MATE664 L05
Jan-19 2026

1. Recap :

Diffusion ⟵ Driving force μ

Homogeneous medium $D = M\cdot k_B T$

$$\underbrace{J}_{\text{Flux}} = c\cdot v = M\cdot c\cdot\underbrace{\nabla\psi}_{\text{driving force}}$$

Fick's 1st law

$$J = -D\nabla c$$

Fick's 2nd law

$$J = -\nabla\cdot(D\nabla c)$$

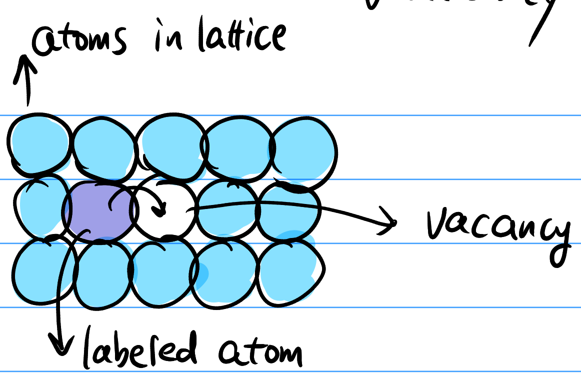
$= D\nabla^2 c$ in homogeneous medium

D values for solid ?

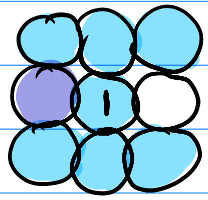
Which reference to use ?

what can affect D?

Vacancy mechanism Cont.ed



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, vacancies can be generated by multiple "sources"

- Surface
- Grain boundary (GB)
- dislocation

We also need to distinguish different "Diffusivities"

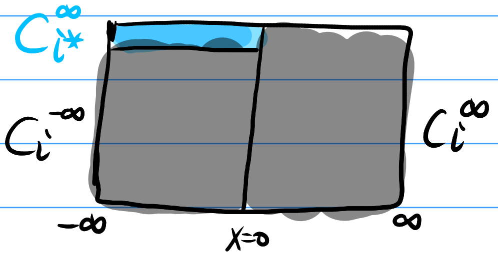
Self-diffusivity $^*D$: atoms diffuse through homogeneous medium

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

Interdiffusivity $\tilde{D}$: 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

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

$$= \text{''} \quad \text{''} \quad \text{''} \quad \text{''} \quad -\mu_V(-dc_i - dc_i^*)$$

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

In such $\boxed{\text{network-constrained}}$ system, identify Flux, Driving Force

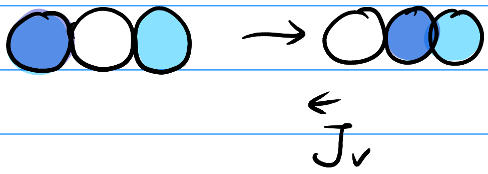
Flux	D.F.
$\vec{J}_i$	$-\nabla(\mu_i - \mu_v)$
$\vec{J}_{i^*}$	$-\nabla(\mu_{i^*} - \mu_v)$

$$\xrightarrow[\text{1D}]{\text{Symmetry}}$$

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

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

Flux of vacancy?



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

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

We thus have $\left(\begin{array}{l} \mu_i = \mu_i^0 + k_BT \ln c_i \Rightarrow \frac{\partial \mu_i}{\partial x} = \frac{k_BT}{c_i}\frac{\partial c_i}{\partial x} \\ \frac{\partial \mu_i^*}{\partial x} = -\frac{\partial \mu_i}{\partial x} \end{array} \right)$

$$J_i = -k_BT\left[\frac{L_{ii}}{c_i} - \frac{L_{ii^*}}{c_{i^*}}\right]\frac{\partial c_i}{\partial x}$$

$$J_{i^*} = -k_BT\left[\frac{L_{i^*i^*}}{c_{i^*}} - \frac{L_{i^*i}}{c_i}\right]\frac{\partial c_{i^*}}{\partial x}$$

$J_V = 0$ (vacancies at equilibrium)

$$J_i + J_{i^*} = 0 \Rightarrow J_{i^*} = -J_i = k_BT\left[\frac{L_{ii}}{c_i} - \frac{L_{ii^*}}{c_{i^*}}\right]\boxed{\frac{\partial c_i}{\partial x}} \leftarrow -\frac{\partial c_{i^*}}{\partial x}$$

$$= -\boxed{k_BT\left[\frac{L_{ii}}{c_i} - \frac{L_{ii^*}}{c_{i^*}}\right]}\frac{\partial c_{i^*}}{\partial x}$$

${}^*D$ → are L_{ii} & L_{ii^*} the same ?

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

But chemical potential is variant !

Why self diffusion happens ⇒ maximizing entropy

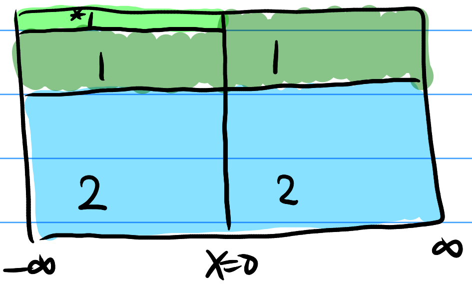
we would assume $L_{ii} \approx L_{ii^*}$ pure $\frac{L_{ii}}{c_i} - \frac{L_{ii^*}}{c_{i^*}}$

But $c_i \gg c_i^*$

$$J = -M_i c_i \nabla \mu_i$$
$$= L_{ii}(-\nabla \mu_i)$$

$L_{ii} = \mu_i c_i \Rightarrow \frac{L_{ii}}{c_i} = \mu_i$ But $\frac{L_{ii^*}}{c_i^*} \neq M_{i^*}$.

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

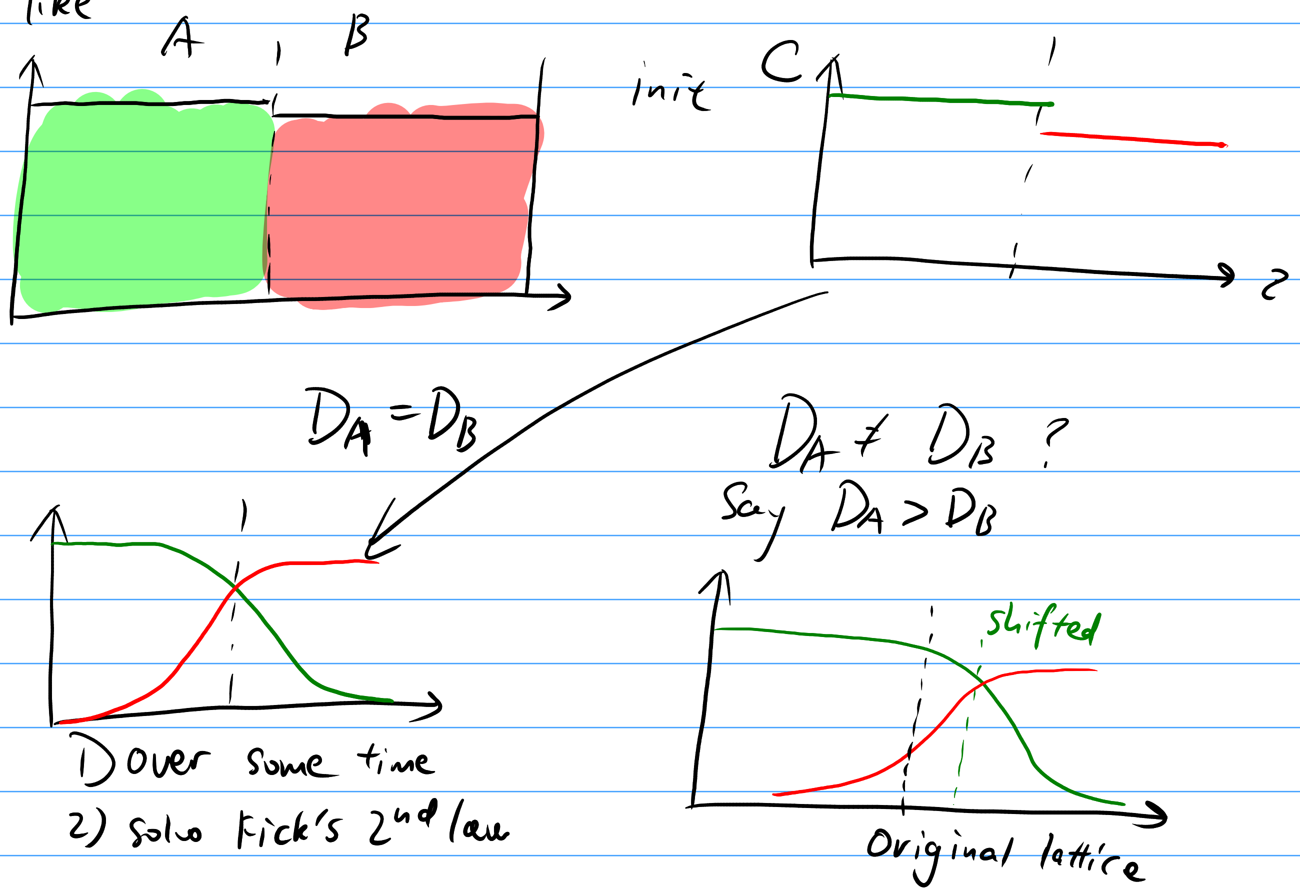
$$J_{1^*} = \underbrace{\boxed{-k_B T \left[\frac{L_{11}}{c_1} - \frac{L_{11^*}}{c_{1^*}} \right]}}_{{}^*D_1 \text{ (self diffusivity of 1 in binary)}} \frac{\partial c_{1^*}}{\partial x}$$

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 => interdiffusion

Interdiffusion of Binay systems

Consider diffusion pair A-B, what will profile looks like



$D_A = D_B$

1) over some time
2) solve Fick's 2nd law

$D_A \neq D_B$?
Say $D_A > D_B$

Intrinsic $D_A > D_B \Rightarrow J_A > -J_B$

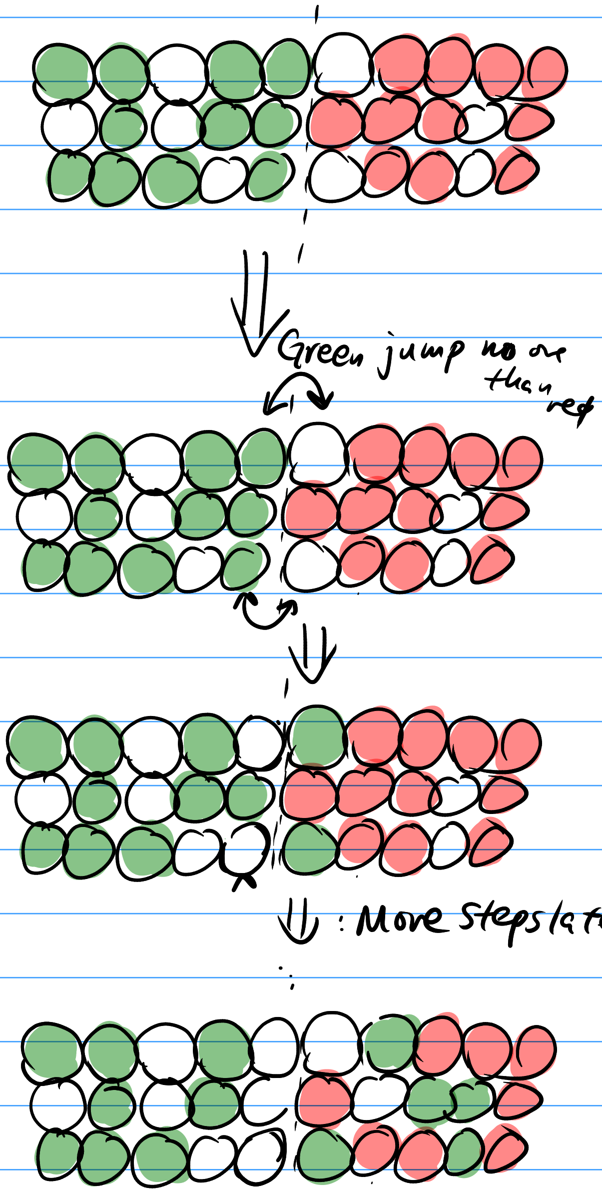
net accumulation on the B side

(First exp Boyle

According to Barr [11], perhaps Robert Boyle (1627 – 1691) reported the first clear experimental evidence for solid-state diffusion in a study called'The Porosity of Bodies'. He observed the penetration of a 'solid and heavy body', probably zinc in a small coin of copper. The side of the coin exposed to zinc took a golden colour, while the other side kept its original colour. He also observed that 'the golden colour had penetrated a pretty way beneath the surface of the coin'. It appears that Boyle has observed the formation of brass by solid-state diffusion between zinc and copper.

Consider vacancy mechanism

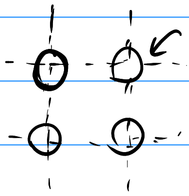
① we don't allow lattice param to change
② we can swap sites with vacancy
③ Maybe interdiffusion isn't eq for vacancy?



① where is A : B interface?
② How do vacancies move?

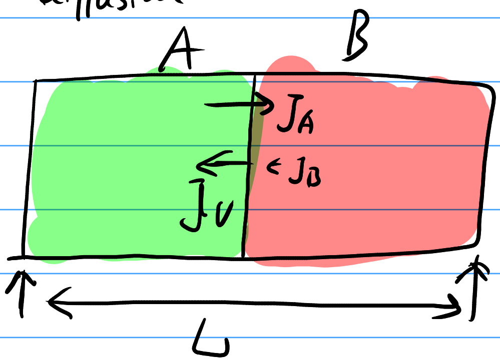
Semi quantitatively, at the local (crystal frame

$$\vec{J}_A^{\,c} + \vec{J}_B^{\,c} + \vec{J}_V^{\,c} = 0$$ still satisfies (In − Out = 0)



relative to this site, total flux = 0

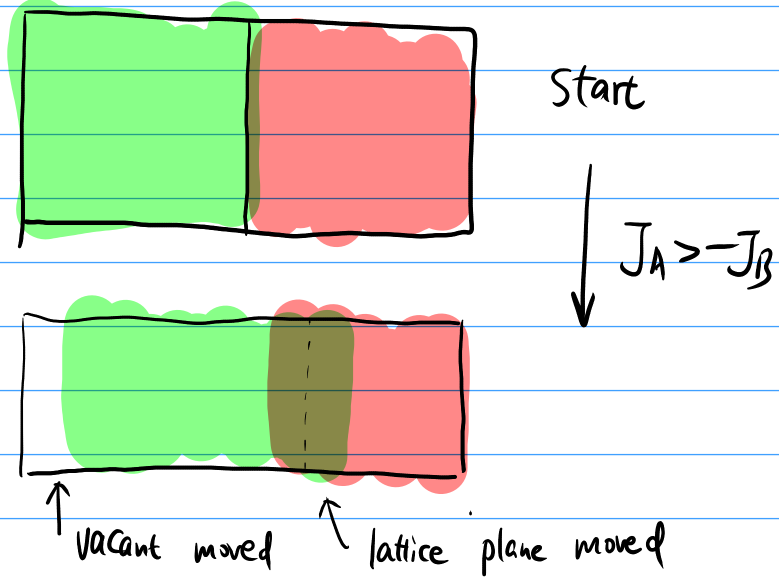
We need to acknowledge lattice change due to diffusion



As $J_A + J_B + J_V = 0$

But $J_A > -J_B$

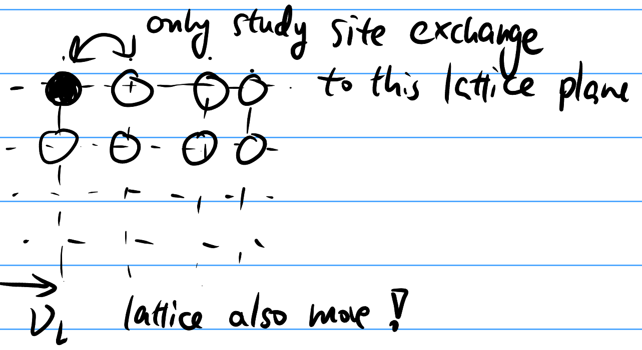
we have $\vec{J_V}$ opposite to fast diffusing component



We have 2 types of reference frames now available

① crystal frame (C)

② volume-fixed frame (V)



Let's see fluxes in C-frame (denote J^c

Use the same condition in self-diffusivity

3 components 1, 2, V

$$J_1^c = -L_{11}\frac{\partial(\mu_1-\mu_v)}{\partial x} - L_{12}\frac{\partial(\mu_2-\mu_v)}{\partial x}$$

$$J_2^c = -L_{21}\frac{\partial(\mu_1-\mu_v)}{\partial x} - L_{22}\frac{\partial(\mu_2-\mu_v)}{\partial x}$$

$$J_v^c = -(J_1^c + J_2^c)$$

Now we have concentration C_1 C_2 varied !

Change of μ_i by n_i in multi-component system

↓ Gibbs-Duhem eqn (local equilibrium)

$$\sum_i n_i d\mu_i = 0$$

$$\Downarrow$$

$$\sum_i c_i d\mu_i = 0$$

Because $U = ST - pV + \sum \mu_i \cdot n_i$

$$dU = SdT + \cancel{Tds} - \cancel{pdV} - Vdp + \cancel{\sum \mu_i dn_i} + \sum n_i d\mu_i$$

And we know

$$dU = \cancel{Tds} - \cancel{pdV} + \cancel{\sum \mu_i dn_i}$$

$$\sum n_i d\mu_i = -\underset{\substack{\Downarrow \\ 0 \text{ const } T}}{SdT} + \underset{\substack{\Downarrow \\ 0 \text{ const } p}}{Vdp}$$

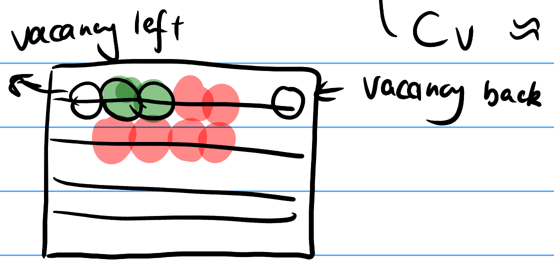
$$C_1\frac{\partial \mu_1}{\partial x} + C_2\frac{\partial \mu_2}{\partial x} + C_v\frac{\partial \mu_v}{dx} = 0$$

At C-frame, the vacancies move fast enough

equilibrated by sinks / sources (e.g. dislocations)

can be regarded $\mu_v = 0$

$C_v \approx C_v^{eq}$



Cont.d

$$c_1 \frac{\partial \mu_1}{\partial x} + c_2 \frac{\partial \mu_2}{\partial x} = 0 \Rightarrow \frac{\partial \mu_2}{\partial x} = -\frac{c_1}{c_2} \frac{\partial \mu_1}{\partial x}$$

$$\Rightarrow J_1^c = -L_{11} \frac{\partial \mu_1}{\partial x} - L_{12} \cdot \left(-\frac{c_1}{c_2}\right) \cdot \frac{\partial \mu_1}{\partial x}$$

$$= -\left[L_{11} - L_{12} \frac{c_1}{c_2}\right] \frac{\partial \mu_1}{\partial x}$$

similarly $J_2^c = -\left[L_{22} - L_{21} \frac{c_2}{c_1}\right] \frac{\partial \mu_2}{\partial x}$

We just want to see

$J_1^c = f(c_1)$ possible ?

General rel. between μ & c

molar fraction

$$\mu_i = \mu_i^0 + k_B T \ln(\gamma_i \cdot x_i)$$

activity coeff

$$= \mu_i^0 + k_B T \ln(\gamma_i \langle \Omega \rangle c_i)$$

$$\Rightarrow \frac{\partial \mu_i}{\partial x} = \frac{\partial k_B T \ln(\gamma_i \langle \Omega \rangle c_i)}{\partial x}$$

$$= \frac{\partial}{\partial x}\left[k_B T(\ln \gamma_i + \ln\langle \Omega \rangle + \ln c_i)\right]$$

$$= \frac{\partial}{\partial \ln c_i}\left[k_B T(\ln \gamma_i + \ln\langle \Omega \rangle + \ln c_i)\right] \cdot \frac{\partial \ln c_i}{\partial x} \quad \text{(chain rule)}$$

$$= k_B T\left(\frac{\partial \ln \gamma_i}{\partial \ln c_i} + \frac{\partial \ln\langle \Omega \rangle}{\partial \ln c_i} + 1\right) \cdot \frac{1}{c_i} \frac{\partial c_i}{\partial x}$$

$$= k_B T\left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} + \frac{\partial \ln\langle \Omega \rangle}{\partial \ln c_i}\right) \cdot \frac{1}{c_i} \frac{\partial c_i}{\partial x}$$

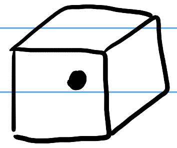
Dimensionless

$c_i \Leftarrow \frac{\text{avg } N\#}{\text{site}}$

$\langle \Omega \rangle \Leftarrow \frac{1}{\text{Vol frac}}$

$\langle \Omega \rangle = V^{tot} / N^{tot}$

$\langle \Omega \rangle$: average site volume



↑ volume $\langle \Omega \rangle \Rightarrow \frac{[\text{vol}]}{[\text{sites}]}$

$c_i \leftarrow$ KoM book fashion

number density

[particles]/[volume]

$x_i = [\text{particles}]/[\text{sites}]$

$= \langle \Omega \rangle \cdot c_i$

If use SI units

$c_i \Rightarrow [\text{mol}]/[\text{volume}]$

$\langle \Omega \rangle \Rightarrow [\text{volume}]/[\text{sites}]$

$x_i = c_i \cdot \Omega / N_A$

↖ avogadro N#

$$J_1^C = -k_BT \cdot \left(L_{11} - \frac{c_1}{c_2} L_{12} \right) \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} + \frac{\partial \ln \langle \Omega \rangle}{\partial \ln c_i} \right) \cdot \frac{1}{c_i} \frac{\partial c_i}{\partial x}$$

$$= \boxed{-k_BT \left(\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2} \right) \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} + \frac{\partial \ln \langle \Omega \rangle}{\partial \ln c_i} \right)} \frac{\partial c_i}{\partial x}$$

$\Downarrow$

D_1 (intrinsic diffusivity ; C-frame)

Comparison

Naive Fick (1 comp)

$$J = -L_{11} \frac{\partial \mu}{\partial x}$$

$$= - \underbrace{\boxed{\frac{L_{11} \cdot k_BT}{c}}}_{D} \frac{\partial c}{\partial x}$$

Self Diffusivity

$$J_1^* = \underbrace{\boxed{-k_BT \left[\frac{L_{11}}{c_1} - \frac{L_{11}^*}{c_1^*} \right]}}_{D_1^*} \frac{\partial c_1^*}{\partial x}$$

It means in C-frame, we have the intrinsic diffusivity related to self-diffusivity

$$D_1 = \boxed{k_BT \left(\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2} \right)} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} + \underbrace{\frac{\partial \ln \langle \Omega \rangle}{\partial \ln c_1}}_{\text{average } \langle \Omega \rangle \text{ conc-independent}} \right)$$

if L_{12}/c_1 is small

$$\doteq D_1^* \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln c_1} \right)$$

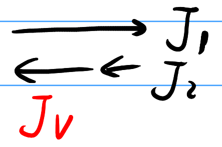
We cannot assume $\gamma_1 = 1$!

(Intrisic diffusivity is self-diffusity but considering mixing activity coeff)

Summary: In all C-frame cases, diffusivity has fick term!

Interdiffusion : V-frame

We know that at C-frame,

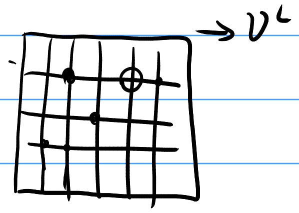


{ vacancy must have a flux.
  c_v μ_v inside diffusion regime is also const.

Contradiction?

No, what's happening is

$$J_v^c = \underbrace{-D_v \frac{dc_v}{dx}}_{\Downarrow \ \text{zero}} + \underbrace{c_v \cdot v_{Ref}^c}_{\Downarrow \ \text{non-zero!}}$$



Vacancies experience a drift velocity in C-frame

⇅

Lattice plane (in lab frame) moves oppositely to J_v^c

The lattice plane must move with velocity v!

Without specifying, we can write

$$J_1^V = J_1^C + C_1 v$$
$$J_2^V = J_2^C + C_2 v$$

How do we know v?
Use volume conservation

What is J_v^V?

$$J_1^V = \frac{[\text{amount}]}{[\text{Area}][\text{time}]} \qquad J_1^V \cdot \Omega_1 \Rightarrow \text{vol change by 1-flux}$$

volume fraction of 1

$$J_1^V \Omega_1 + J_2^V \Omega_2 = 0 \quad (\text{Because } C_1\langle\Omega_1\rangle + C_2\langle\Omega_1\rangle = 1)$$

$$\Rightarrow \left(-D_1 \frac{dc_1}{dx} + c_1 v\right) \cdot \Omega_1 + \left(-D_2 \frac{dc_2}{dx} + c_2 v\right) \cdot \Omega_2 = 0$$

Cont.d

$$\Rightarrow \left(-D_1 \cdot \frac{dc_1}{dx} + c_1 v\right)\cdot \Omega_1 + \left(-D_2 \frac{dc_2}{dx} + c_2 v\right)\cdot \Omega_2 = 0$$

$$-D_1 \Omega_1 \frac{dc_1}{dx} + \boxed{c_1\Omega_1}\, v - D_2\Omega_2 \frac{dc_2}{dx} + \boxed{c_2\Omega_2} \cdot v = 0$$

$c_1\Omega_1 + c_2\Omega_2 = 1$

$$\Rightarrow v = D_1\Omega_1 \frac{dc_1}{dx_1} + D_2\Omega_2 \frac{dc_2}{dx} \quad \left(\text{also } \Omega_1 dc_1 = -\Omega_2 dc_2 \;.\right)$$

$$= (D_1 - D_2)\, \Omega_1 \frac{dc_1}{dx_1}$$

This is the latice drift in the V-frame ?

Sign ? $D_1 > D_2$ $v > 0$ ⇒ lattice plane drift to right ✓

Eventually, we want a V-frame flux equ.

$$J_1^V = \boxed{\text{C-diff}} + \boxed{\text{V-drift}}$$

$$= -D_1 \frac{\partial c}{\partial x} + v \cdot c_1$$

$$= -D_1 \frac{\partial c}{\partial x} + (D_1 - D_2)\cdot \Omega_1 \cdot c_1 \cdot \frac{\partial c_1}{\partial x}$$

$$= -\left(D_1 - (D_1 - D_2)\cdot \Omega_1 \cdot c_1\right) \frac{\partial c_1}{\partial x}$$

$$= -\left(D_1 \Omega_2 \cdot c_2 + D_2 \Omega_1 c_1\right) \frac{\partial c_1}{\partial x}$$

$$= -\left(D_1 X_2 + D_2 X_1\right) \cdot \frac{\partial c_1}{\partial x}$$

molar fraction

$$= -\tilde{D} \frac{\partial c_1}{\partial x}$$

So $J_1^V = -\tilde{D}\frac{\partial c_1}{\partial x}$

symmetry ⇒ $J_2^V = -\tilde{D}\frac{\partial c_2}{\partial x}$ ($J_V^V = 0$!)

$\tilde{D}$ => interdiffusivity

$$= \underbrace{D_1}_{\text{intrinsic } D_1}\underbrace{\Omega_2 c_2}_{\text{fraction } 2} + D_2\Omega_1 c_1$$

Summary:

1' C-frame ⇒ 1 & 2 have different diffusivity (intrinsic)
frame drift seen for vacancy

2' V-frame ⇒ Only 1 diffusivity interdiff
frame velocity implicit

(Undergrad mass transfer course

$$N_A = -D_A\frac{dc}{dx} + (N_A + N_B)\cdot c/c_T$$)

What effect do we see from lattice drift?

- Kirkendall effect

Interstitial diffusion

fast moving particle $\Longrightarrow$ immobile solvent

Interdiffusivity $\tilde{D} = D_1 \Omega_2 C_2 + \underset{\Rightarrow 0}{\cancel{D_2}} \Omega_1 C_1$

$= D_1 \Omega_2 C_2$