MATE 664 Lecture 05

Diffusion (II)

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Recap of Lecture 04

Key ideas from last lecture:

- Driving forces for diffusion
- Fick's 1st and 2nd laws of diffusion
- Time-dependent behavior of Fick's 2nd equation
- Temperature-dependency of diffusivity and activation mechanism
- Introduction to diffusivity measurements

Learning Outcomes

After today's lecture, you will be able to:

- Recall different types of diffusivities in solids
- Describe basic mechanism in interdiffusion systems
- Analysis the driving force for various diffusion mechanisms
- Analysis of change of reference system in diffusion experiments.

Recap: Fick's Laws of Diffusion

- 1st law: steady-state diffusion

$$\vec{J}_i = -D_i \nabla c_i$$

- 2nd law: time-dependent diffusion

$$\frac{\partial c}{\partial t} = D_i \nabla^2 c_i$$

Recap: Different definitions of diffusivities

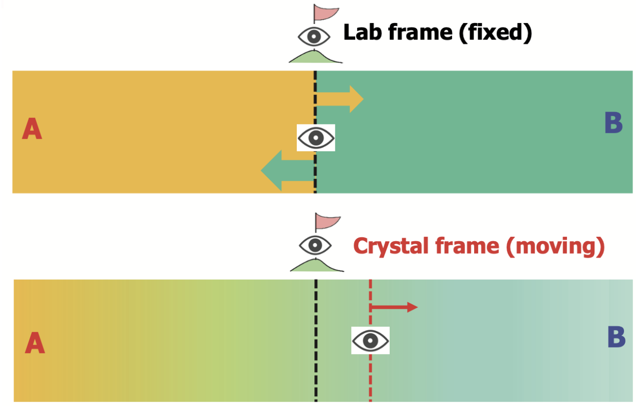


Figure 1: Lattice (C) vs Lab (V) frame

- Self-diffusivity D^*
- Intrinsic diffusivity D_i (lattice frame / C-frame; `C` crystal)
- Inter-diffusivity $\tilde{D}$ (laboratory frame / V-frame; `V` volume-fixed)

We will see a few examples today for more clarification.

Self-Diffusion: Chemically Homogeneous Material

- Isotope tracer experiments
- Lattice constraint:

$$c_i + c_i^* + c_v = \text{const}$$

  - General "network-constrained" problem

- Vacancy concentration often at equilibrium
  - Vacancy balance with the source (surface / grain boundary / dislocation)

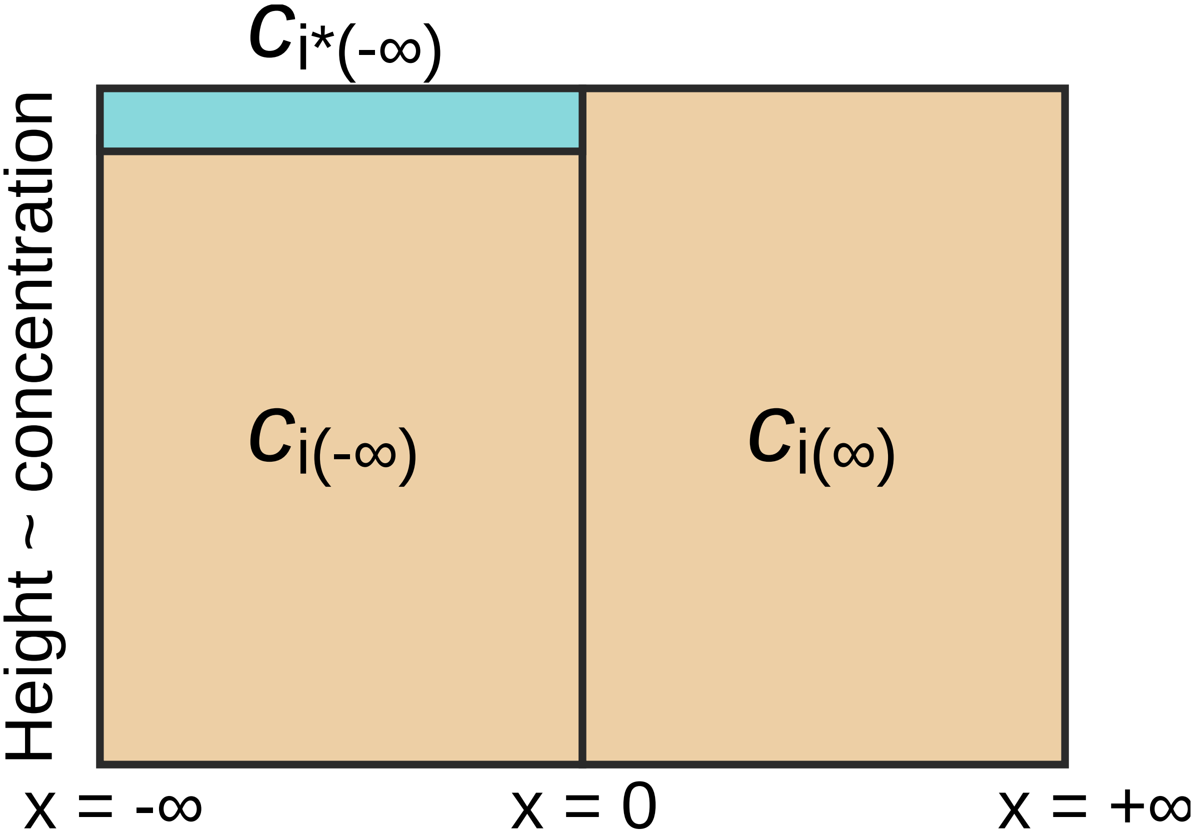


Figure 2: Setup for isotope diffusion

Flux Relations in Network-Constrained Systems

- Flux driven by chemical potential differences (1D)
  - Non-radioactive species:

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

  - Radioactive species:

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

  - Vacancy (zero-flux, why?):

$$J_v = 0$$

Vacancy Equilibrium Assumption

- $\mu_v = \text{const}$
- $J_v = 0$
- total flux balance:

$$J_i + J_i^* + J_v = 0$$

Resulting Self-Diffusion Flux

- Chemical potential gradient:

$$\frac{\partial \mu_{i^*}}{\partial x} = k_B T \frac{1}{c_i} \frac{\partial c_i}{\partial x}$$

- Self-diffusion coefficient:

$$D^* = k_B T \left(\frac{L_{ii}}{c_i} - \frac{L_{ii^*}}{c_{i^*}} \right)$$

Self-diffusion summary

- **No** macroscopic concentration gradient!
- Chemical potential varies locally for i and i^*
- Follows the Fick equation!

Self-diffusion in a homogeneous binary solution

- Binary alloy / solution between 1 and 2
- Isotope tracer for 1
- Chemically homogeneous, no lattice change during diffusion

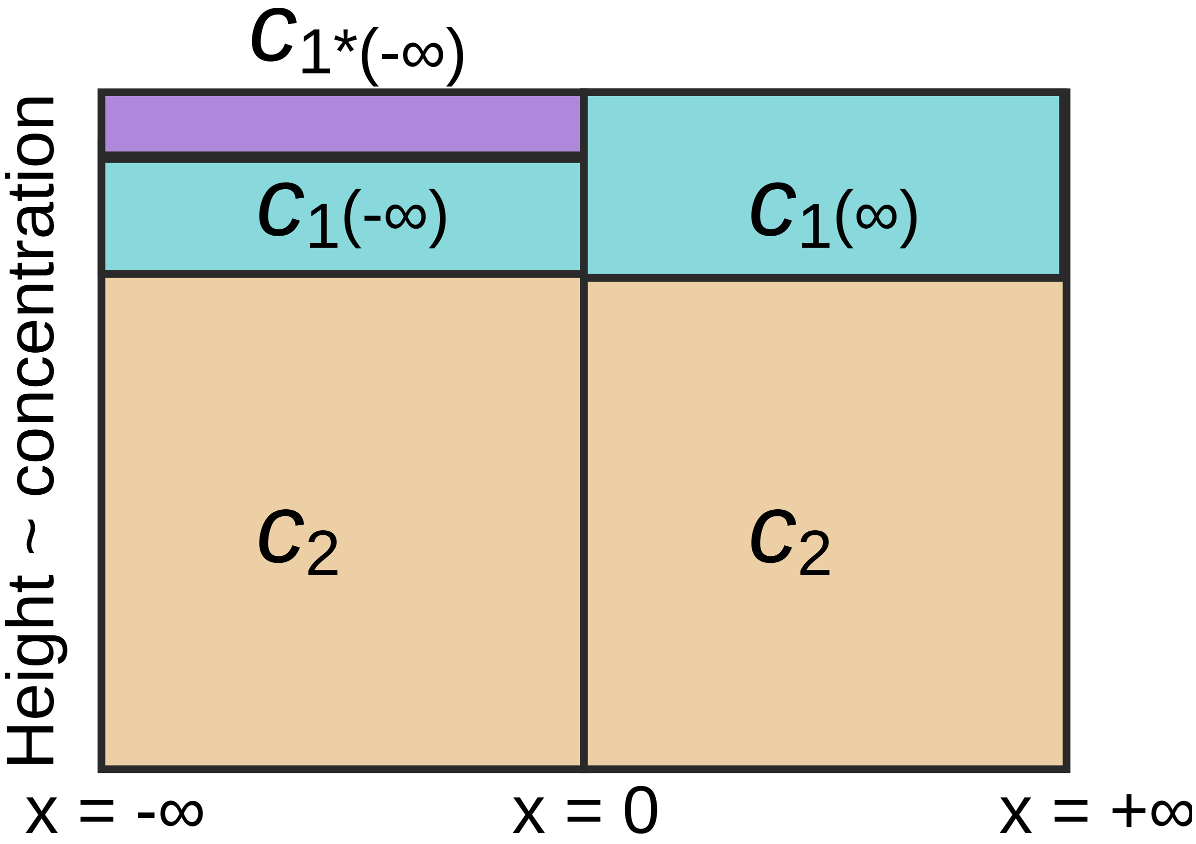


Figure 3: Setup for isotope diffusion for binary mixture

Self-diffusion in binary solution: diffusivity

- We have self-diffusion for 4 species (1, 1^*, 2 and V)
- General flux balance still holds
- Vacancy concentration is uniform
- Still follows Fick's law.

$$\begin{aligned} J_{1^*} &= -k_B T\left[\frac{L_{11}}{c_1} - \frac{L_{11^*}}{c_{1^*}}\right]\frac{\partial c_{1^*}}{\partial x} \quad (1) \\ &= -D_1^*\frac{\partial c_{1^*}}{\partial x} \quad (2) \end{aligned}$$

Diffusion in Inhomogeneous Materials

- Real materials are rarely homogeneous

- Concentration gradients exist by construction
- Diffusion fluxes differ locally in space
- Leads to imbalance of material transport

Historical Observation: Boyle (17th Century)

- Robert Boyle observed solid-state diffusion
- Zn penetration into Cu coin → brass formation
- Clear macroscopic evidence of diffusion in solids
- Mechanism not understood until 20th century

Imbalance of Diffusion Fluxes

- Consider a binary diffusion couple A–B
- If $D_A \neq D_B$
- Then intrinsic fluxes differ:
$$J_A^C \neq -J_B^C$$
- Mass transport is locally unbalanced

Vacancy Mechanism and Imbalance

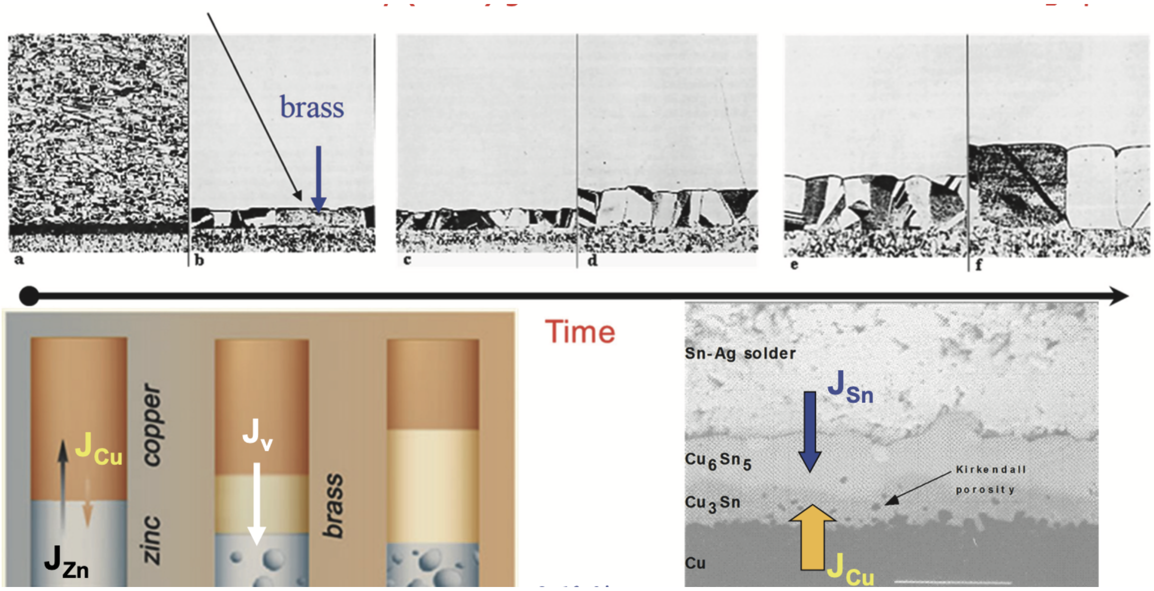
- Substitutional diffusion proceeds via vacancies
- Site conservation:
$$J_A^C + J_B^C + J_v^C = 0$$
- Unequal atomic fluxes force a vacancy flux
- Vacancy flux is opposite to faster species

Vacancy Accumulation Issue

- Vacancy flux implies transport of empty sites
- But vacancy concentration remains near equilibrium
- Fast sources/sinks (dislocations, GBs, surfaces)
- Therefore: no long-term vacancy buildup

Kirkendall Effect

- Unequal intrinsic diffusivities
- Net vacancy flux in crystal frame
- Lattice planes shift to accommodate vacancy flow
- Inert markers move relative to sample ends



C-frame View: Inhomogeneous Materials

- Crystal (C) frame attached to lattice sites
- Atomic fluxes are Fick-like:

$$J_i^C = -D_i \frac{\partial C_i}{\partial x}$$

- Vacancy flux is kinematically constrained
- Lattice assumed locally intact

Intrinsic Diffusivity

- Defined in the crystal frame
- Measures diffusion relative to lattice sites
- Denoted D_i
- Depends on:
    - jump frequency
    - vacancy availability
    - thermodynamic factor

$$\begin{aligned} J_1^C &= -k_B T[\frac{L_{11}}{c_1} - \frac{L_{12}}{c_2}]\Phi \frac{\partial c}{\partial x} \\ &= -D_1 \frac{\partial c}{\partial x} \end{aligned}$$

Relation to Self-Diffusivity

- Self-diffusion: tracer in homogeneous system
- No net chemical potential gradient
- Intrinsic diffusivity reduces to self-diffusivity:

$$D_i = D_i^* \, \Phi$$

- Φ: thermodynamic factor

Thought Experiment: Vacancy Diffusion (C-frame)

- Assume $C_v \approx C_{v,\mathrm{eq}}$
- Yet $J_v^C \neq 0$
- Continuity cannot be satisfied by accumulation
- Requires an additional velocity

Origin of Lattice Velocity

- Transform flux to lab frame:

$$J_v^{\mathrm{lab}} = J_v^C + C_v v$$

- Impose no net vacancy transport in lab frame:

$$J_v^{\mathrm{lab}} = 0$$

- Lattice velocity:

$$v = -\frac{J_v^C}{C_v}$$

Vacancy (V) Frame Basics

- V-frame moves with vacancy flux
- By definition:

$$J_v^V = 0$$

- Atomic fluxes include convective term:

$$J_i^V = J_i^C + C_i v$$

Governing Equation in V-frame

- Impose volume conservation:
$$J_1^V\Omega_1 + J_2^V\Omega_2 = 0$$
- Leads to single interdiffusion coefficient
- Darken equation emerges naturally

Interdiffusivity

- Defined in volume-fixed (V) frame
- Flux form:
$$J_i^V = -\tilde{D}\frac{\partial C_i}{\partial x}$$
- Interdiffusivity:
$$\tilde{D} = D_1X_2 + D_2X_1$$

Special Case: Interstitial Diffusion

- Interstitial atoms do not occupy lattice sites
- No site conservation constraint
- No lattice drift required
- Interdiffusivity reduces to:
$$\tilde{D} \approx D_{\text{interstitial}}$$

Summary: Types of Diffusivities

Diffusivity	Frame	Meaning
D_i^*	lattice	tracer / self-diffusion
D_i	C-frame	intrinsic diffusivity
$\tilde{D}$	V-frame	interdiffusivity

Summary

- Inhomogeneity leads to flux imbalance
- Vacancy mechanism enforces site conservation
- Lattice velocity resolves vacancy continuity
- Choice of reference frame is essential
- Kirkendall effect is a frame-dependent phenomenon