MATE 664 L10
Diffusion in solids

Recap: Atomic model for diffusion
Einstein equation (random walk ; point source)

$$D = \frac{\Gamma \langle r^2 \rangle}{6} \cdot \boxed{f} \Rightarrow \text{Correction for correlated motion}$$

Gas $D = \frac{1}{3} \langle u \rangle \lambda \propto T^{1.5}/p$

Liquid $D = M k_B T \overset{\text{Stokes}}{=\!=} \frac{k_B T}{6\pi \eta R}$

η could be $\propto \exp(\frac{B}{T})$

Diffusion model in solids

- Multiple mechanisms exist (What is mechanism? abstracted atomic motion)
- Mechanism depends on lattice / bonding / size difference / charge
- Species to diffuse?
  1. substitutional "replace sites"
  2. interstitial "between sites"

Substitutional: vacancy take over

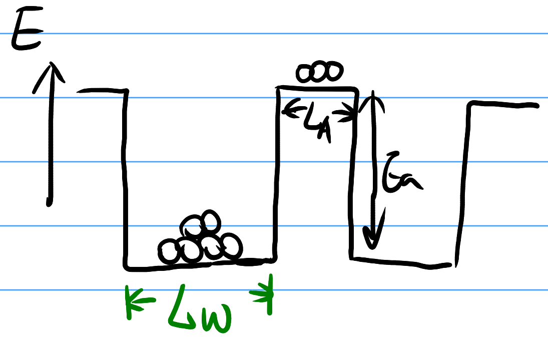
Interstitial: solute atom squeeze in

Both encounters a "Barrier"!

Remember our goal is still $D = \frac{\Gamma \langle r^2 \rangle}{6}$

there are simplified models to choose from

Generalized well potential (where does well come from?)



From Boltzmann distribution

$$\frac{P_{activated}}{P_{well}} = \exp\left(-\frac{E_a}{k_B T}\right)$$

1) Γ: how frequent do one particle move over barrier?

$$\tau_{cross} = \frac{L_A}{\langle v \rangle} = \frac{L_A}{\sqrt{\frac{k_B T}{2\pi m}}}$$

Stat Mech $\langle v \rangle$ from $\langle p \rangle$

$$\left(\langle p \rangle = \frac{\int_0^\infty p e^{-\frac{p^2}{2mk_BT}} dp}{\int_0^\infty e^{-\frac{p^2}{2mk_BT}} dp} = \sqrt{\frac{mk_BT}{2\pi}} \quad E_{kin} = \frac{p^2}{2m} \right)$$

1D

$$= L_A \cdot \sqrt{\frac{2\pi m}{k_B T}}$$

✓ wider L_A longer

heavier particle longer ✓

higher T shorter ✓

2) How many particles can move?

rate of crossing $R_{cross} = \frac{[N^\# \text{ of particles at activated}]}{[\tau_{cross}]}$

Similarly a particle spent $\begin{cases} \tau_A & \text{in activated} \\ \tau_W & \text{in well} \end{cases}$

$$N^\# \text{at activated} = \frac{N \cdot \frac{\tau_A}{\tau_W + \tau_A + \tau_{cross}}}{\tau_{cross}} \approx \frac{N \cdot \frac{\tau_A}{\tau_W}}{\tau_{cross}}$$

Rate of crossing

$$R_{cross} = N \cdot \left(\frac{\tau_A/\tau_W}{\tau_{cross}}\right)$$ like 1^{st} order reaction

Frequency

$$\Gamma' \text{ (jump freq)} = \boxed{\frac{\tau_A}{\tau_W}} \cdot \frac{1}{\tau_{cross}}$$

From Boltzmann dist

$$\tau_{cross} \Rightarrow \sqrt{\frac{2\pi m}{k_B T}} \cdot L_A$$

Length of activated / well states
Probability
$\Rightarrow \tau$

(trick: $\int$ prob $dx \Rightarrow \tau$)

$$\frac{\tau_A}{\tau_W} = \frac{L_A}{L_W} e^{\left(-\frac{E_a}{k_B T}\right)}$$

Finally

$$\Gamma' = \sqrt{\frac{k_B T}{2\pi m}} \cdot \frac{1}{L_W} e^{-\frac{E_a}{k_B T}}$$

length of well

No dependly on L_A any more

Arrhenius frequency

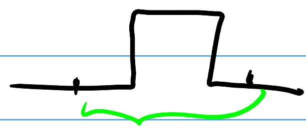
$$\nu = \sqrt{\frac{k_B T}{2\pi m}} \cdot \frac{1}{L_W} \Rightarrow \Gamma' = \nu e^{-\frac{E_a}{kT}}$$

To get D:

$$D = \frac{\Gamma \langle r^2 \rangle}{2}$$

(1D)

$\langle r^2 \rangle$?

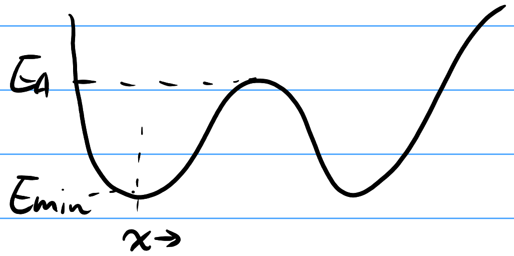


$r \approx L_{well} + L_A$

$$= \underbrace{\sqrt{\frac{k_B T}{8\pi m}} \frac{1}{L_W} \cdot (L_W + L_A)^2}_{D_0} \cdot \exp\left(-\frac{E_a}{k_B T}\right)$$

Very simplified, but works

More complex landscape?



Parabolic well

$$E(x) = E_{min} + \frac{\beta}{2}(x - x_{min})^2$$

$$\frac{\beta}{2}\left(\frac{L_w}{2}\right)^2 = E_a$$

$\Rightarrow$ modify Γ (or ν)

$$\Gamma' = \frac{1}{2\pi}\sqrt{\frac{\beta}{m}}\, e^{\left(-\frac{E_a}{k_B T}\right)}$$

$\Downarrow$

ν parabolic well

What are potentially missing?

1) One particle picture $\longrightarrow$ landscape can be "many body"

2) Static landscape $\longrightarrow$ $E(\vec{x})$ depends on local env

3) Many particle system $\longrightarrow$ Same E_a diff configurations

$\hookrightarrow$ Entropy effect

4) Real lattice $\longrightarrow$ symmetry factors to Γ

5) Correlated jump? $\longrightarrow$ f-factor

General solution for Γ' (KoM eq 7.25)

$$\Gamma' = \nu e^{-\frac{G^a}{k_B T}} = \nu e^{-\frac{H^a - TS^a}{k_B T}}$$

$$= \nu e^{\frac{S^a}{k_B}} e^{-\frac{H^a}{k_B T}}$$

$\nu = \frac{\omega_J}{2\pi}$ $\quad \omega_J$: angular frequency

Note: contribution from entropy

$$S^a = k_B \left[2\ln\frac{\omega_J}{\omega_J^A} + \sum_{f=1}^{3N^A} \ln\left(\frac{\omega}{\omega_i^A}\right) \right]$$

$\Uparrow$ varies little in T

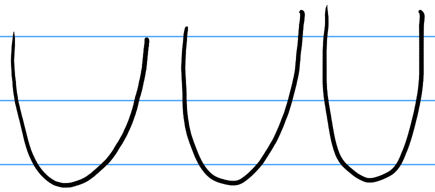
$\leftarrow$ 3D frequencies

$\Longrightarrow$ Arrhenius equation $D = D_0 \exp\left(-\frac{H_a}{k_B T}\right)$

{ Activation enthalpy !
{ Fundation for theoretical calculations

What are ω ?

Think about multiple potential well "landscape"



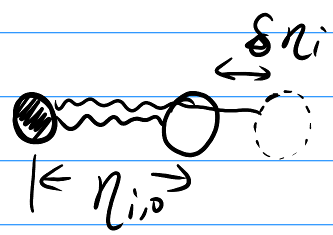
From KOM terms

$$\phi^{well}(\eta_1, \eta_2 \cdots \eta_{3N}) = N\phi^0 + \frac{1}{2}\underbrace{\sum_{i=1}^{N=3} m_i \omega_i^2 \cdot (\delta\eta_i)^2}_{\text{quadratic}}$$

(x, y, z)

$\Uparrow$ average ϕ

Just like spring experiments



restoring force $F = m\frac{\partial^2\eta}{\partial t^2} = -k\,\delta\eta_i$

$$\omega_i^2 = \frac{k_i}{m_i}$$

$$\Delta\omega = \omega_i^A - \omega$$

$\uparrow$ activated $\quad$ $\uparrow$ stable

In all cases, we have

$$D = \nu \cdot \exp\left(-\frac{E^a}{k_B T}\right)$$

E^a → activation energy

ν ⇑ attempted Frequency

How about application in real materials?

$$D = \frac{\Gamma \langle r^2 \rangle}{6} \cdot f$$

$$= \frac{z \cdot \Gamma' \langle r^2 \rangle}{6} \cdot f$$

z → multiplier for events

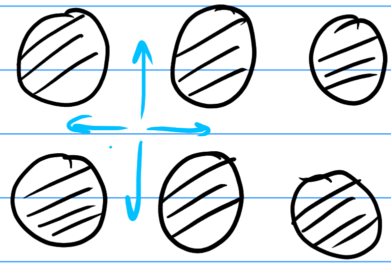
Γ' → frequency single event

$\langle r^2 \rangle$ → length single jump

f → factor for correlated jump

Case 1 interstitial D_I (intrinsic, interstitial)

$z = 4$ in this case not $\tilde{D}$



$$D_I = \frac{z \Gamma_I' \langle r^2 \rangle}{6} f$$

$$= \frac{z \cdot \nu \langle r^2 \rangle}{6} \exp\left(\frac{S_I^m}{k_B}\right) \exp\left(-\frac{H_I^m}{k_B T}\right)$$

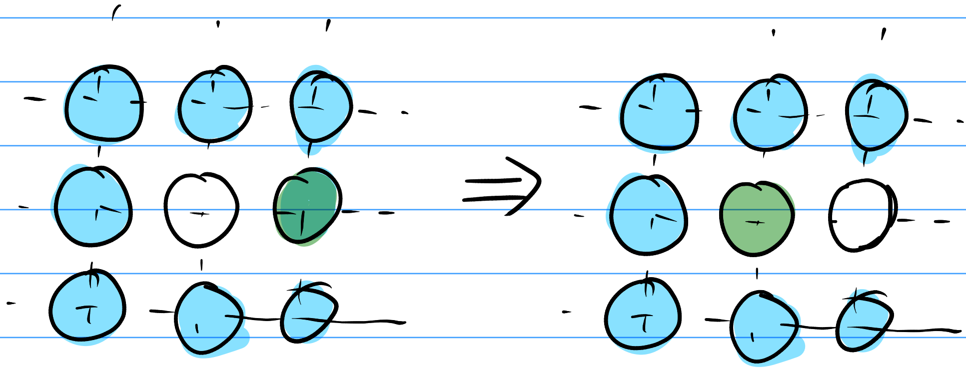
S_I^m → migration entropy

H_I^m → migration entalpy

ν → From latice

$f = 1$ because uncorrelated

Case 2: vacancy self diffusion



Looks like vacancy moves → Right

$$D_v = \frac{z\,\nu\langle r^2\rangle}{6}\exp\left(\frac{S_v^m}{k_B T}\right)\exp\left(-\frac{H_v^m}{k_B T}\right)$$

$f = 1$ because uncorrelated

Case 3 vacancy-assited diffusion

[Random walk of vancany] [Random walk of Solute]

↘ vicinity ↙

Probability of vacancy in vicinity

vacancy formation entropy

va form enthalpy

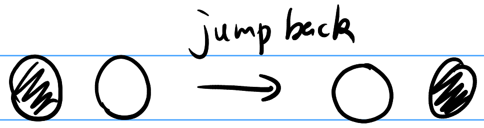
$$D_A = X_v \cdot D_v \quad ; \quad X_v = \exp\left(-\frac{G_v^f}{k_B T}\right) = \exp\left(\frac{S_v^f}{k_B}\right)\exp\left(-\frac{H_v^f}{k_B T}\right)$$

$$\Rightarrow D_A = \frac{z\langle r^2\rangle\nu}{6}\exp\left(\frac{S_v^f + S_v^m}{k_B}\right)\exp\left[\frac{-(H_v^f + H_v^m)}{k_B T}\right]\cdot f$$

$f \neq 1$

Why $f \neq 1$ (Correlated jump)?

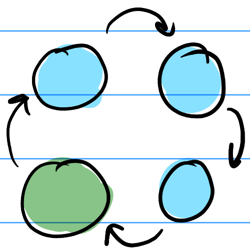
Approximation $f \simeq \dfrac{1+\langle\cos\theta\rangle}{1-\langle\cos\theta\rangle} \simeq \dfrac{1+\frac{1}{z}}{1-\frac{1}{z}}$



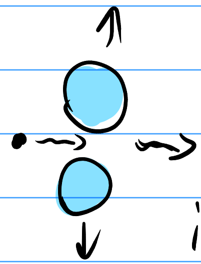
$\cos\theta = -1$ probability $= \frac{1}{z}$

From symmetry $\begin{cases} f \simeq 0.85 & \text{for f.c.c} \\ f \simeq 0.7 & \text{common} \end{cases}$

Other mechanisms



ring



interstitialcy

Correlated, $f \neq 1$

Next we'll discuss some complex mechanisms

- diffusion in ionic solid
- diffusion in imperfection $\Rightarrow$ short-cut