

Chapter Outline

Diffusion - how do atoms move through solids?

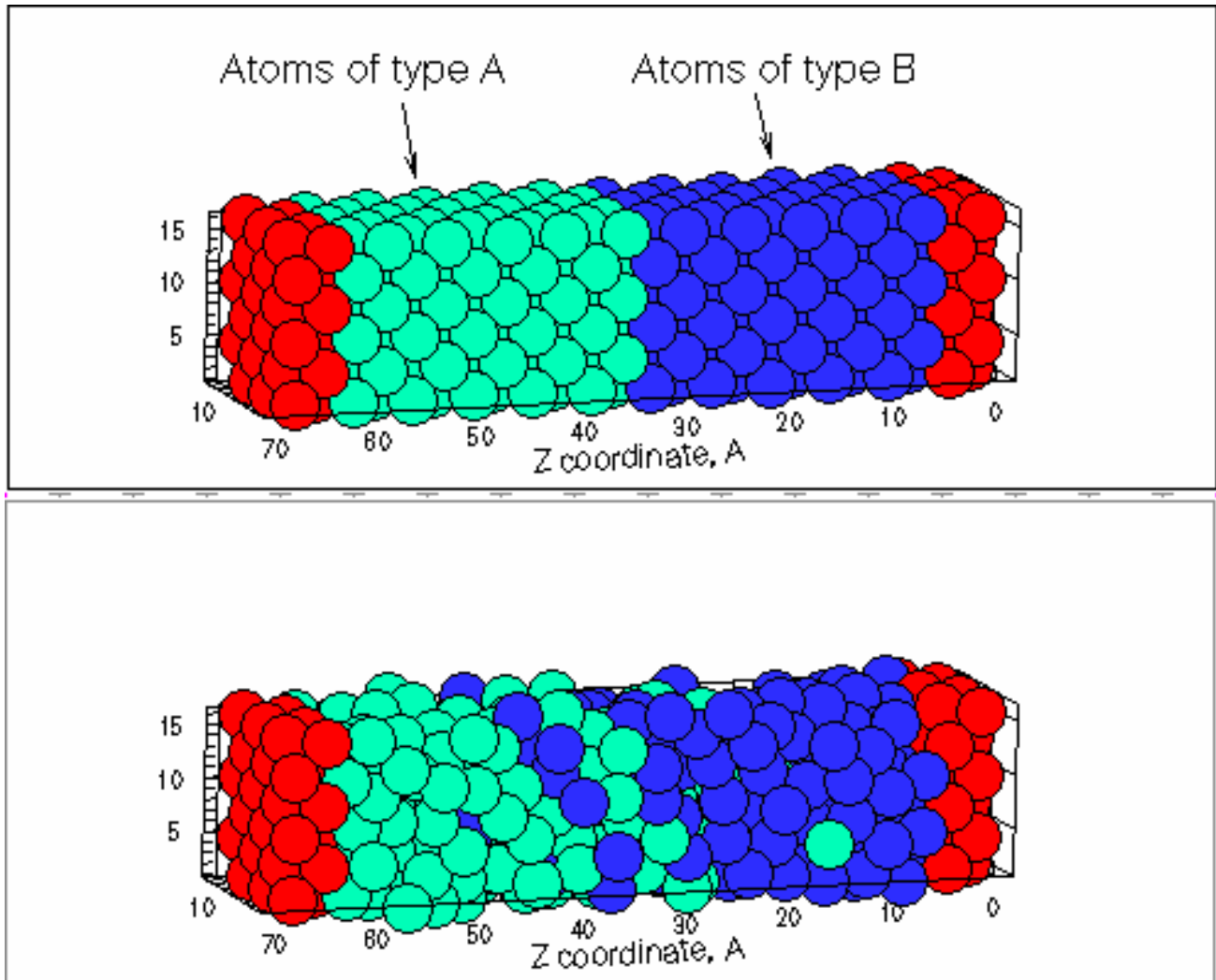
- **Diffusion mechanisms**
 - **Vacancy diffusion**
 - **Interstitial diffusion**
 - **Impurities**

- **The mathematics of diffusion**
 - **Steady-state diffusion** (Fick's first law)
 - **Nonsteady-State Diffusion** (Fick's second law)

- **Factors that influence diffusion**
 - **Diffusing species**
 - **Host solid**
 - **Temperature**
 - **Microstructure**

What is diffusion?

Diffusion is material transport by atomic motion.

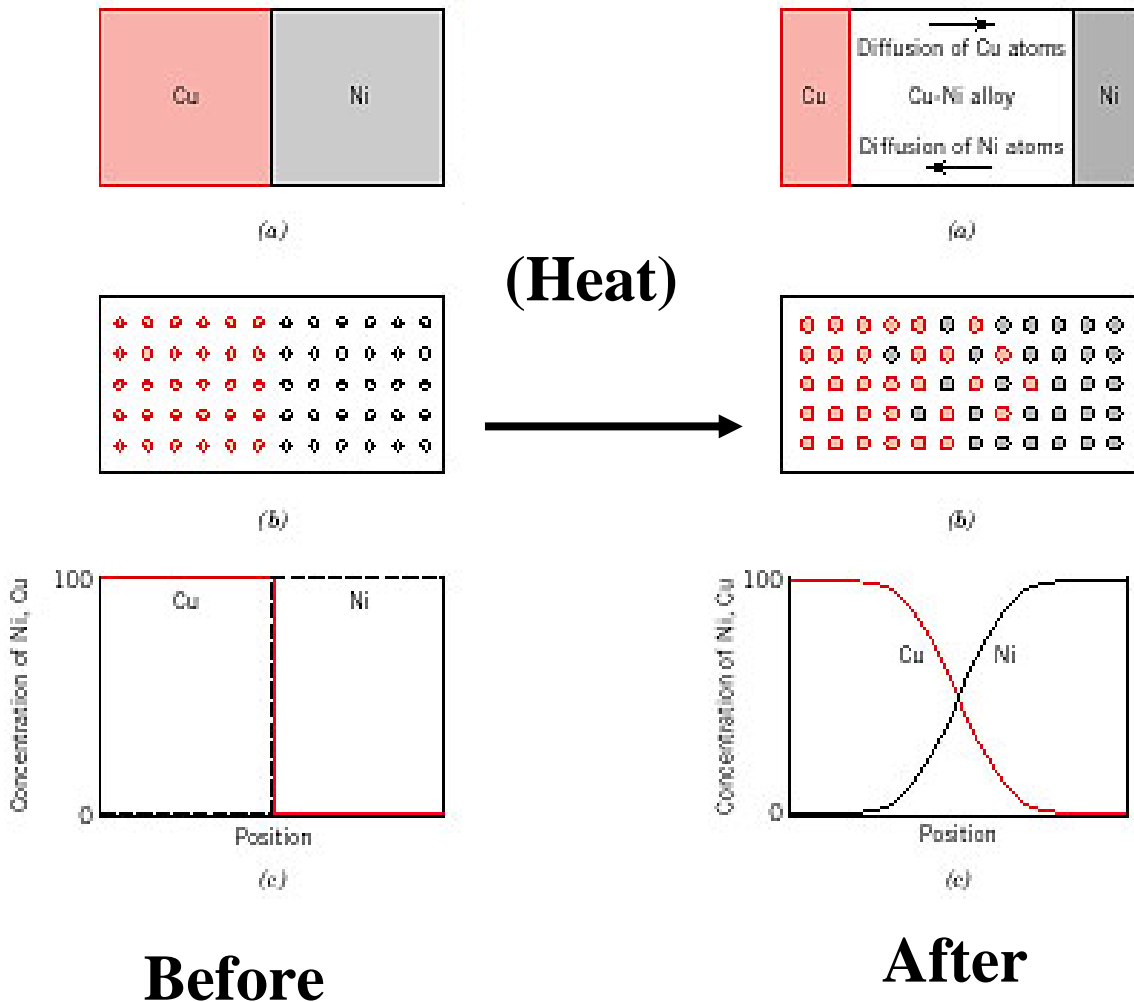


results of an atomistic simulation of atomic mixing
homework project in MSE 4592/6270

Inhomogeneous materials can become homogeneous by diffusion. For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion.

Interdiffusion and Self-diffusion

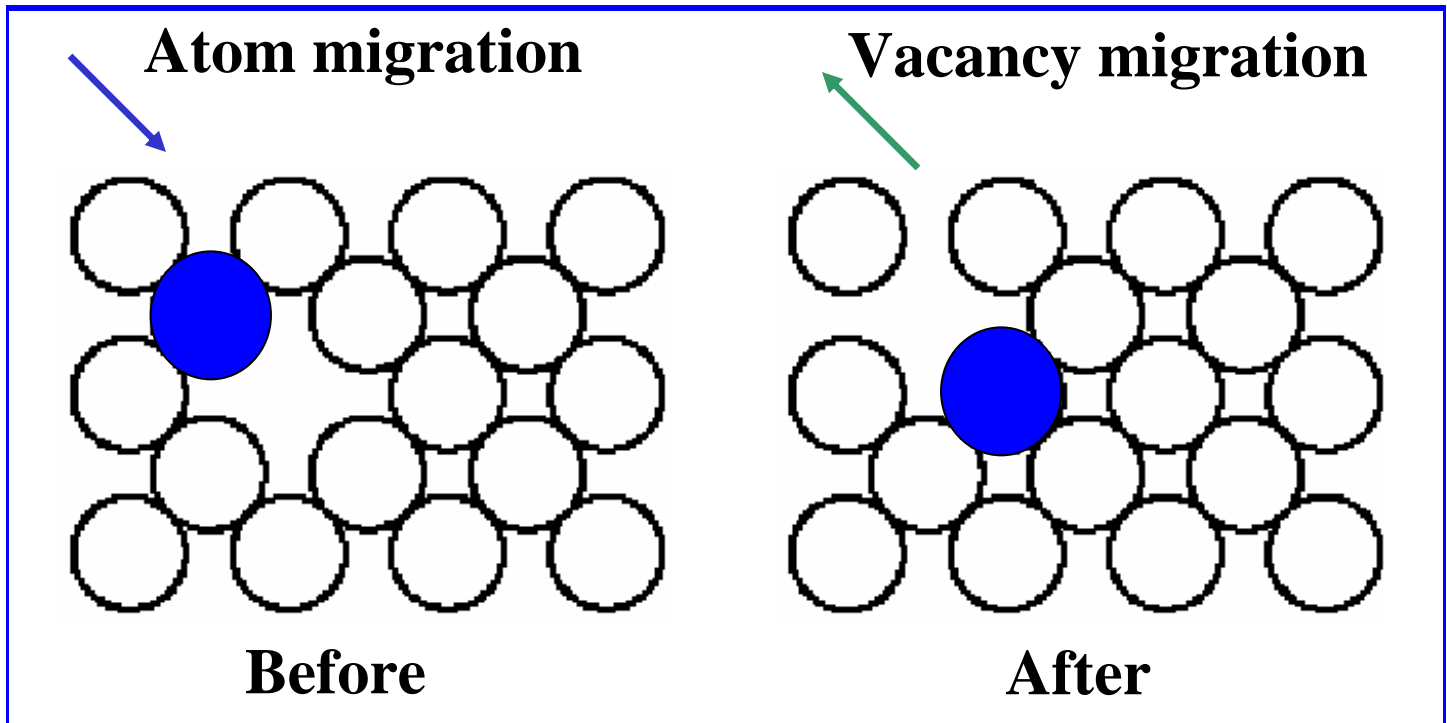
Interdiffusion (or impurity diffusion) occurs in response to a **concentration gradient**.



Self-diffusion is diffusion in one-component material, when all atoms that exchange positions are of the same type.

Diffusion Mechanisms (I)

Vacancy diffusion mechanism

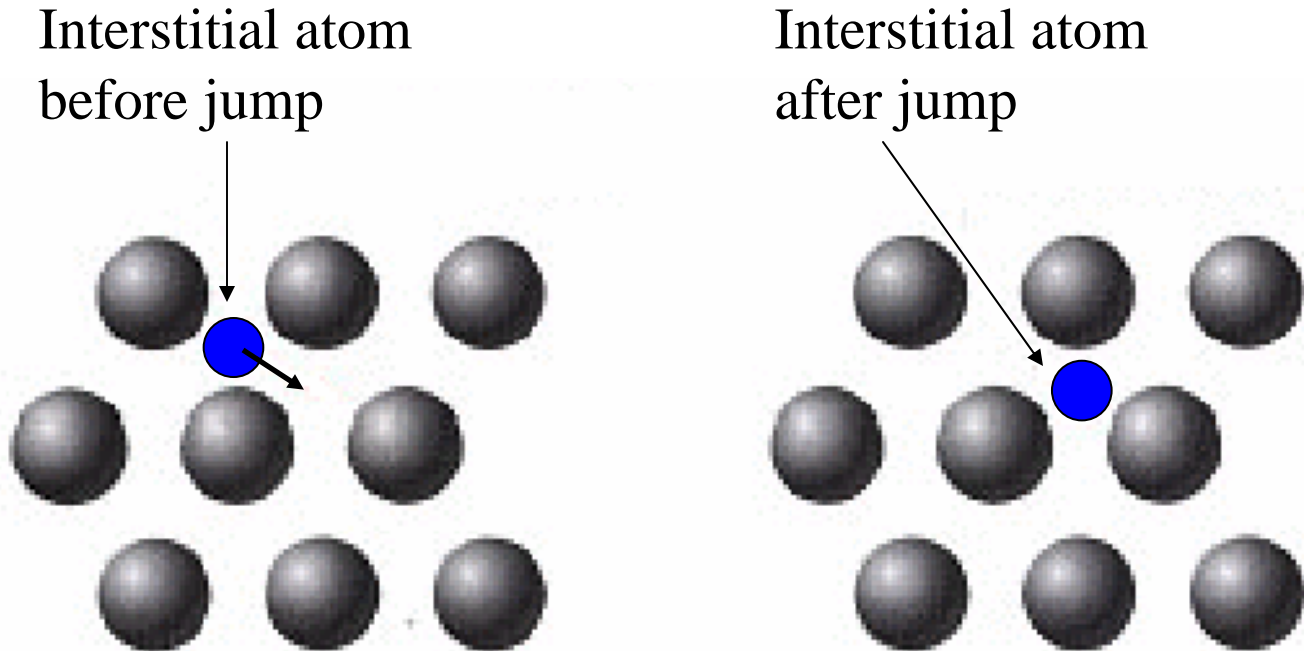


To jump from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during jump. This energy comes from the thermal energy of atomic vibrations ($E_{av} \sim k_B T$)

The direction of flow of atoms is opposite the vacancy flow direction.

Diffusion Mechanisms (II)

Interstitial diffusion mechanism



Interstitial diffusion is generally faster than vacancy diffusion because bonding of interstitials to the surrounding atoms is normally weaker and there are many more interstitial sites than vacancy sites to jump to.

Requires small impurity atoms (e.g. C, H, O) to fit into interstices in host.

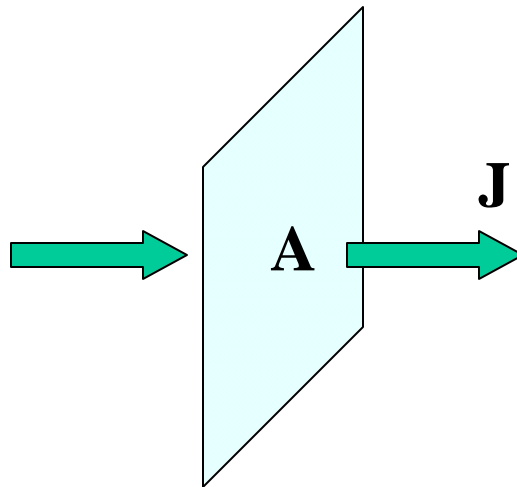
Diffusion Flux

The flux of diffusing atoms, J , is used to quantify how fast diffusion occurs. The flux is defined as either the number of atoms diffusing through unit area per unit time (atoms/m²-second) or the mass of atoms diffusing through unit area per unit time, (kg/m²-second).

For example, for the mass flux we can write

$$\mathbf{J} = \mathbf{M} / \mathbf{A}t \cong (1/A) (dM/dt) \text{ (Kg m}^{-2} \text{ s}^{-1}\text{)}$$

where M is the mass of atoms diffusing through the area A during time t .



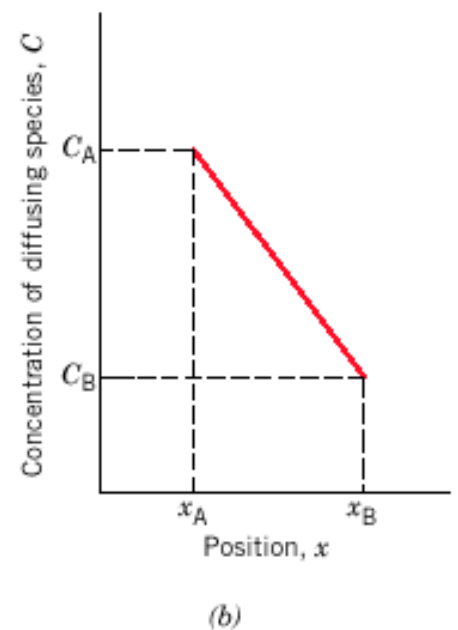
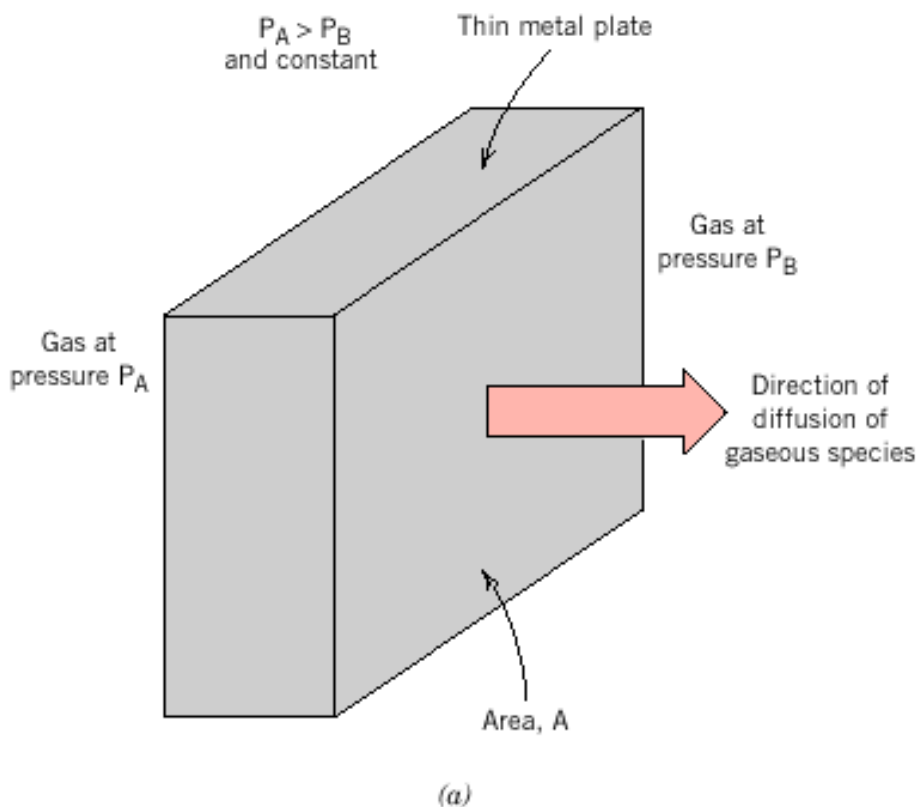
Steady-State Diffusion

Steady state diffusion: the diffusion flux does not change with time.

Concentration profile: concentration of atoms/molecules of interest as function of position in the sample.

Concentration gradient: dC/dx (Kg m^{-4}): the slope at a particular point on concentration profile.

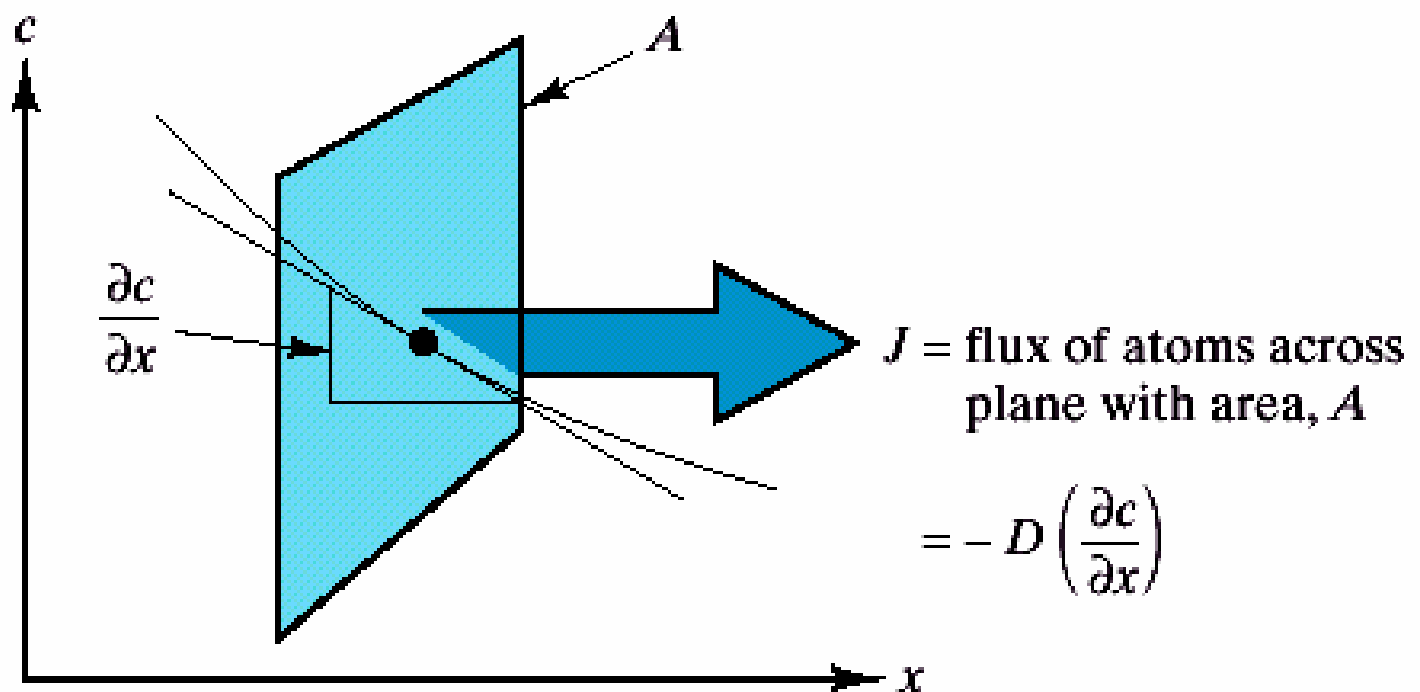
$$\frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B}$$



Steady-State Diffusion: Fick's first law

Fick's first law: the diffusion flux along direction x is proportional to the concentration gradient

$$J = -D \frac{dC}{dx} \quad \text{where } \mathbf{D} \text{ is the diffusion coefficient}$$



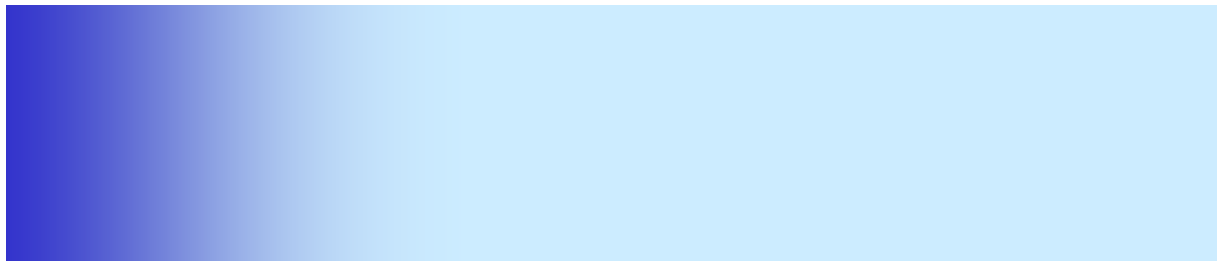
The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense).

The minus sign in the equation means that diffusion is down the concentration gradient.

Diffusion down the concentration gradient

$$J = -D \frac{dC}{dx}$$

Why do the random jumps of atoms result in a flux of atoms from regions of high concentration towards the regions of low concentration?



↑
Atoms here jump randomly both right and left

↑
But there are not many atoms here to jump to the left

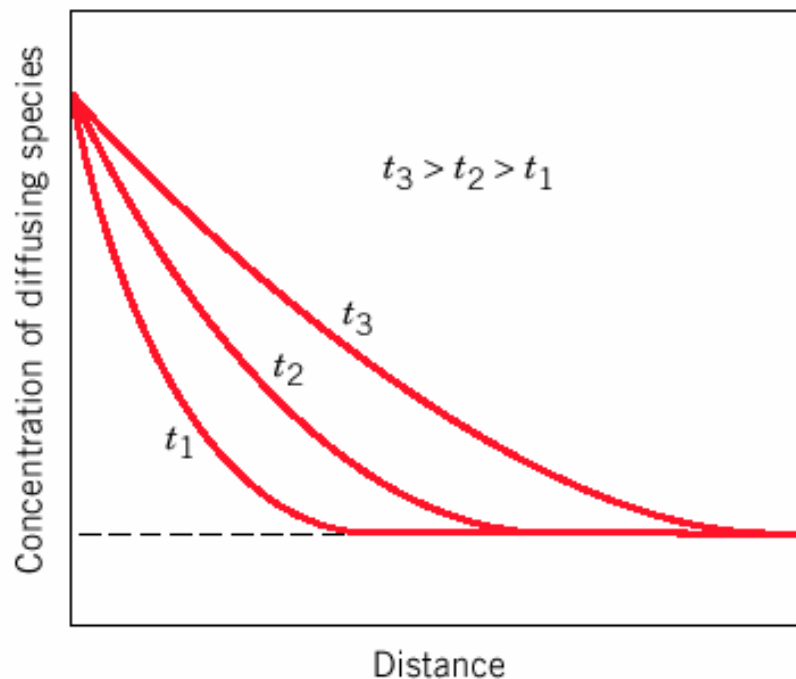
As a result there is a net flux of atoms from left to right.

Nonsteady-State Diffusion: Fick's second law

In many real situations the concentration profile and the concentration gradient are changing with time. The changes of the concentration profile can be described in this case by a differential equation, **Fick's second law**.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = D \frac{\partial^2 C}{\partial x^2}$$

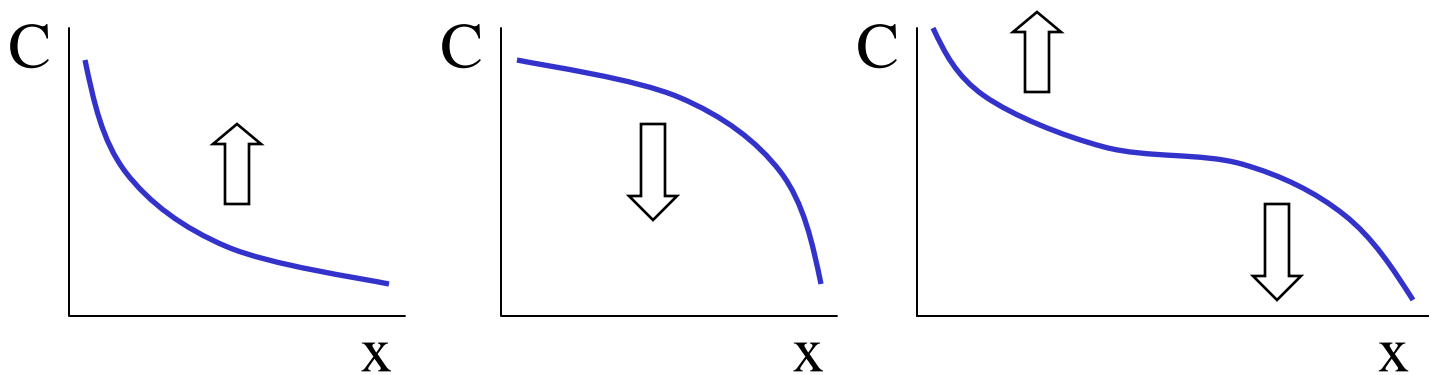
Solution of this equation is concentration profile as function of time, $C(x,t)$:



Nonsteady-State Diffusion: Fick's second law

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

Fick's second law relates the rate of change of composition with time to the curvature of the concentration profile:

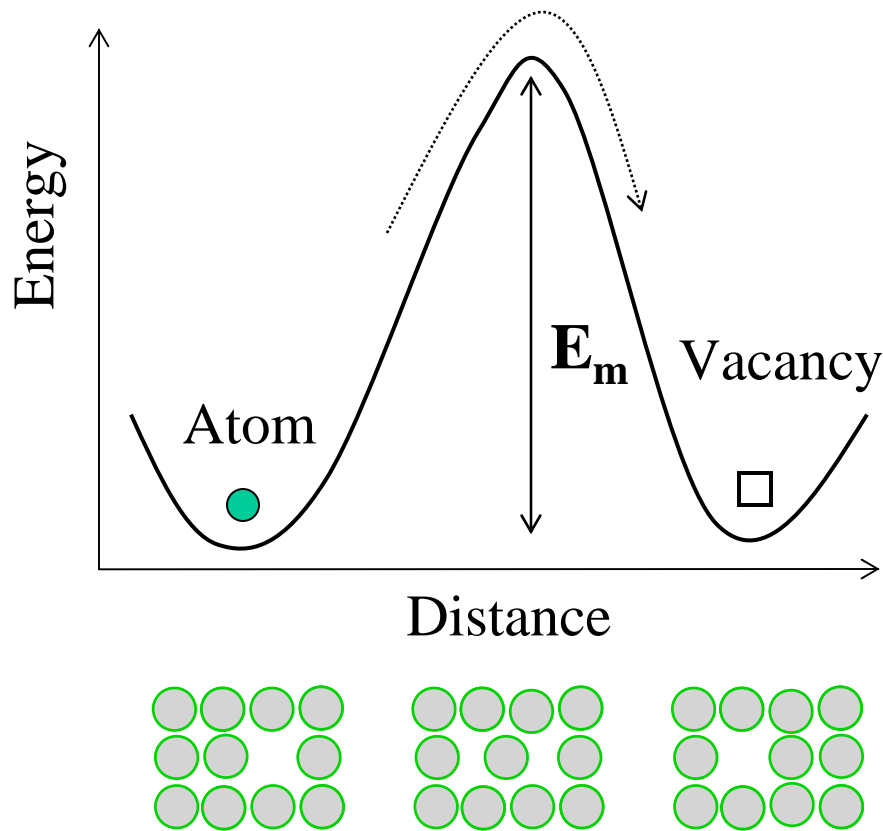


Concentration increases with time in those parts of the system where concentration profile has a positive curvature. And decreases where curvature is negative.

The phenomenological description based on the Fick's laws is valid for any atomic mechanism of diffusion. Understanding of the atomic mechanisms is important, however, for predicting the dependence of the atomic mobility (and, therefore, diffusion coefficient) on the type of interatomic bonding, temperature, and microstructure.

Diffusion – Thermally Activated Process (I) (*not tested*)

To jump from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during jump. The energy necessary for motion, E_m , is called **the activation energy** for vacancy motion.



Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. Activation energy E_m has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

Diffusion – Thermally Activated Process (II) (*not tested*)

The average thermal energy of an atom ($k_B T = 0.026$ eV for room temperature) is usually much smaller than the activation energy E_m (~ 1 eV/atom) and a large fluctuation in energy (when the energy is “pooled together” in a small volume) is needed for a jump.

The probability of such fluctuation or frequency of jumps, R_j , depends exponentially on temperature and can be described by equation that is attributed to Swedish chemist **Arrhenius**:

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

where R_0 is so-called “attempt frequency” proportional to the frequency of atomic vibrations.

Diffusion – Thermally Activated Process (III) (*not tested*)

For the vacancy diffusion mechanism the probability for any atom in a solid to move is the product of

the probability of finding a vacancy in an adjacent lattice site (see Chapter 4):

$$P = z \exp\left(-\frac{Q_v}{k_B T}\right) \quad \begin{array}{l} z \text{ is coordination number} \\ \text{(number of atoms adjacent to} \\ \text{the vacancy)} \end{array}$$

and the frequency of jumps (probability of thermal fluctuation needed to overcome the energy barrier for vacancy motion):

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

The diffusion coefficient can be estimated as

$$\begin{aligned} D &\approx z R_0 a^2 \exp\left(-\frac{E_m}{k_B T}\right) \exp\left(-\frac{Q_v}{k_B T}\right) = \\ &= D_0 \exp\left(-\frac{(E_m + Q_v)}{k_B T}\right) = D_0 \exp\left(-\frac{Q_d}{k_B T}\right) \end{aligned}$$

Temperature dependence of the diffusion coefficient, follows the Arrhenius dependence.

Diffusion – Temperature Dependence (I)

$J = -D \frac{dC}{dx}$ Diffusion coefficient is the measure of mobility of diffusing species.

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

D_0 – temperature-independent preexponential (m^2/s)

Q_d – the activation energy for diffusion (J/mol or eV/atom)

R – the gas constant (8.31 J/mol-K or 8.62×10^{-5} eV/atom-K)

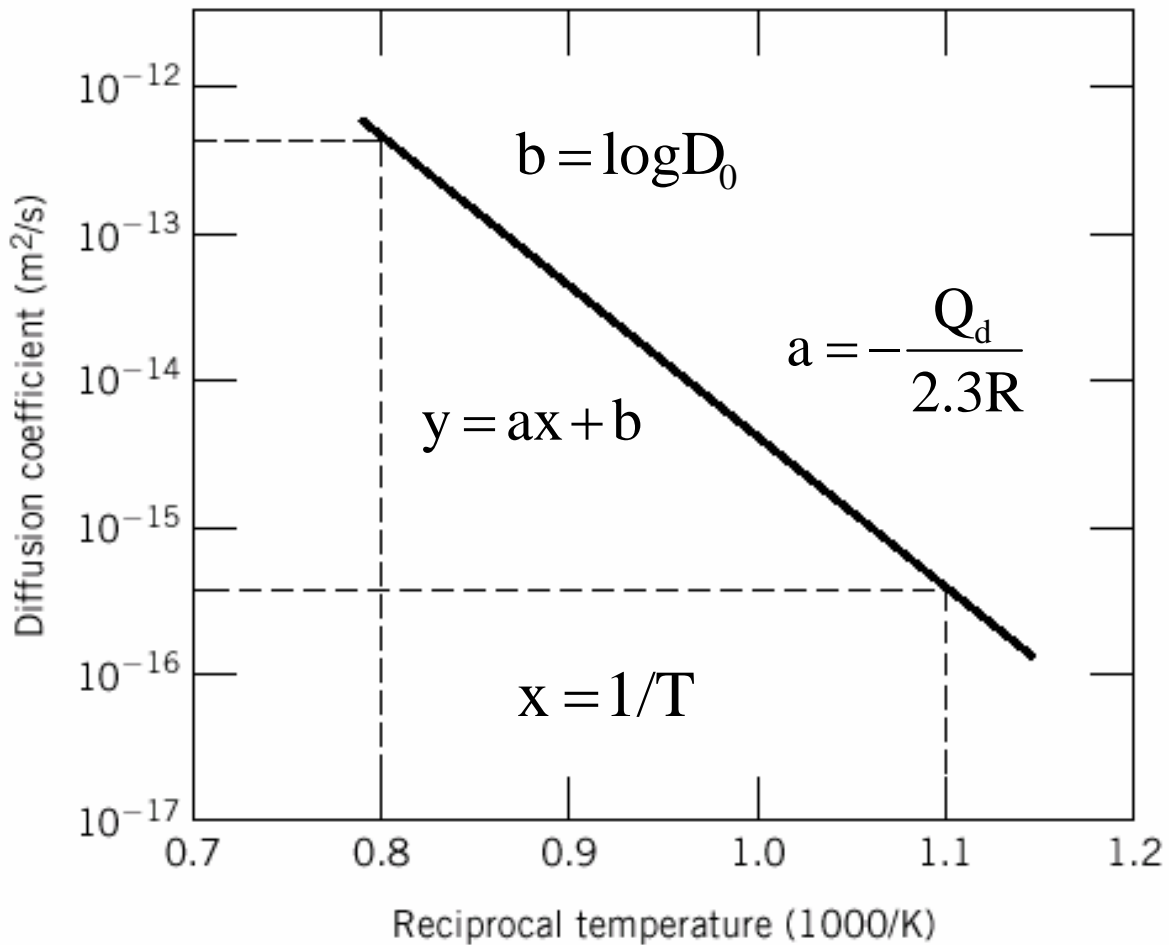
T – absolute temperature (K)

The above equation can be rewritten as

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right) \quad \text{or} \quad \log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T}\right)$$

The activation energy Q_d and preexponential D_0 , therefore, can be estimated by plotting $\ln D$ versus $1/T$ or $\log D$ versus $1/T$. Such plots are called Arrhenius plots.

Diffusion – Temperature Dependence (II)

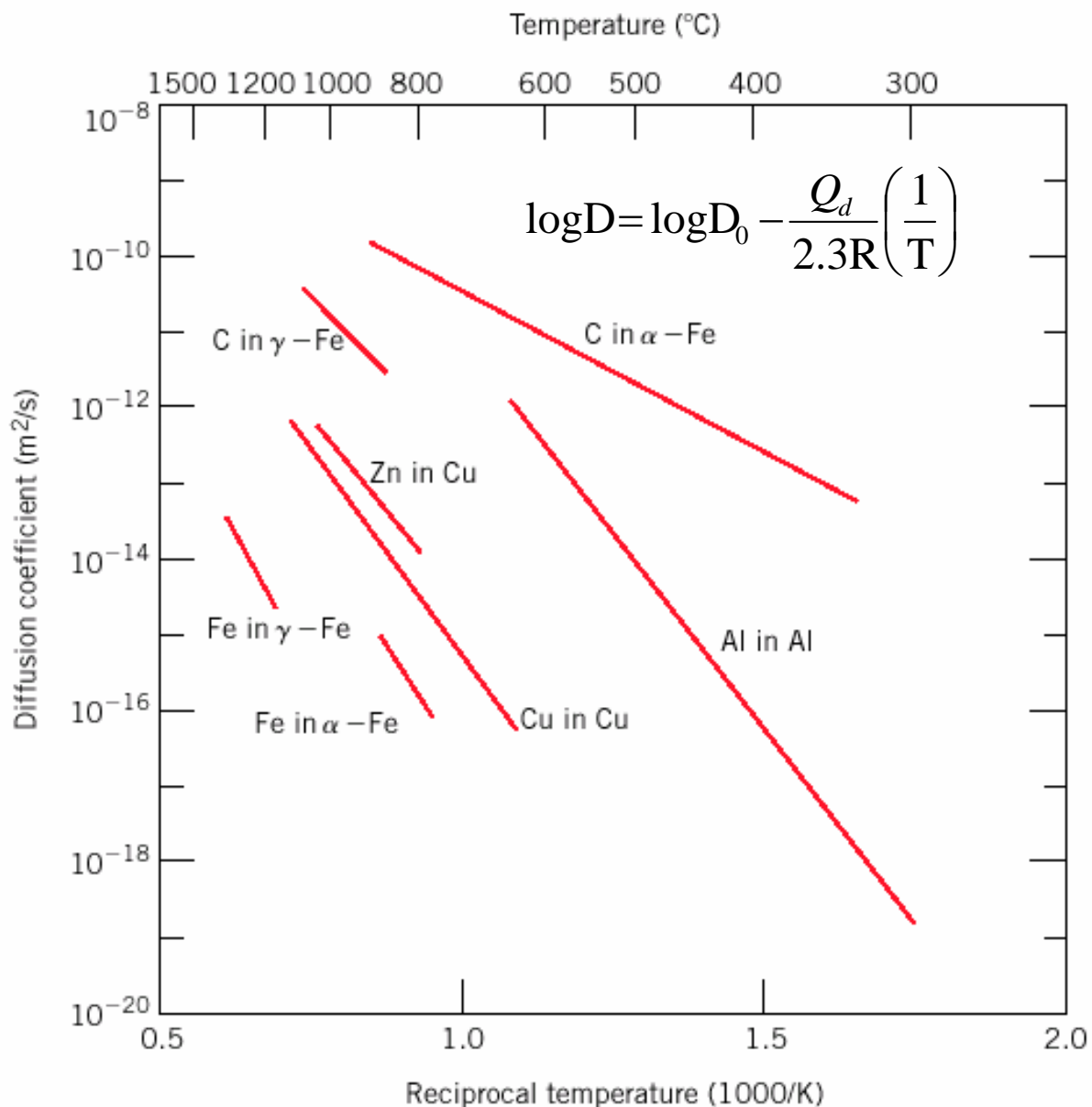


Graph of $\log D$ vs. $1/T$ has slope of $-Q_d/2.3R$,
intercept of $\log D_0$

$$\log D = \log D_0 - \frac{Q_d}{2.3R} \left(\frac{1}{T} \right)$$

$$Q_d = -2.3R \left[\frac{\log D_1 - \log D_2}{1/T_1 - 1/T_2} \right]$$

Temperature dependence: Interstitial and vacancy diffusion mechanisms (I)



Diffusion of interstitials is typically faster as compared to the vacancy diffusion mechanism (self-diffusion or diffusion of substitutional atoms).

Temperature dependence: Interstitial and vacancy diffusion mechanisms

$$D = D_0 \exp\left(-\frac{Q_d}{k_B T}\right)$$

Interstitial diffusion mechanism

Impurity	D_0 , mm ² /s ⁻¹	Q_d , kJ/mol
C in FCC Fe	23	138
C in BCC Fe	1.1	87
N in FCC Fe	0.34	145
N in BCC Fe	0.47	77
H in FCC Fe	0.63	43
H in BCC Fe	0.12	15

Smaller atoms cause less distortion of the lattice during migration and diffuse more readily than big ones (the atomic diameters decrease from C to N to H).

Diffusion is faster in open lattices or in open directions

Vacancy diffusion mechanism

	D_0 , mm ² /s ⁻¹	Q_d , kJ/mol
Fe in FCC Fe	65	279
Fe in BCC Fe	410	246
Ni in Cu	230	242
Si in Si	180000	460

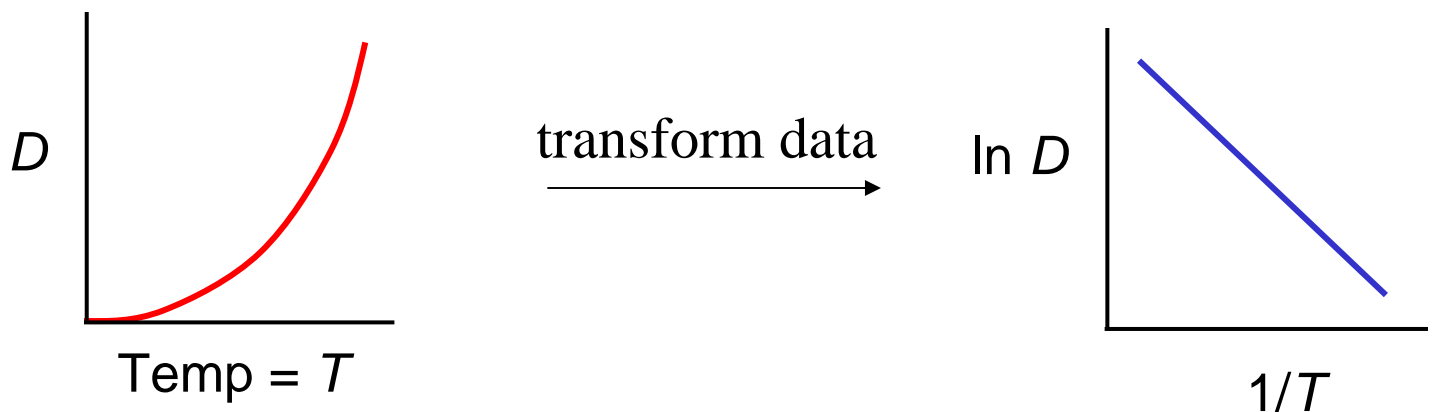
Example: Temperature dependence of D

At 300°C the diffusion coefficient and activation energy for Cu in Si are

$$D(300^\circ\text{C}) = 7.8 \times 10^{-11} \text{ m}^2/\text{s}$$

$$Q_d = 41.5 \text{ kJ/mol}$$

What is the diffusion coefficient at 350°C?



$$D = D_0 \exp\left(-\frac{Q_d}{k_B T}\right)$$

$$\ln D = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T}\right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T_2}\right) \quad \text{and} \quad \ln D_1 = \ln D_0 - \frac{Q_d}{R} \left(\frac{1}{T_1}\right)$$

$$\ln D_2 - \ln D_1 = \ln \frac{D_2}{D_1} = -\frac{Q_d}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Example: Temperature dependence of **D** (continued)

$$\ln \frac{D_2}{D_1} = -\frac{Q_d}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$D_2 = D_1 \exp \left[-\frac{Q_d}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

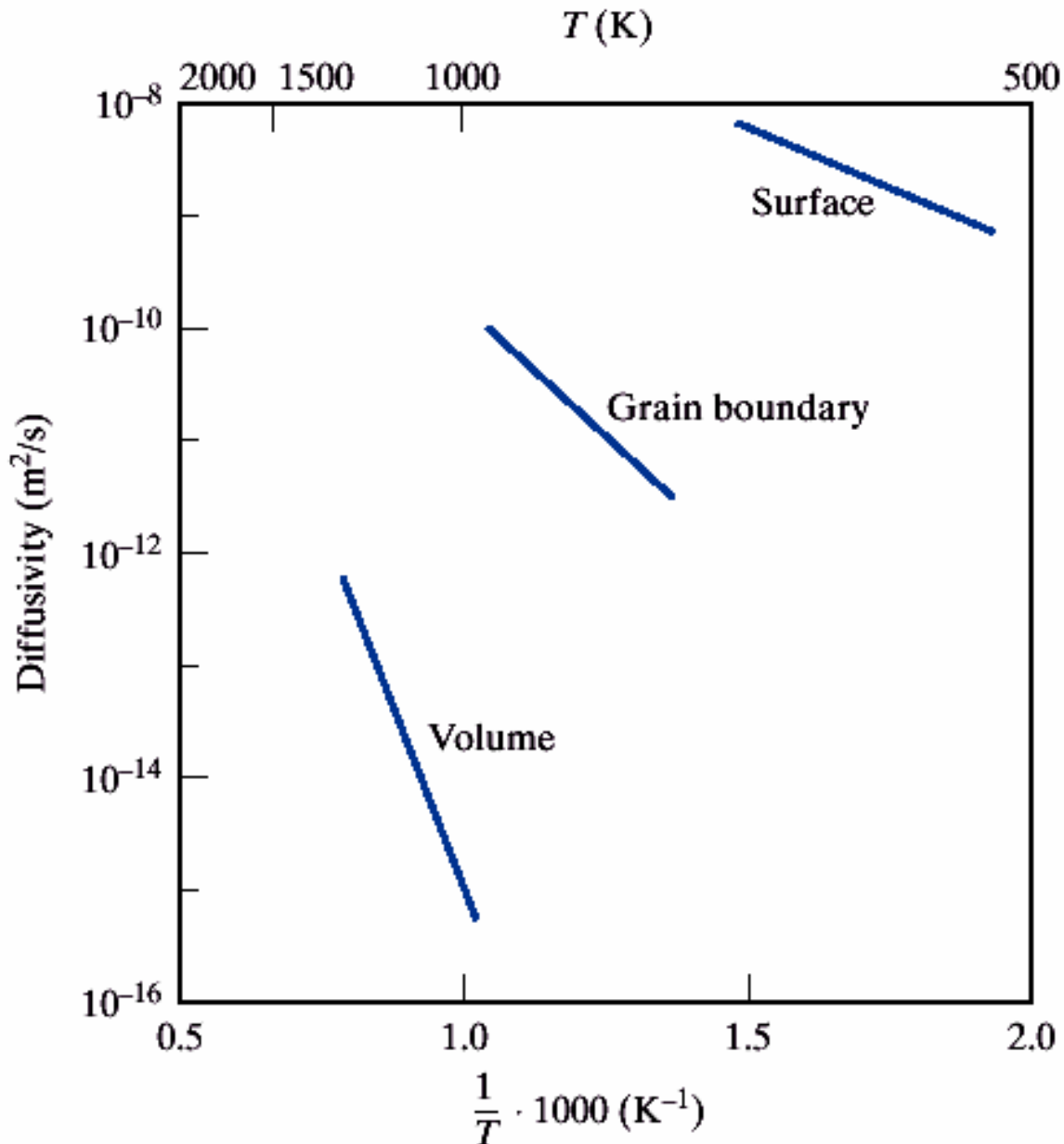
$$T_1 = 273 + 300 = 573 \text{ K}$$

$$T_2 = 273 + 350 = 623 \text{ K}$$

$$D_2 = (7.8 \times 10^{-11} \text{ m}^2/\text{s}) \exp \left[\frac{-41,500 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{623 \text{ K}} - \frac{1}{573 \text{ K}} \right) \right]$$

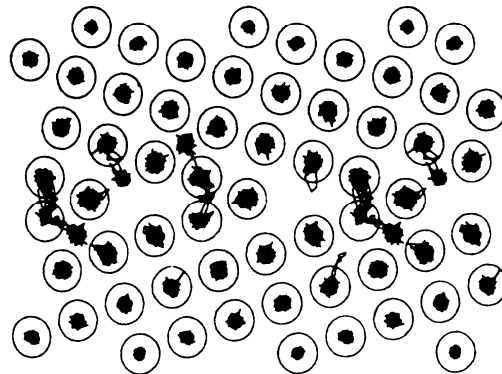
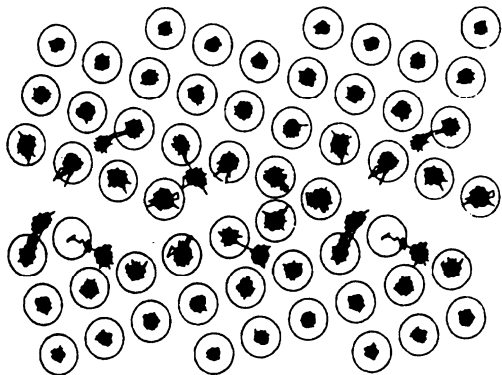
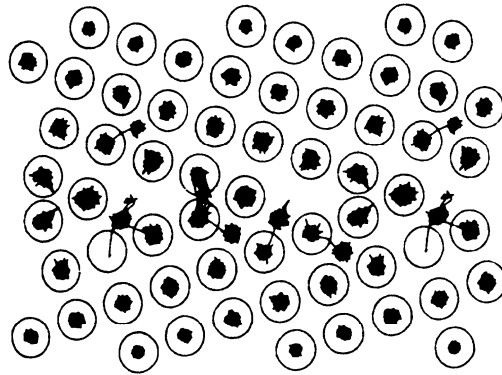
$$D_2 = 15.7 \times 10^{-11} \text{ m}^2/\text{s}$$

Diffusion: Role of the microstructure (I)



Self-diffusion coefficients for Ag depend on the diffusion path. In general the diffusivity is greater through less restrictive structural regions – grain boundaries, dislocation cores, external surfaces.

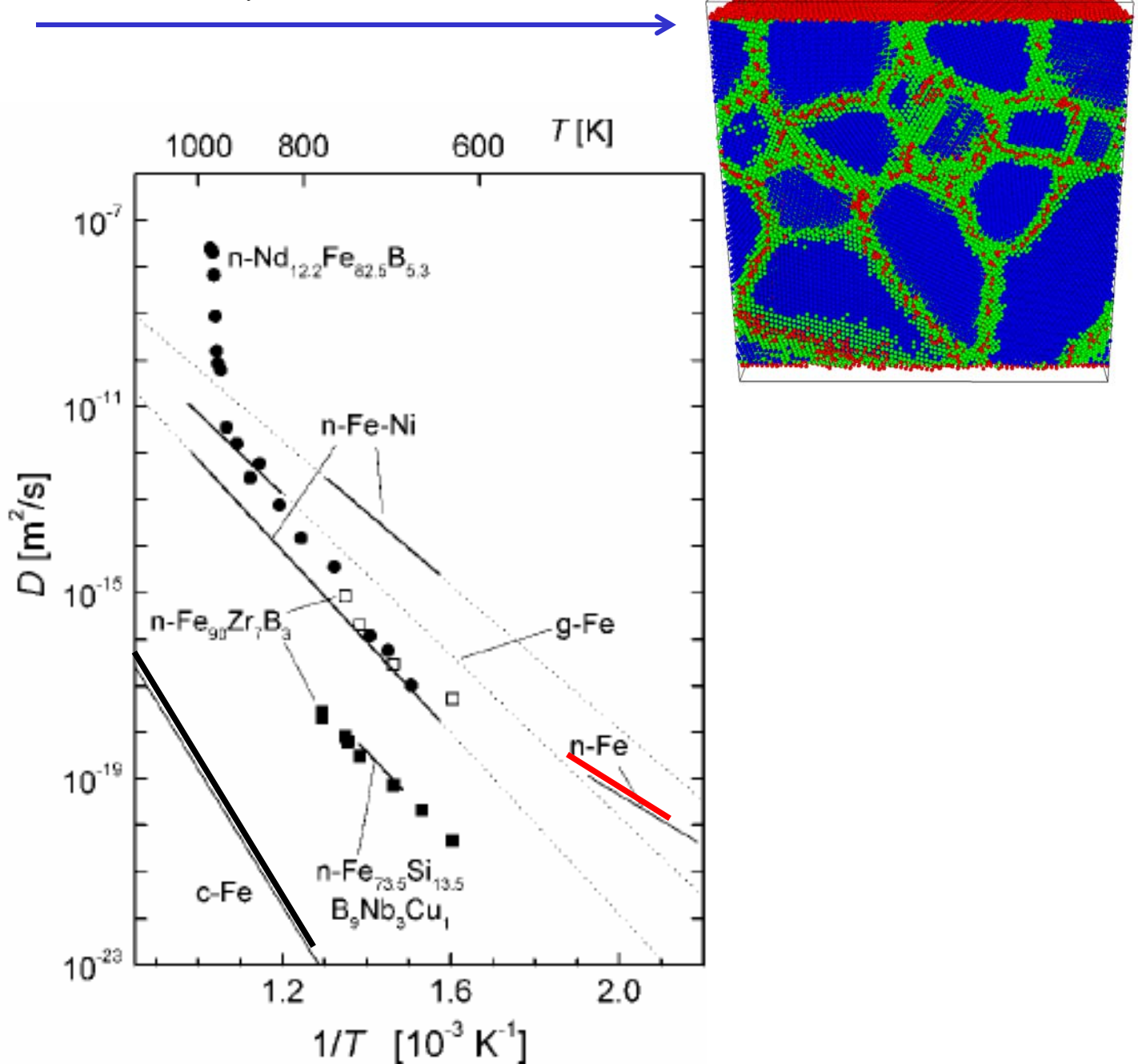
Diffusion: Role of the microstructure (II)



The plots below are from the computer simulation by T. Kwok, P. S. Ho, and S. Yip. Initial atomic positions are shown by the circles, trajectories of atoms are shown by lines. We can see the difference between atomic mobility in the bulk crystal and in the grain boundary region.

Example: Diffusion in nanocrystalline materials

Lin *et al.* *J. Phys. Chem. C* **114**, 5686, 2010



Arrhenius plots for ⁵⁹Fe diffusivities in nanocrystalline Fe and other alloys compared to the crystalline Fe (ferrite).

[Wurschum *et al.* *Adv. Eng. Mat.* **5**, 365, 2003]

Factors that influence diffusion: Summary

- **Temperature** - diffusion rate increases very rapidly with increasing temperature
- **Diffusion mechanism** – diffusion by interstitial mechanism is usually faster than by vacancy mechanism
- **Diffusing and host species** - D_o , Q_d are different for every solute, solvent pair
- **Microstructure** - diffusion is faster in polycrystalline materials compared to single crystals because of the accelerated diffusion along grain boundaries.

Diffusion in material processing

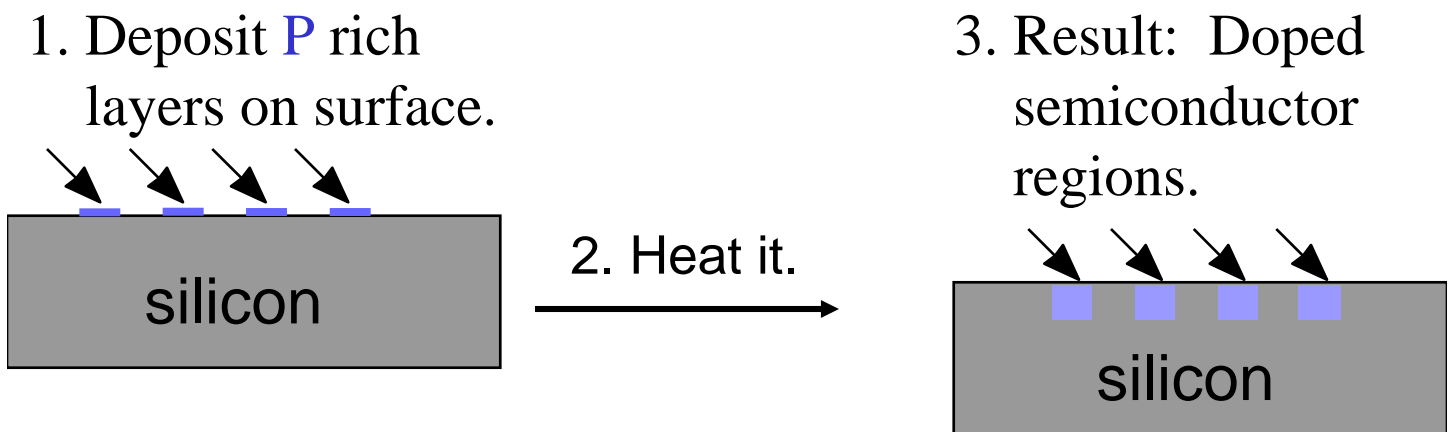
Case Hardening: Hardening the surface of a metal by exposing it to impurities that diffuse into the surface region and increase surface hardness.

Common example of case hardening is **carburization of steel**. Diffusion of carbon atoms (interstitial mechanism) increases concentration of C atoms and makes iron (steel) harder.



Doping silicon with phosphorus for *n*-type semiconductors.

Process of doping:



Summary

Make sure you understand language and concepts:

- Activation energy
- Concentration gradient
- Diffusion
- Diffusion coefficient
- Diffusion flux
- Driving force
- Fick's first and second laws
- Interdiffusion
- Interstitial diffusion
- Self-diffusion
- Steady-state diffusion
- Nonsteady-state diffusion
- Temperature dependence of D
- Vacancy diffusion

Homework #3: 5.7, 5.8, 5.22, 5.23, 5.D2

Due date: Monday, September 20.

Reading for next class:

Chapter 6: Mechanical Properties of Metals

➤ Stress and Strain

- ✓ Tension
- ✓ Compression
- ✓ Shear
- ✓ Torsion

➤ Elastic deformation

➤ Plastic Deformation

- ✓ Yield Strength
- ✓ Tensile Strength
- ✓ Ductility
- ✓ Resilience
- ✓ Toughness
- ✓ Hardness

Optional reading (not tested): *details of the different types of hardness tests, variability of material properties (starting from the middle of page 174)*