MATE 664 Lecture 06

Solution to Diffusion Equations (I)

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Recap of Lecture 05

Key ideas from last lecture:

- Different forms of diffusivities
- Deriving diffusivity from driving force terms
- Differentiate reference frames used for diffusion equations

Recap: Intrinsic Diffusivity Expression

For component i (notation from notes)

$$D_i^* = k_B T \left(\frac{L_{ii}}{c_i} - \frac{L_{ij}}{c_j} \right)$$

$$D_i = k_B T \left(\frac{L_{ii}}{c_i} - \frac{L_{ij}}{c_j} \right) \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \right)$$

whereas

$$\Phi(c) = 1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i}$$

Recap: Interdiffusivity (Binary)

Binary mixture

$$\tilde{D}_{12} = D_1 c_2 \Omega_2 + D_2 c_1 \Omega_1$$

- Ω_i: partial molar volume factor in your notation
- Both C-frame and V-frame still lead to Fick-type equations

Learning Outcomes

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

- Interpret Kirkendall effect using lattice (C-frame) vs lab (V-frame)
- Solve steady-state diffusion (Laplace equation) in common geometries
- Use non-steady solutions: Gaussian / error function / superposition
- Use separation of variables and Laplace transform as solution strategies

Remaining Question 1: Kirkendall Effect

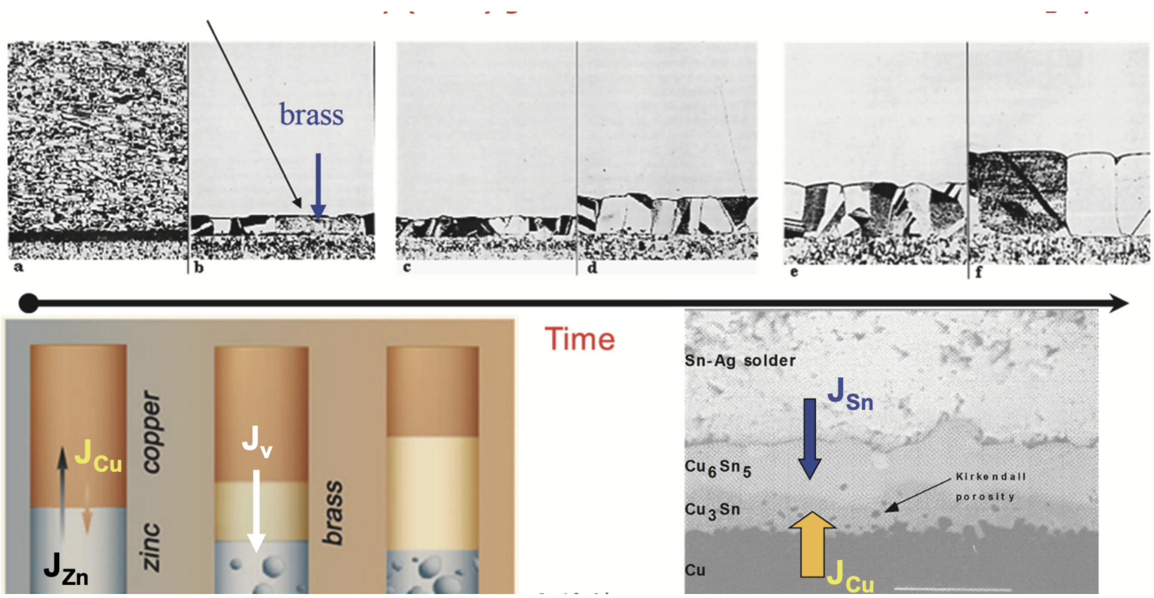

Figure 1: Kirkendall effect demo

Key observation

- In diffusion couple, markers move relative to lab frame
- Indicates unequal intrinsic fluxes in lattice frame

C-frame vs V-frame Fluxes

C-frame (lattice frame)

- net lattice flux can be nonzero: $J_V^* \neq 0$

V-frame (lab frame)

$$J_A^V = -J_B^V, \qquad J_V^V = 0$$

Interpretation

- $J_V^* \neq 0$ but $J_V^V = 0$ implies defect accumulation / depletion

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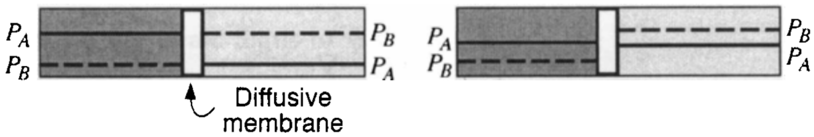
Kirkendall Effect: Physical Meaning

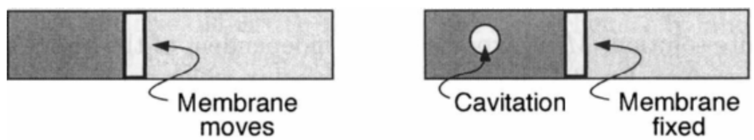
Experimentally measured lattice shift

- Markers track lattice (or marker plane)
- Unequal intrinsic fluxes ⇒ vacancy flux
- Vacancy imbalance ⇒ defect accumulation in control volume
- Can produce porosity (Kirkendall voids)

Kirkendall Effect: Analog



(a) (b)



(a) (b)

- A diffuse faster than B across the membrane
- $p_i = c_i RT$
- Fixed membrane   expanding voids

Kirkendall Effect: Simulations

See simulation of vacancy mechanism

Credit: Dissemination of IT for the Promotion of Materials Science (DoITPoMS), University of Cambridge

Remaining Question 2: Interstitial Diffusion Setup

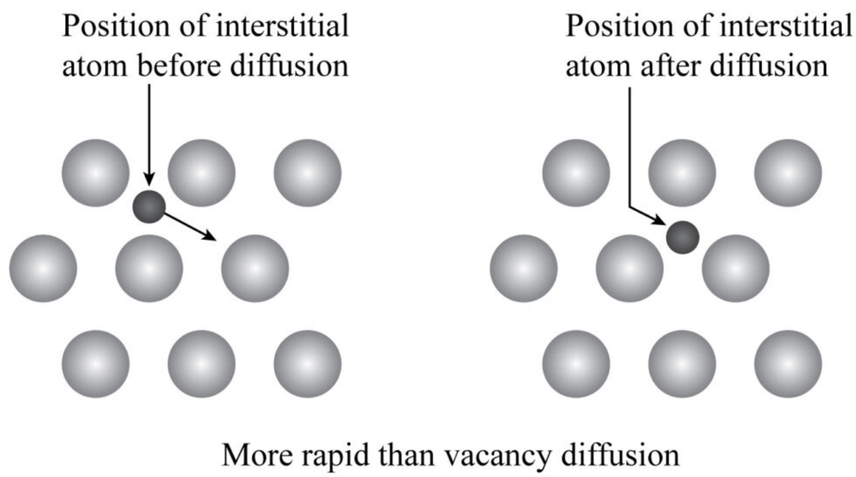


Figure 2: Interstitial diffusion

Model ideas:

- species 1 diffuses through sites of 2 (interstitial)
- atoms of 2 are much heavier than 1
- what is the interdiffusivity $\tilde{D}$?

Mobility and Diffusivity in C-frame

C-frame velocity

$$v_s^* = \frac{M_1}{c_1} \nabla \mu_1$$

Then

$$D_1 = M_1 k_B T$$

and (using Onsager coefficient notation)

$$D_1 = \frac{L_{11}}{c_1} k_B T$$

Connection

- this matches Nernst–Einstein type relation

V-frame Analysis

Special Case: Diffusivity of 2 $\to$ 1 with $D_2 = 0$

- species 2 immobile: $D_2=0
- drift velocity related to $\partial c_1 / \partial x$
- similar to "diffusion through solvent" in mass transfer

$$J_1^V = -D_1 \frac{\partial c_1}{\partial x} + c_1 (D_1 - 0) \Omega_1 \frac{\partial c_1}{\partial x} \tag{1}$$

$$= -D_1 \left(1 - c_1 \Omega_1\right) \frac{\partial c_1}{\partial x} \tag{2}$$

$$\tag{3}$$

V-frame: Effective Diffusivity

The interdiffusivity now becomes:

$$\tilde{D} = D_1 \Omega_2 c_2 \tag{4}$$

$$= D_1 x_2 \tag{5}$$

- x_2 is the fraction of lattice particles (usually 1).
- interdiffusivity depends on "how many sites" the smaller species can use
- this expression only applicable for interstitial diffusion!

Driving Forces Beyond Chemical Potential

We often used μ_i as driving force for diffusion, but other contributions exist.

Generalized "diffusion potential":

$$\Phi_i = \mu_i + \sum_j \eta_j$$

- vacancy mechanism / site availability
- electromigration
- external pressure / stress effects
- capillarity / surface curvature effects
- etc.

How Do We Determine D?

General experimental workflow:

- impose initial concentration + geometry
- evolve for time $t > 0$
- measure profile $c(x,t)$ (or length scale)
- fit to model solution $\Rightarrow D$

Forward Problem vs Inverse Problem

Given

- geometry + initial/boundary conditions
- candidate D

Predict

- concentration profile $c(x,t)$

Inverse

- infer D from measured $c(x,t)$

What Do We Learn In The Following Lectures?

- We want **analytical** + **numerical** solutions to the diffusion equations (Fick's laws)
- Start with steady state, then non-steady state.
- Covering general formula, and geometries

Fick's Second Law (1D, constant D)

Assuming homogeneous isotropic constant D

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

To solve we must specify

- initial condition: $c(x, 0)$
- boundary conditions: $c(0, t)$, $c(L, t)$ or flux BC

Part I: Steady State Diffusion

Steady state

$$\frac{\partial c}{\partial t} = 0 \quad \Rightarrow \quad \nabla^2 c = 0$$

This is Laplace equation, having solution in 1D:

$$\frac{d^2 c}{dx^2} = 0 \Rightarrow c(x) = C_1 x + C_2$$

1D Steady State: Dirichlet BC Example

If $c(0) = c^0$ and $c(L) = c^L$

Then

$$c(x) = c^0 + \frac{c^L - c^0}{L} x$$

and flux

$$J = -D\frac{dc}{dx} = -D\frac{c^L - c^0}{L}$$

Cylindrical Steady State (Radial)

For axisymmetric $c = c(r)$

$$\nabla^2 c = \frac{1}{r}\frac{d}{dr}\left(r\frac{dc}{dr}\right) = 0$$

Integrate twice

$$c(r) = k_1 \ln r + k_2$$

Cylinder: Apply BC at r_1, r_2

If $c(r_1) = c_1$ and $c(r_2) = c_2$

Then

$$c(r) = c_1 + \frac{c_2 - c_1}{\ln(r_2/r_1)} \ln\left(\frac{r}{r_1}\right)$$

Spherical Steady State (Radial)

For $c = c(r)$

$$\nabla^2 c = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dc}{dr}\right) = 0$$

Integrate to get

$$c(r) = -\frac{k_1}{r} + k_2$$

Sphere: Apply BC at r_1, r_2

If $c(r_1) = c_1$, $c(r_2) = c_2$

One convenient form

$$c(r) = c_1 + \frac{c_2 - c_1}{\left(\frac{1}{r_2} - \frac{1}{r_1}\right)}\left(\frac{1}{r} - \frac{1}{r_1}\right)$$

Spatially Varying Diffusivity in Steady State

Notes: still solvable if D depends on 1 variable (e.g. x or r)

Steady 1D with constant flux J

$$J = -D(x)\frac{dc}{dx} = \text{const}$$

So

$$\frac{dc}{dx} = -\frac{J}{D(x)} \Rightarrow c(x) = c(x_0) - J\int_{x_0}^{x} \frac{1}{D(\xi)}\, d\xi$$

Often requires numerical integration for $D(\xi)$.

- Dirchlet boundary   directly integration
- Neumann boundary   need to fix dc/dx at boundary

Part II: Non-steady State Diffusion

Different strategies

- superposition with known "source" solutions
- separation of variables (finite domains)
- Laplace transform (initial condition handling)
- numerical methods (general geometry / $D(c)$)

Method 1: Superposition of Known Solutions

Use linearity of diffusion equation

If c_a and c_b satisfy the PDE and BCs, then

$$c = c_a + c_b$$

also satisfies (with compatible IC/BC decomposition).

Inifinite Space: Half-Half Situation

Geometry: $x \geq 0$

I.C.

- $c(x < 0, t = 0) = c_L$
- $c(x > 0, t = 0) = c_R$

Solution form

$$c(x,t) = \frac{c_L + c_R}{2} + \frac{c_L - c_R}{2} \operatorname{erf}\left(\frac{x}{\sqrt{2Dt}}\right)$$

How do we get here?

Limits and Checks

- $t \to 0^+$: $\text{erfc}(x/(2\sqrt{Dt})) \to 0$ for $x > 0 \quad c \to c_B$
- $x \to 0$: $\text{erfc}(0) = 1 \quad c(0,t) = c_A$
- $x \to \infty$: $\text{erfc}(\infty) = 0 \quad c \to c_B$

Next Steps

- Apply these solutions to real diffusion experiments
- Extract D by fitting measured $c(x,t)$
- Extend to variable $D(c)$ and coupled diffusion (later)