MATE 664 Lecture 10

Atomic Models for Diffusion (III): Ideal Crystals

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Recap: atomic model for diffusion

- Random walk picture
- Einstein relation links jump statistics to diffusivity
- Correlation factor f corrects for non-independent motion

$$D = \frac{\Gamma \langle r^2 \rangle}{6} f \tag{1}$$

Recap: diffusion in gases and liquids

- Gas diffusion from kinetic theory ($D = f(T, p)$)
- Liquid diffusion from mobility and viscous drag ($D = f(\mu, T)$)
  - Often $\eta \propto \exp(B/T)$

$$D_{\text{gas}} = \frac{1}{3}\langle u \rangle \lambda \propto T^{3/2}/p \tag{2}$$

$$D_{\text{liquid}} = M k_B T \approx \frac{k_B T}{6\pi\eta R} \tag{3}$$

Learning outcomes

After this lecture, you will be able to:

- Link thermodynamic properties to the diffusivity in ideal solids
- Recall the potential well model for solid diffusivity
- Analysis of the Arrhenius equation / plot for solids

Diffusion models in solids

- Multiple mechanisms exist (*what is a machanism*?)
- Mechanism depends on lattice, bonding, charge, and size mismatch
- Two broad classes of diffusing species:
  - substitutional: A occupies the lattice site of B
    - interstitial: A is inserted between neighbouring B-sites

Two basic mechanisms

Substitutional diffusion - atom replaces a lattice site - usually vacancy-mediated

Interstitial diffusion - atom moves between host sites - solute squeezes through interstitial positions

Barrier picture for diffusion

- Both mechanisms encounter an energy barrier
- Goal remains to estimate jump frequency and jump length

$$D = \frac{\Gamma \langle r^2 \rangle}{6} \tag{4}$$

Generalized well potential

- Particle resides in a potential well
- It must cross an activation barrier E_a
- Activated population follows Boltzmann statistics

$$\frac{P_{\text{activated}}}{P_{\text{well}}} = \exp\left(-\frac{E_a}{k_B T}\right) \tag{5}$$

Step 1: crossing time

- Ask how long one activated particle needs to cross the barrier region
- Estimate by distance over average speed

$$\tau_{\text{cross}} = \frac{L_A}{\langle v \rangle} \approx \frac{L_A}{\sqrt{k_B T/(2\pi m)}} = L_A \sqrt{\frac{2\pi m}{k_B T}} \tag{6}$$

Does it make sense? A few implications: - Larger L_A gives longer crossing time - Higher T gives shorter crossing time - Heavier particles cross more slowly

Step 2: how many particles can cross?

Crossing rate is number of activated particles divided by crossing time

$$R_{\text{cross}} = \frac{N^{\#}}{\tau_{\text{cross}}} \tag{7}$$

where the total number of crossing $N^{\#}$ follows

$$N^{\#} \approx N \frac{\tau_A}{\tau_W} \tag{8}$$

- τ_A: time spent in activated region
- τ_W: time spent in well

Step 3: crossing rate and jump frequency

- Combine activated fraction with crossing time
- Jump frequency behaves like a first-order rate constant

$$R_{\text{cross}} = N \left(\frac{\tau_A/\tau_W}{\tau_{\text{cross}}} \right) \tag{9}$$

$$\Gamma' = \frac{\tau_A}{\tau_W} \frac{1}{\tau_{\text{cross}}} \tag{10}$$

Step 4: probability ratio from the well shape

Ratio of residence times scales with probability of occupying each region For a simple well model, we have

$$\frac{\tau_A}{\tau_W} = \frac{L_A}{L_W} \exp\left(-\frac{E_a}{k_B T}\right) \tag{11}$$

- L_W: well width
- L_A: activated-region width

Arrhenius jump frequency

Substituting the crossing time removes explicit dependence on L_A, so that the jump frequency Γ' follows a Boltzmann distribution!

$$\Gamma' = \sqrt{\frac{k_B T}{2\pi m}} \frac{1}{L_W} \exp\left(-\frac{E_a}{k_B T}\right) \tag{12}$$

If we define the attempt frequency ν (frequency dependent on thermal kinetic energy and well geometry)

$$\nu = \sqrt{\frac{k_B T}{2\pi m}} \frac{1}{L_W} \tag{13}$$

Final form for the jump frequency:

$$\Gamma' = \nu \exp\left(-\frac{E_a}{k_B T}\right) \tag{14}$$

From jump frequency to diffusivity

In 1D, the random-walk expression becomes

$$D = \frac{\Gamma' \langle r^2 \rangle}{2} \tag{15}$$

What is $\langle r^2 \rangle$? For this well, $r \sim L_W + L_A$:

$$D = \sqrt{\frac{k_B T}{8\pi m}} \frac{(L_W + L_A)^2}{L_W} \exp\left(-\frac{E_a}{k_B T}\right) \tag{16}$$

More realistic potential landscape

- Real barriers are not rectangular
- Near a minimum, a parabolic approximation is often better parabolic well model

$$E(x) = E_{\min} + \frac{\beta}{2}(x - x_{\min})^2 \tag{17}$$

- Barrier height (activation energy) E_a approximated by:

$$\frac{\beta}{2}\left(\frac{L_W}{2}\right)^2 = E_a \tag{18}$$

Modified attempt frequency for a parabolic well

The jump frequency in a parabolic well follows:

$$\Gamma' = \frac{1}{2\pi}\sqrt{\frac{\beta}{m}} \exp\left(-\frac{E_a}{k_B T}\right) \tag{19}$$

- Can be rewritten with $\nu = \frac{1}{2\pi}\sqrt{\beta/m}$
- Still follows the Boltzmann distribution!

What is missing from the simple picture?

- One-particle picture may be too simple
- Energy landscape can be many-body
- Landscape may change with local environment
- Many configurations can share the same barrier
- Real lattices add symmetry factors
- Jumps may be correlated

General activated form

- More generally, write the jump frequency using activation free energy

$$\Gamma' = \nu \exp\left(-\frac{G^m}{k_B T}\right) \tag{20}$$

$$= \nu \exp\left(\frac{S^m}{k_B}\right) \exp\left(-\frac{H^m}{k_B T}\right) \tag{21}$$

- $G^m = H^m - TS^m$: superscript m denotes *migration*

Entropy contribution in migration

- Activation entropy S^m modifies the prefactor
- It usually varies weakly with temperature, because it's usually estimated from all vibrational modes with angular momenta ω

$$S^m = k_B \left[2 \ln\left(\frac{\omega_J^\ddagger}{\omega_J}\right) + \sum_{i=1}^{3N-7} \ln\left(\frac{\omega_i}{\omega_i^\ddagger}\right)\right] \tag{22}$$

Analog: angular momenta of springs near the stationary point.

Arrhenius equation for diffusion

Using our previous analysis, it can be shown that plugging the jump frequency into the random-walk diffusivity equation is basically the famous Arrhenius form of diffusivity

$$D = D_0 \exp\left(-\frac{H^m}{k_B T}\right) \tag{23}$$

- D_0 contains geometric and entropic terms
- H^m is the activation **enthalpy**
- In an Arrhenius plot ($\ln D$ vs $1/T$), the slope is only related with H^m! (see Lecture 01)

Application to real materials

For real materials, the Einstein relation / random-walk analog still holds, while a few more factors need to be considered:

$$D = \frac{\Gamma \langle r^2 \rangle}{6} f = \frac{z\,\Gamma' \langle r^2 \rangle}{6} f \tag{24}$$

- z counts equivalent jump paths (e.g. equivalent neighbouring sites in f.c.c. lattice)
- f is the correlation factor (usually around 0.7)

Case 1: interstitial diffusion

Interstitial jumps are often uncorrelated - After one interstitial jump, the next jump is not strongly biased - No vacancy left behind to pull the atom back - Successive jumps are approximately independent

$$D_I = \frac{z\,\nu \langle r^2 \rangle}{6} \exp\left(\frac{S_I^m}{k_B}\right) \exp\left(-\frac{H_I^m}{k_B T}\right) \tag{25}$$

Case 2: vacancy self-diffusion

- Atom-vacancy exchange makes the vacancy appear to move
- Diffusion still uses the migration barrier (*for vacancy*)
- Usually uncorrelated ($f \approx 1$)

$$D_V = \frac{z\,\nu \langle r^2 \rangle}{6} \exp\left(\frac{S_V^m}{k_B}\right) \exp\left(-\frac{H_V^m}{k_B T}\right) \tag{26}$$

Case 3: vacancy-assisted solute diffusion

- Solute motion requires a nearby vacancy
- Combine vacancy availability with vacancy migration
- Correlated motion!

$$D_A = X_V \, D_V f \tag{27}$$

- Vacancy concentration is related with the vacancy formation free energy G_V^f

$$X_V = \exp\left(-\frac{G_V^f}{k_B T}\right) = \exp\left(\frac{S_V^f}{k_B}\right) \exp\left(-\frac{H_V^f}{k_B T}\right) \tag{28}$$

Vacancy-assisted diffusion: final form

After combining vacancy formation and migration, D_A becomes dependent on both vacancy formation enthalpy and vacancy migration barrier!

$$D_A = \frac{z \, \nu \langle r^2 \rangle}{6} \exp\left(\frac{S_V^f + S_m}{k_B}\right) \exp\left(-\frac{H_V^f + H_m}{k_B T}\right) \, f \tag{29}$$

Why can $f < 1$ in vacancy-mediated diffusion?

- Vacancy jumps create "memory"
- A just-moved atom is likely to **jump back** into the nearby vacancy
  - This reduces net transport efficiency
- Approximate estimate from jump-back bias:

$$f \simeq \frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} \tag{30}$$

Correlation factor in practice

Simple estimate with z

$$f \simeq \frac{1-\frac{1}{z}}{1+\frac{1}{z}} \tag{31}$$

- For substitutional diffusion, f is commonly below 1
- For fcc, a typical value is about 0.78
- In many cases, using $f \sim 0.7$–0.8 is reasonable

Other correlated mechanisms

- Ring mechanisms
- Interstitialcy mechanisms
- Cooperative multi-atom motion (e.g. push-out mechanism)

Summary

After today's lecture, you should be able to - recognize diffusion in solids as an process associated with activation energy - link diffusivity with potential well picture - analyze the enthalpy dependency in the Arrhenius-type diffusivity equations

Next topics

In next lecture, we will discuss diffusion processes with varied energy barriers, in particular:

- Diffusion in ionic solids
- Diffusion in imperfect solids
- Short-circuit diffusion