ($\mu_i = \mu_i^\circ + k_B T \ln C_i \Rightarrow \frac{\partial \mu_i}{\partial x} = \frac{k_B T}{C_i}\frac{\partial C_i}{\partial x}$)

$$\frac{\partial \mu_i^*}{\partial x} = -\frac{\partial \mu_i}{\partial x}$$

$$J_i = -k_B T \left[\frac{L_{ii}}{C_i} - \frac{L_{ii^*}}{C_{i^*}}\right]\frac{\partial C_i}{\partial x}$$

$$J_{i^*} = -k_B T \left[\frac{L_{i^*i^*}}{C_{i^*}} - \frac{L_{i^*i}}{C_i}\right]\frac{\partial C_{i^*}}{\partial x}$$

$J_V = 0$ (vacancies at equilibrium)

$$J_i + J_{i^*} = 0 \Rightarrow J_{i^*} = -J_i = k_B T \left[\frac{L_{ii}}{C_i} - \frac{L_{ii^*}}{C_{i^*}}\right]\frac{\partial C_i}{\partial x}$$

$-\frac{\partial C_{i^*}}{\partial x}$

$$= -\left[k_B T \left[\frac{L_{ii}}{C_i} - \frac{L_{ii^*}}{C_{i^*}}\right]\right]\frac{\partial C_{i^*}}{\partial x}$$

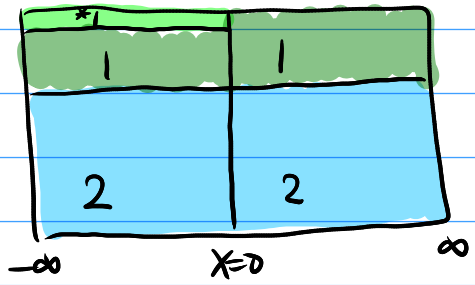
$*D$

If we consider concentration of "chemical species" there is no chemical conc gradient

But chemical potential is variant !

Why self diffusion happens $\Rightarrow$ maximizing entropy

The results can be obtained for isotope self diffusion in homogeneous binary mixture



Again even 4 species 1, 1*, 2, V are moving, we have fixed lattice plane so

$$J_{1^*} = -k_B T \left[\frac{L_{11}}{c_1} - \frac{L_{11^*}}{c_{1^*}} \right] \frac{\partial c_{1^*}}{\partial x}$$

$^*D_1$ (self diffusivity of 1 in binary)

Summary:
self diffusion happens as result of random walk (even if no chemical inhomogenity)

We'll see how to deal with systems having lattice change during diffusion