Diffusion

Macroscopic picture (Fick 1880)

1st law: $J = -D \nabla C$

flux | diff. coeff. | grad. conc.

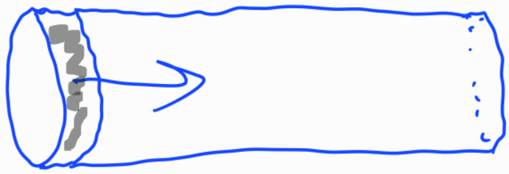
1D: $\left(J_x = -D \frac{\partial C}{\partial x} \right)$

2nd law: $\frac{\partial C}{\partial t} = \nabla \cdot J = -\nabla \cdot D \nabla C$

If D is not func. of C $\Rightarrow$ $\boxed{\frac{\partial C}{\partial t} = -D \nabla^2 C}$

Measure:

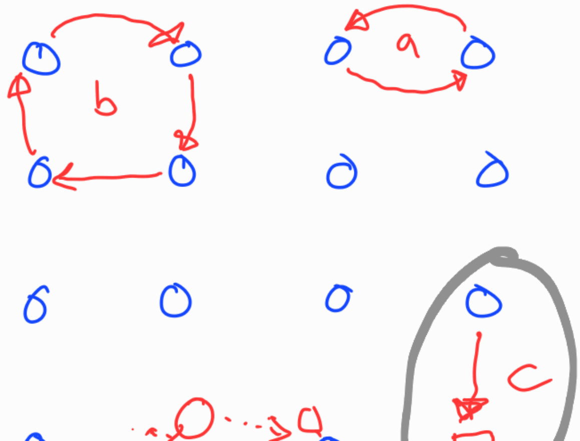
ex Tracer diffusion



activate

Microscopic picture

Diffusion mechanism:



a) Exchange (very high E_m)

b) Ring exchange (correlation problems)

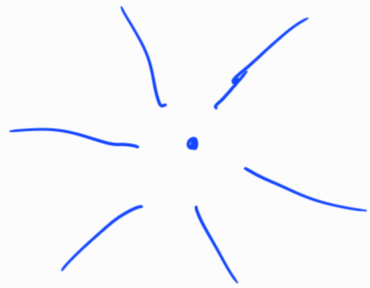
c) defect mediated

Mean-square displacement

$$\overline{r^2} = \underset{\substack{\uparrow \\ \text{jump length}}}{\lambda^2}\ \underset{\substack{\uparrow \\ \text{jump freq}}}{\Gamma}\ \underset{\substack{\uparrow \\ \text{time}}}{t}$$

Connect micro/macro scales

$$\frac{\partial C}{\partial t} \underset{\substack{\uparrow \\ \text{(minus sign?)}}}{=} D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right)$$



$c(r,t)$

$$\Rightarrow C(r,t) = \frac{N e^{-r^2/4Dt}}{(4\pi D t)^{3/2}}$$

(in 3D)

$\left\{ C(r,0) = 0 \quad r \neq 0 \right.$

$\left\{ c(\infty,t) = 0 \right.$

$\left\{ \begin{array}{l} \text{Constraint:} \\ N = \int_0^\infty 4\pi r^2 C(r,t)\, dr \end{array} \right.$

MSD:

$$\overline{r^2} = 4\pi \int_0^\infty r^2 r^2 \frac{C(r,t)}{N}\, dr = \underset{\substack{\uparrow \\ \text{(EX)}}}{\ldots} = 6Dt \Rightarrow 6Dt = \lambda^2 \Gamma t$$

$$\Rightarrow \boxed{D = \frac{\lambda^2 \Gamma}{6}} = \frac{\lambda^2 \Gamma}{2 \cdot \underset{\substack{\uparrow \\ N_D = \#\text{dim.}}}{N_D}}$$

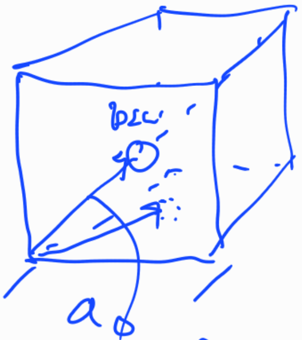
Jump frequency:

Depends on coordination number, z

probability to find defect, p_v,   fractional n.n. dist the attempt freq, ω

$$\Rightarrow \Gamma = z p_v \omega \quad \Rightarrow \quad D_a^v = \frac{\lambda^2 z p_v \omega}{6} = \left\{ \begin{array}{l} \lambda = A a_0 \\ \alpha = \frac{z A^2}{6} \end{array} \right\}$$

atom



$$= \alpha a_0^2 p_v \omega \simeq \alpha a_0^2 c_v \omega$$

in dilute limit

$p_v \simeq c_v$

$$A_{bcc} = \frac{\sqrt{3}}{2}$$

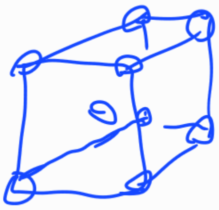
$$A_{fcc} = \frac{\sqrt{2}}{2}$$

EX Determine α for vacancies in bcc and fcc:

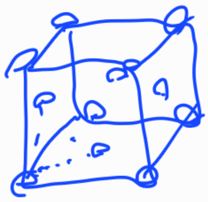
$$\alpha = \frac{z A^2}{6}$$

$z_{bcc} = 8$

$z_{fcc} = 12$



bcc



fcc

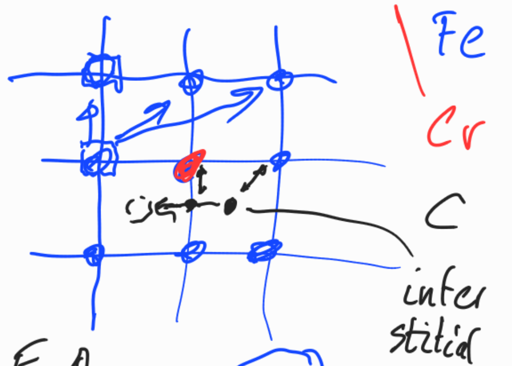
z = # of 1st nearest neighbours

$$\begin{cases} \alpha_{bcc}^{vac} = 8 \cdot \frac{3}{4} \cdot \frac{1}{6} = 1 \\ \alpha_{fcc}^{vac} = 12 \cdot \frac{2}{4} \cdot \frac{1}{6} = 1 \end{cases}$$

Continuation 15/4-21

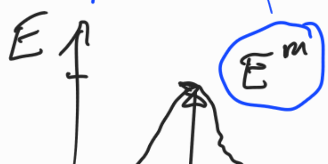
- Controlled by defects

(except int. impurities)



$$D_a^v = \alpha a_0^2 c_v \omega$$

$$c_v = e^{-G_v^f / k_B T} \quad \text{(thermal cond.)}$$



Saddlepoint state, similar TD reasoning $\Rightarrow$

$$\omega = \nu \underbrace{e^{-G_v^m/k_BT}}_{\text{barrier}}$$

ν: vibration of lattice (~ Debye freq.)

Debye

$$D_a^v = \alpha a_0^2 c_v \omega =$$

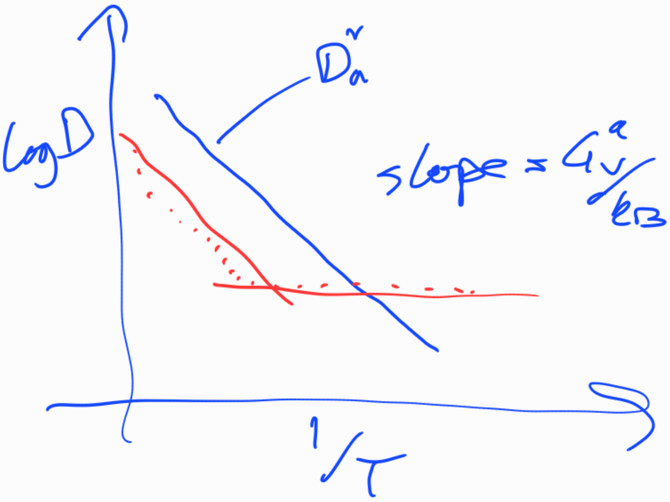
$$\alpha a_0^2 e^{-G_v^f/k_BT} \nu e^{-G_v^m/k_BT} =$$

$$= \left\{ G^f + G^m = G^a \right\} =$$

G^a: activation

$$= \alpha a_0^2 \nu e^{-G_v^a/k_BT} =$$

$$= D_0 e^{-G_v^a/k_BT} \left(= D_0 e^{-Q/k_BT} \right)$$



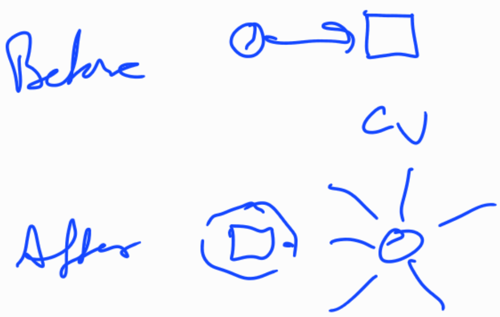
Irradiation

c_v has to be modelled!

Have to add mechanisms!

$$D_a = D_a^v + D_a^{2v} + D_a^i + \dots\dots$$

Small correction $\left(D_a^v = f \alpha a_0^2 c_v \omega \right)$



Correlation factor $f = \frac{z-1}{z+1}$

$$\begin{cases} f_{bcc} \sim 0{,}78 \\ f_{fcc} \sim 0{,}85 \end{cases}$$