MATE 664 Lecture 04

Introduction to Diffusion

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Recap of Lecture 03

Key ideas from last lecture:

- Entropy flux and production
- Rewritting entropy production in flux and driving force terms
- Direct and coupling coefficients
- Analysis of several cross-coupling effects in material science

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Learning Outcomes

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

- Identify driving forces and fluxes for diffusive mass transport
- Derive Fick's first law from irreversible thermodynamics using chemical potential
- Estimate magnitudes of diffusivity in gases, liquids, and solids
- Explain temperature dependence of diffusivity using Arrhenius-type relations
- explain the thermodynamic origin of self-diffusion

Recap: Driving Forces in Irreversible Thermodynamics

- entropy balance:
$$\frac{ds}{dt} = -\nabla \cdot \vec{J}_s + \dot{\sigma}$$
- entropy flux:
$$\vec{J}_s = \sum_i \frac{\psi_i}{T} \vec{J}_i$$
- entropy production:
$$T\dot{\sigma} = -\sum_i \vec{J}_i \cdot \nabla \psi_i \geq 0$$

When Do $\dot{\sigma}$ Diminish? Orthogonality of Flux and Driving Force

We will show one example that has non-trivial solution to $\dot{\sigma} = 0$

- entropy production vanishes if:
$$\vec{J}_i \cdot \nabla \psi_i = 0$$
- Example: Hall effect
  - Current flows while electric potential gradient is orthogonal
  - Generalized for thermomagnetic and galvanomagnetic effects (Callen *Phys. Rev.* **1948**, 73, 1349)
  - Magnetic field induced symmetry breaking
  - $L_{ij}(H) = L_{ji}(-H)$

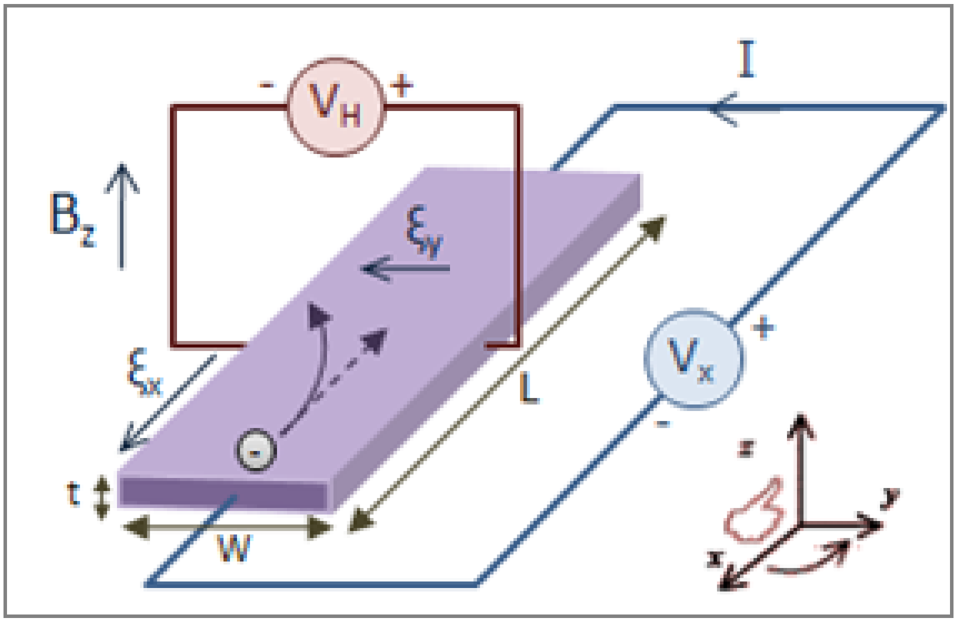

Figure 1: Hall effect scheme

Chemical Potential as Driving Force

- Consider one chemical species with chemical potential μ
- Definition:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

- μ represents energy cost of adding more molecules
- Diffusion driven by gradients in μ

See analog to a water tank in handwritten notes

Entropy Production and Mass Flux

- Entropy production due to diffusion:

$$T\dot{\sigma} = -\vec{J}_m \cdot \nabla \mu$$

- Linear law:
$$\vec{J}_m = -L_{MM}\nabla\mu$$

- L_{MM}: phenomenological mobility coefficient

From Mobility to Fick's Law (Determine L_MM)

See analog in handwritten notes

- Force balance and drift velocity (M: mobility):
$$v = M\nabla\mu$$

- Mass flux:
$$\vec{J} = cv = -Mc\nabla\mu$$

- Diffusion coefficient:
$$D = Mk_BT$$

Chemical Potential in Mixtures

See analog in handwritten notes

- For constant T, P:
$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P}$$

- Chemical potential in a mixture solution:
$$\mu_i = \mu_i^0 + k_BT\ln\gamma_i x_i$$

- activity coefficient $\gamma_i = 1$ for ideal solution (Raoult's law)

Fick's First Law

- Substitute μ_i into flux. For species i

$$\vec{J} = -D\nabla c$$

- Assumptions:
  - ideal solution
  - constant T
  - isotropic medium ($D_{\alpha\beta} = D = \text{Const}$)
- concentration gradient is a special case of $\nabla\mu$

What Does Diffusivity Depend On?

- temperature
- concentration
- spatial position (??)
- general diffusion driven by $\nabla\mu$
- Fick's law valid under restricted conditions

Fick's Second Law

- Mass conservation (no source term)

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}$$

- Substitution:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c)$$

- If D_i is constant:

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

  - ∇^2: Laplace operator

One-Dimensional Diffusion in Isotropic Homogeneous Medium

- 1D equation:

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

- Steady state:

$$\frac{\partial^2 c}{\partial x^2} = 0$$

  - Linear concentration profile!

Physical Meaning of Laplace Operator

- $\nabla^2 c$ measures curvature (sort of...)
- Steady state implies zero curvature
- Transient diffusion requires nonzero curvature
- Curvature and Second Derivative
  - concave profile:

$$\frac{d^2 c}{dx^2} < 0$$

  - convex profile:

$$\frac{d^2 c}{dx^2} > 0$$

  - curvature determines smoothing direction

Typical Magnitudes of Diffusivity

- gases:

$$D \sim 10^{-5}\ \mathrm{m^2/s}$$

- liquids:

$$D < 10^{-9}\ \mathrm{m^2/s}$$

- solids:

$$D < 10^{-13}\ \mathrm{m^2/s}$$

Typical D Range

A Common Misconception

Search for any youtube video with *"diffusion experiment dye"*

Example Video

Can we **verify** whether the scenario seen is Ficknian diffusion?

Diffusion vs Convection Length Scale

Length L traveled in time t:

- **Diffusion:** $L = 6\sqrt{D_{AB}\, t}$ *(Einstein, ~1905)*
- **Convection:** $L = v_m\, t$

What is typical D_{AB} in a liquid?
- Often $D_{AB} \sim 10^{-9}$ to $10^{-10}\,\mathrm{m}^2/\mathrm{s}$

Assuming $D_{AB} = 10^{-10}\mathrm{m}^2/\mathrm{s}$ $v_m = 10^{-3}\mathrm{m/s}$

Temperature Dependence of Diffusivity

- Arrhenius form:

$$D = D_0 \exp\left(-\frac{\Delta H^a}{k_B T}\right)$$

- ΔH^a: activation enthalpy
- Why do we measure ΔH_a, not the ΔG^a?
- How can you read the plot?

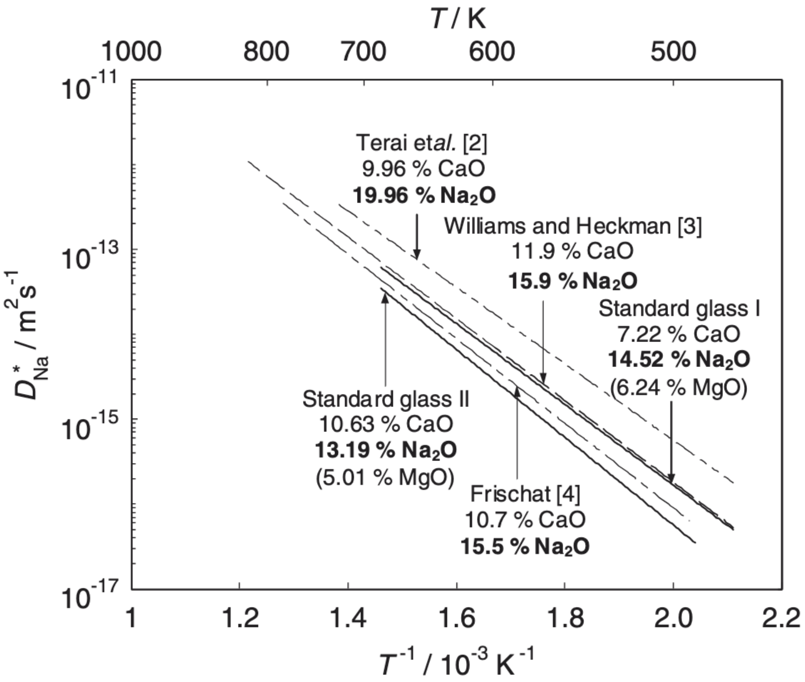

Fig. 8. Comparison of the ^{22}Na diffusivity in various soda-lime glasses. [1]

Physical Interpretation of Activation

- atoms hop between sites
- energy barrier must be overcome
- jump frequency:

$$\Gamma = \nu \exp\left(-\frac{\Delta G^{\ddagger}}{k_B T}\right)$$

- diffusion proportional to hop rate and distance

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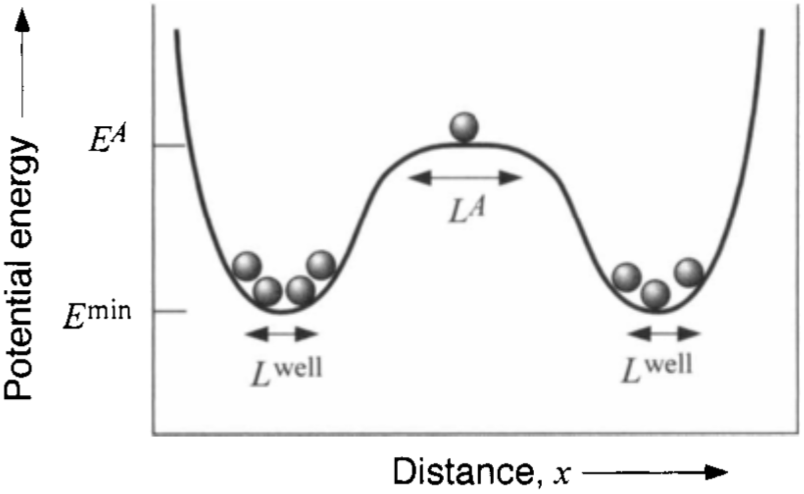
[1] *Solid. State Ionics* **2006**, 177, 2839



Multiple Diffusion Mechanisms

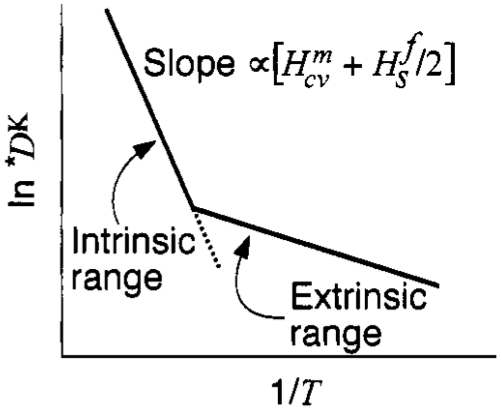


Figure 2: Intrinsic and extrinsic mechanism in doped halides

- Different diffusion paths
- Different activation energies
- Dominant mechanism controls slope of $\ln D$ vs $1/T$

Diffusion in Gases

- Kinetic theory description
- Chapman–Enskog result:

$$D \propto \frac{T^{3/2}}{P}$$

- Collisions limit transport

Diffusion in Liquids

- Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r}$$

- η: viscosity
- r: particle radius
- Is it accurate enough in polymer solutions?

Diffusion in Solids

- Diffusion in solids is much more complex!
- Discrete lattice sites
- Mechanisms (non-exhaustive)
  - Vacancy
  - Ring mechanism
  - Push-out mechanism
  - Interstitial
- Strong temperature dependence

Vacancy Diffusion Mechanism

- Atoms exchange with vacancies
- Jump only if vacancy is adjacent
- Vacancy sources:
    - Surfaces
    - Grain boundaries
    - Dislocations

Types of Diffusivity

As the previous example of diffusion + convection video shows, the measurement of diffusivity really depends on which reference frame we use.

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

Measuring Self-Diffusion

- 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)

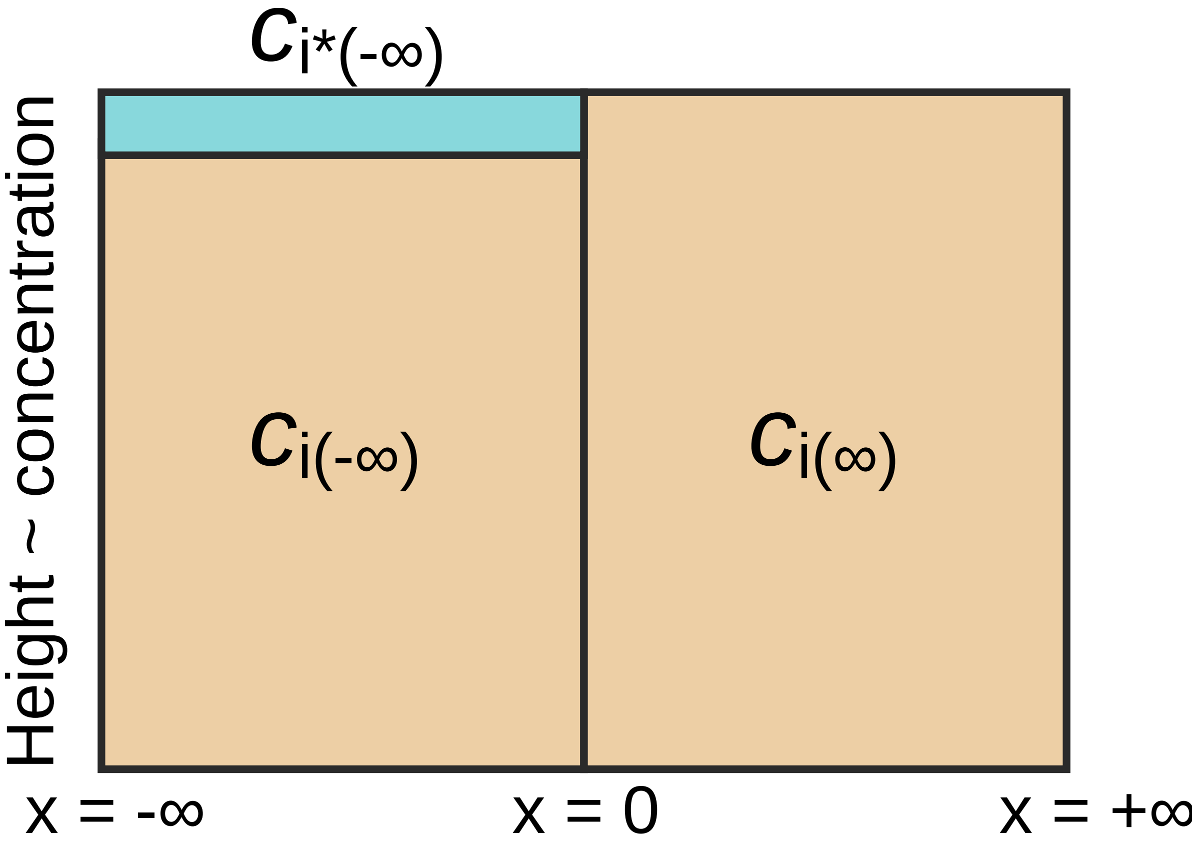


Figure 3: Setup for isotope diffusion

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:

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

Why Self-Diffusion Occurs

- **No** macroscopic concentration gradient!
- Chemical potential varies locally
- Random walk lowers free energy
- Entropy maximization drives motion

Summary

- Diffusion is driven by chemical potential gradients
- Fick's laws follow from irreversible thermodynamics
- Laplace operator reflects curvature and smoothing
- Diffusivity varies strongly with phase and temperature
- Self-diffusion exists even in homogeneous systems