

Kinetics and Diffusion

Basic concepts in kinetics

Kinetics of phase transformations
Activation free energy barrier
Arrhenius rate equation

Atomic mechanisms of diffusion

How do atoms move through solids?

- Substitutional diffusion
- Interstitial diffusion
- High diffusivity paths, diffusion along grain boundaries, free surfaces, dislocations

Factors that influence diffusion

- Diffusing species and host solid (size, bonding)
- Temperature
- Microstructure

Diffusion in Solids - Phenomenological description

Flux, steady-state diffusion, Fick's first law
Nonsteady-state diffusion, Fick's second law

Kinetics and Diffusion

Driving force for diffusion

Diffusion in ideal and real solutions

Thermodynamic factor

Diffusion against the concentration gradient

Spinodal decomposition

Solutions to the diffusion equation

Numerical integration

Analytical solution

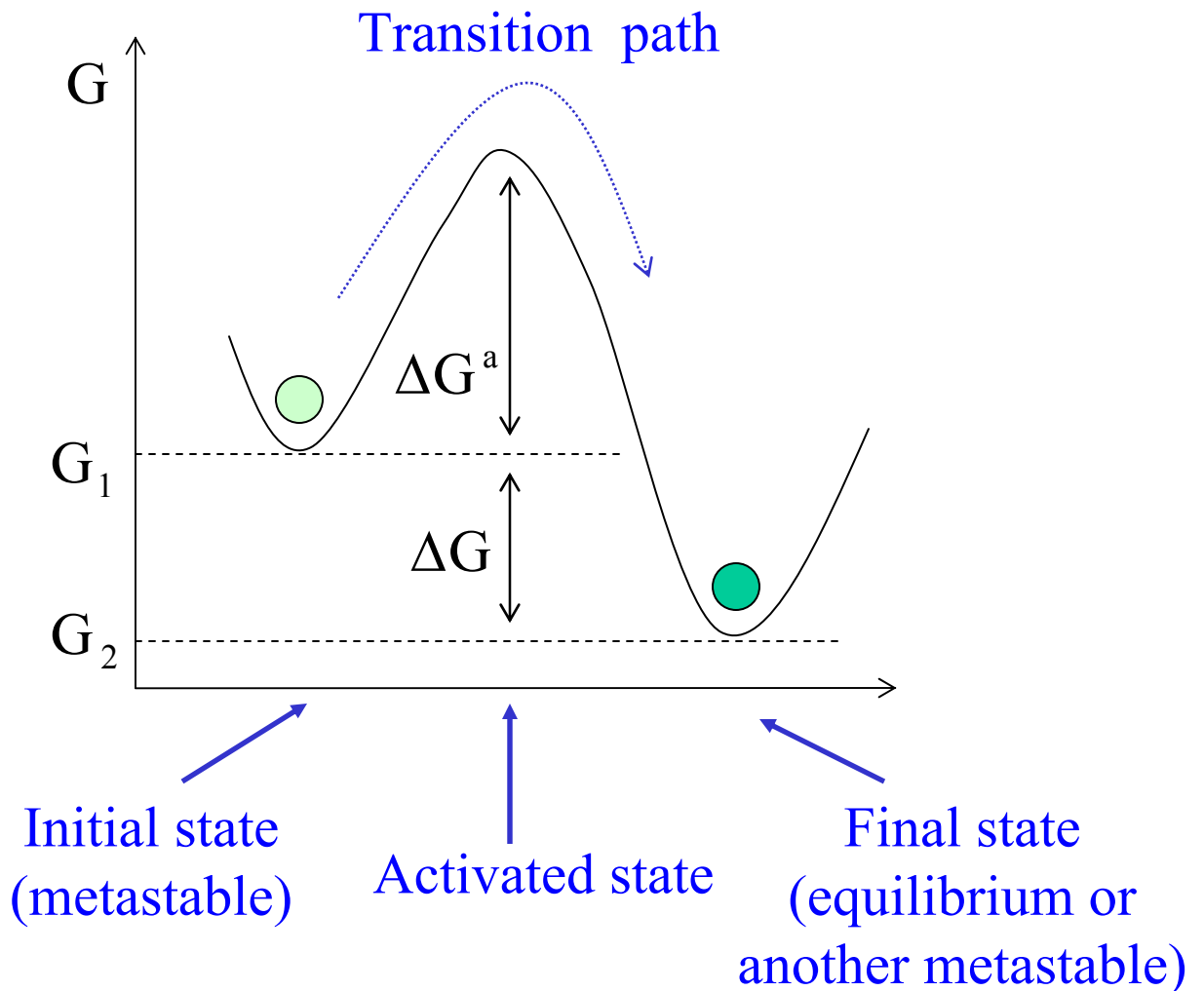
Kinetics: basic concepts

Thermodynamics can be used to predict what is the equilibrium state for a system and to calculate the driving force (ΔG) for a transformation from a metastable state to a stable equilibrium state.

How fast the transformation occurs is the question addressed by **kinetics**.

Let's consider transition from a metastable to the equilibrium state. The transformation between the initial and final states involves rearrangement of atoms – the system should go through a *transformation (or reaction) path*. Since the initial and final states are metastable or stable ones, the energy of the system increases along any transformation path between them

Kinetics: basic concepts



G_1 and G_2 are the Gibbs free energies of the initial and final states of the system

$\Delta G = G_2 - G_1$ is the *driving force for the transformation*.

ΔG^a is **the activation free energy barrier** for the transition - the maximum energy along the transformation path relative to the energy of the initial state.

Kinetics: basic concepts

In order for a system to proceed through the transition path to the equilibrium state, it has to obtain the energy that is sufficient to overcome the activation barrier.

The energy can be obtained from thermal fluctuation (when the thermal energy is “pooled together” in a small volume). Statistical mechanics can be used to predict the probability that a system gets an energy that exceeds the activation energy. This process is called **thermal activation**.

The probability of such thermal fluctuation or the rate at which a transformation occurs, depends exponentially on temperature and can be described by equation that is attributed to Swedish chemist Svante Arrhenius*:

$$\text{rate} \sim \exp\left(-\frac{\Delta G^a}{k_B T}\right) \sim \exp\left(-\frac{\Delta H^a}{k_B T}\right)$$

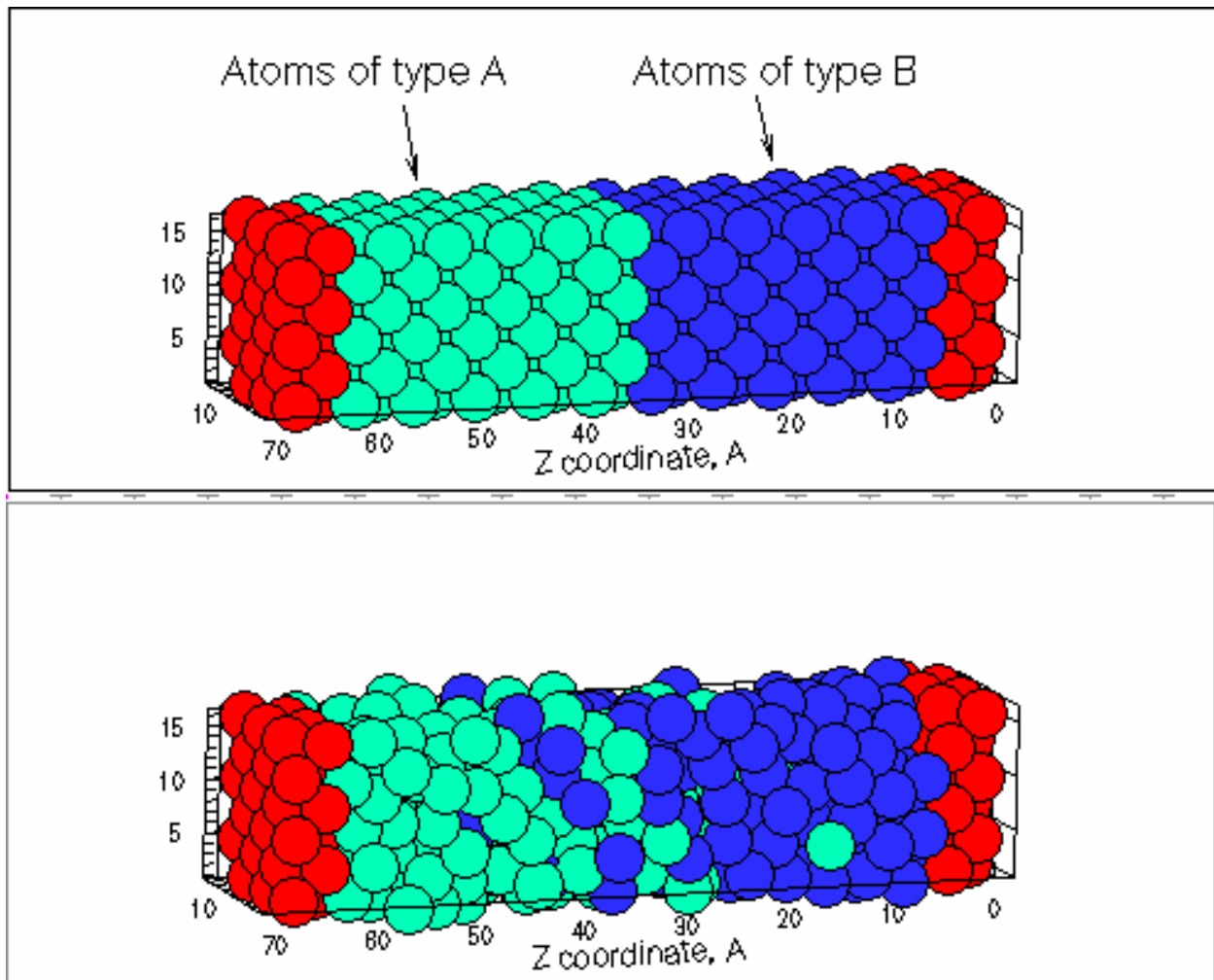
$$\Delta G^a = \Delta H^a - T\Delta S^a$$

Arrhenius equation can be applied to a wide range of thermally activated processes, including diffusion that we consider next.

* Arrhenius equation was first formulated by J. J. Hood on the basis of his studies of the variation of rate constants of some reactions with temperature. Arrhenius demonstrated that it can be applied to any thermally activated process.

What is diffusion?

Diffusion is material transport by atomic motion.



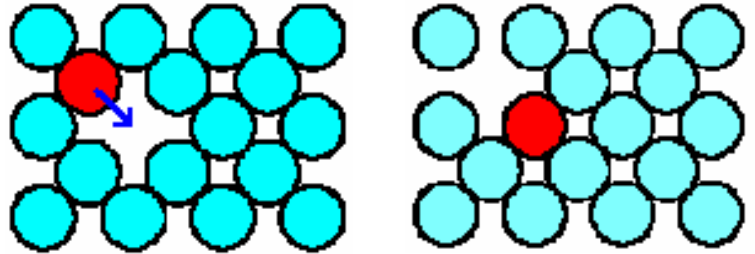
Most kinetic processes in materials involve diffusion. Inhomogeneous materials can become homogeneous by diffusion, compositions of phases can change by diffusion, etc.

For an active diffusion to occur, the temperature should be high enough to overcome energy barriers to atomic motion.

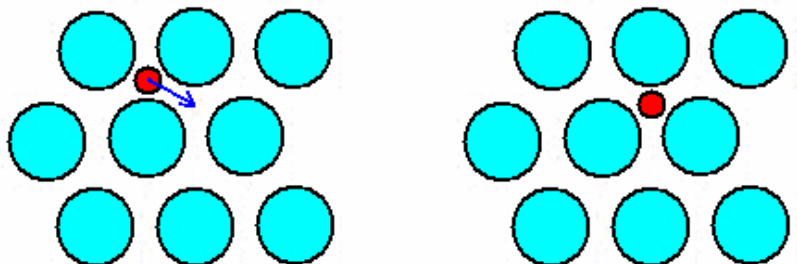
Atomic mechanisms of diffusion

Two main mechanisms of atomic diffusion *in crystals*:

Atoms located at the crystal lattice sites, solvent atoms or solute atoms (substitutional impurities), usually diffuse by a **vacancy mechanism**.



Interstitial atoms diffuse by jumping from one interstitial site to another interstitial site without permanently displacing any of the matrix/solvent atoms – **interstitial mechanism**.

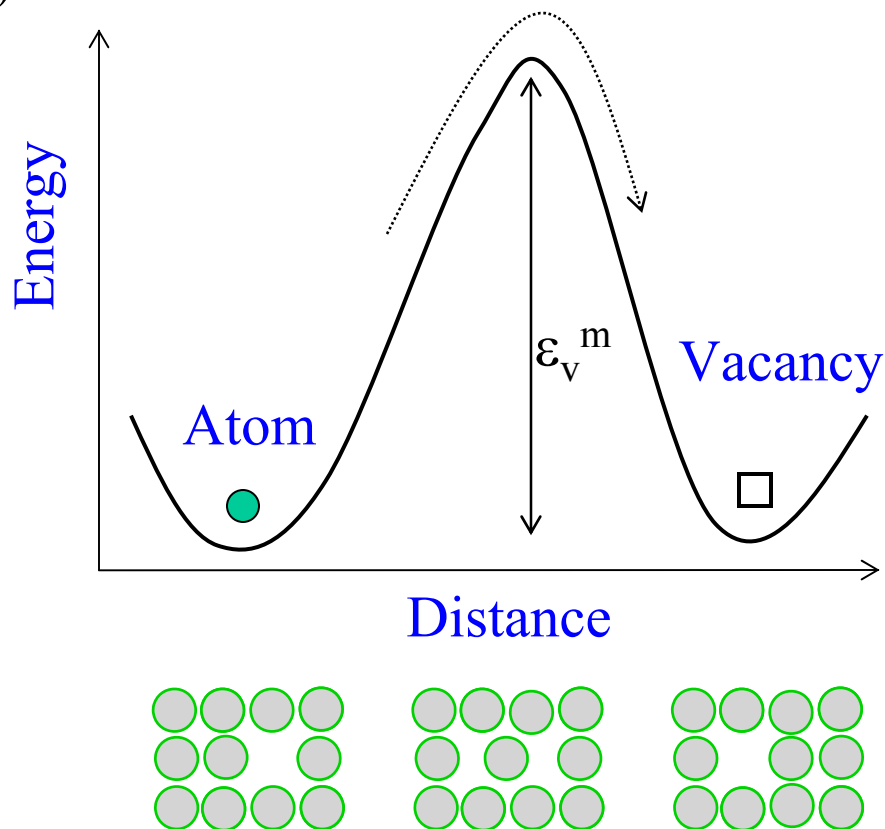


In both cases the moving atom must pass through a state of high energy – this creates energy barrier for atomic motion.

The phenomenological description considered in the previous lectures 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 Mechanisms: Vacancy diffusion

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 necessary for the jump, ϵ_v^m , is called **the activation energy** for vacancy motion. It comes from the thermal energy of atomic vibrations (**remember our discussion of the average thermal energy of an atom in a solid $E_{av} = 3kT$**).



Vacancy mechanism of diffusion:

- Substitutional impurities
- Self-diffusion (diffusion of an atom in a lattice of the same atoms) – can be studied by depositing of a small amount of radioactive isotope of the element (tracer diffusion)

Diffusion – Thermally Activated Process (I)

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

For a simple one-dimensional case, shown in the previous page, the probability of such fluctuation or frequency of jumps, R_j , depends exponentially on temperature and can be described by the Arrhenius equation:

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

where R_0 is an attempt frequency proportional to the frequency of atomic vibrations.

To relate this to the diffusion of atoms we have to consider the jump frequency of a given atom in a 3D crystal. For an atom to jump, there must be a vacancy next to it.

Diffusion – Thermally Activated Process (II)

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 (remember the derivation based on statistical thermodynamics):

$$P = \frac{n_{\text{eq}}}{N} z = z \exp\left(-\frac{\epsilon_v^f}{k_B T}\right)$$

where z is coordination number (number of atoms adjacent to the vacancy), n_{eq} is the number of vacancies, N is the number of the lattice sites in the system, ϵ_v^f is the vacancy formation energy.

- and the probability of thermal fluctuation needed to overcome the energy barrier for vacancy motion

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

The rate at which atom jumps from place to place in the crystal is therefore

$$R_j^{\text{atom}} = \frac{1}{\tau_j} \approx R_0 z \exp\left(-\frac{\epsilon_v^f}{k_B T}\right) \exp\left(-\frac{\epsilon_v^m}{k_B T}\right)$$

where τ_j is the average time between jumps for atoms.

Diffusion – Thermally Activated Process (III)

If the distance atoms cover in each jump is a , we can use the Einstein relation $\langle \Delta \vec{r}_i(t)^2 \rangle_i = 6Dt$ to estimate the diffusion coefficient from the average time between jumps:

$$D = \frac{a^2}{6\tau_j} = \frac{a^2 R_0 z}{6} \exp\left(-\frac{(\epsilon_v^f + \epsilon_v^m)}{k_B T}\right) = D_0 \exp\left(-\frac{E_d}{k_B T}\right)$$

where D_0 is a parameter of material (both matrix and diffusing species) and is independent of temperature, E_d is activation energy for diffusion.

Let's estimate the average time between jumps and the diffusion coefficient for self-diffusion in aluminum

$$\epsilon_v^f = 0.72 \text{ eV} \quad \text{at } T = 0^\circ\text{C} = 273 \text{ K} \quad k_B T = 2.4 \times 10^{-2} \text{ eV}$$

$$\epsilon_v^m = 0.68 \text{ eV} \quad \text{at } T = 650^\circ\text{C} = 923 \text{ K} \quad k_B T = 8 \times 10^{-2} \text{ eV}$$

$$R_0 \approx 10^{13} \text{ s}^{-1} \quad \tau_j \approx \frac{1}{R_0 z} \exp\left(\frac{\epsilon_v^f + \epsilon_v^m}{k_B T}\right)$$

$$z \approx 12$$

$$a \approx 3 \times 10^{-10} \text{ m} \quad D = \frac{a^2 R_0 z}{6} \exp\left(-\frac{(\epsilon_v^f + \epsilon_v^m)}{k_B T}\right)$$

$$\tau_j \approx 2 \times 10^{11} \text{ s at } T = 0^\circ\text{C} \text{ and } \tau_j \approx 3 \times 10^{-7} \text{ s at } T = 650^\circ\text{C}$$

$$D \approx 8 \times 10^{-32} \text{ m}^2/\text{s at } T=0^\circ\text{C} \text{ and } D \approx 4 \times 10^{-14} \text{ m}^2/\text{s at } T = 650^\circ\text{C}$$

17 orders of magnitude difference!

Diffusion – Temperature Dependence

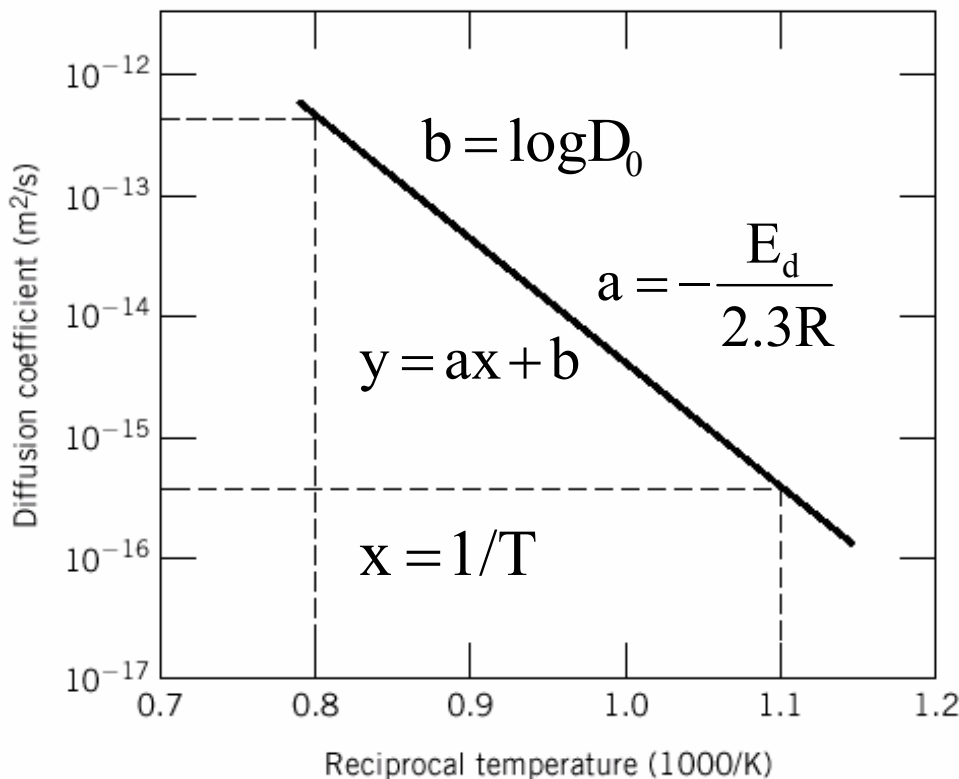
$$D = D_0 \exp\left(-\frac{E_d}{RT}\right)$$

D_0 – T-independent pre-exponential (m^2/s)
 E_d – activation energy for diffusion (J/mol)
 R – the gas constant (8.31 J/mol-K)
 T – absolute temperature (K)

The above equation can be rewritten as

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

The activation energy E_d and pre-exponential D_0 , therefore, can be estimated by plotting $\ln D$ vs. $1/T$ or $\log D$ vs. $1/T$. Such plots are called Arrhenius plots.



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

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

Coefficient of self-diffusion and melting temperature

For a given crystal structure and bonding type the ratio E_d/RT_m is roughly constant, and, therefore $D(T/T_m) \approx \text{const}$

Example: for most closely packed metals $E_d/RT_m \approx 18$.

$D_0 \approx 1 \text{ cm}^2/\text{s}$ and $D(T_m) \approx 10^{-12} \text{ m}^2/\text{s} = 1 \text{ }\mu\text{m}^2/\text{s}$

Self-diffusion data for FCC metals

Metal	T_m , K	D_0 , $10^{-6} \text{ m}^2/\text{s}$	E_d/RT_m	$D(T_m)$, $10^{-12} \text{ m}^2/\text{s}$
Al	933	170	18.3	1.9
Cu	1356	31	17.8	0.59
Ni	1726	190	19.5	0.65
γ -Fe	1805	49	18.9	0.29

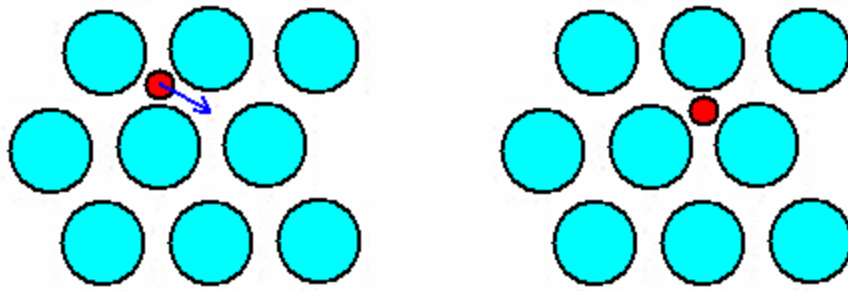
from Porter and Easterling textbook

For a diamond cubic lattice, $E_d/RT_m \approx 34$.

and $D(T_m) \approx 10^{-16} \text{ m}^2/\text{s}$

The correlation between T_m and E_d is not surprising – stronger interatomic bonds make it more difficult to melt material and increase ϵ_v^f and ϵ_v^m

Diffusion of interstitial atoms



Interstitial diffusion also involve transition through the energy barrier and can be discussed in a manner similar to the vacancy diffusion mechanism.

The difference is that there are always sites for an interstitial atom to jump to.

$$D = \frac{a^2 R_0 p}{6} \exp\left(-\frac{\epsilon_i^m}{k_B T}\right) = D_0 \exp\left(-\frac{\epsilon_i^m}{k_B T}\right)$$

where p is number of neighbor interstitial sites.

Small interstitial atoms of a foreign (extrinsic) type, e.g. C in Fe or O in Si may diffuse directly through the lattice (i.e. without the help of vacancies) and play an important role in defining properties of materials.

Diffusion of self-interstitials

Intrinsic interstitials, also called “self-interstitials” are interstitial atoms of the same kind as the atoms of the crystal.

Self-interstitials in most materials introduce strong deformations into the lattice and have very high formation energy, $\varepsilon_i^f \approx 3\varepsilon_v^f \approx 27k_B T_m$ for metals. The number of equilibrium interstitials can be estimated by an equation similar to the one derived for vacancies:

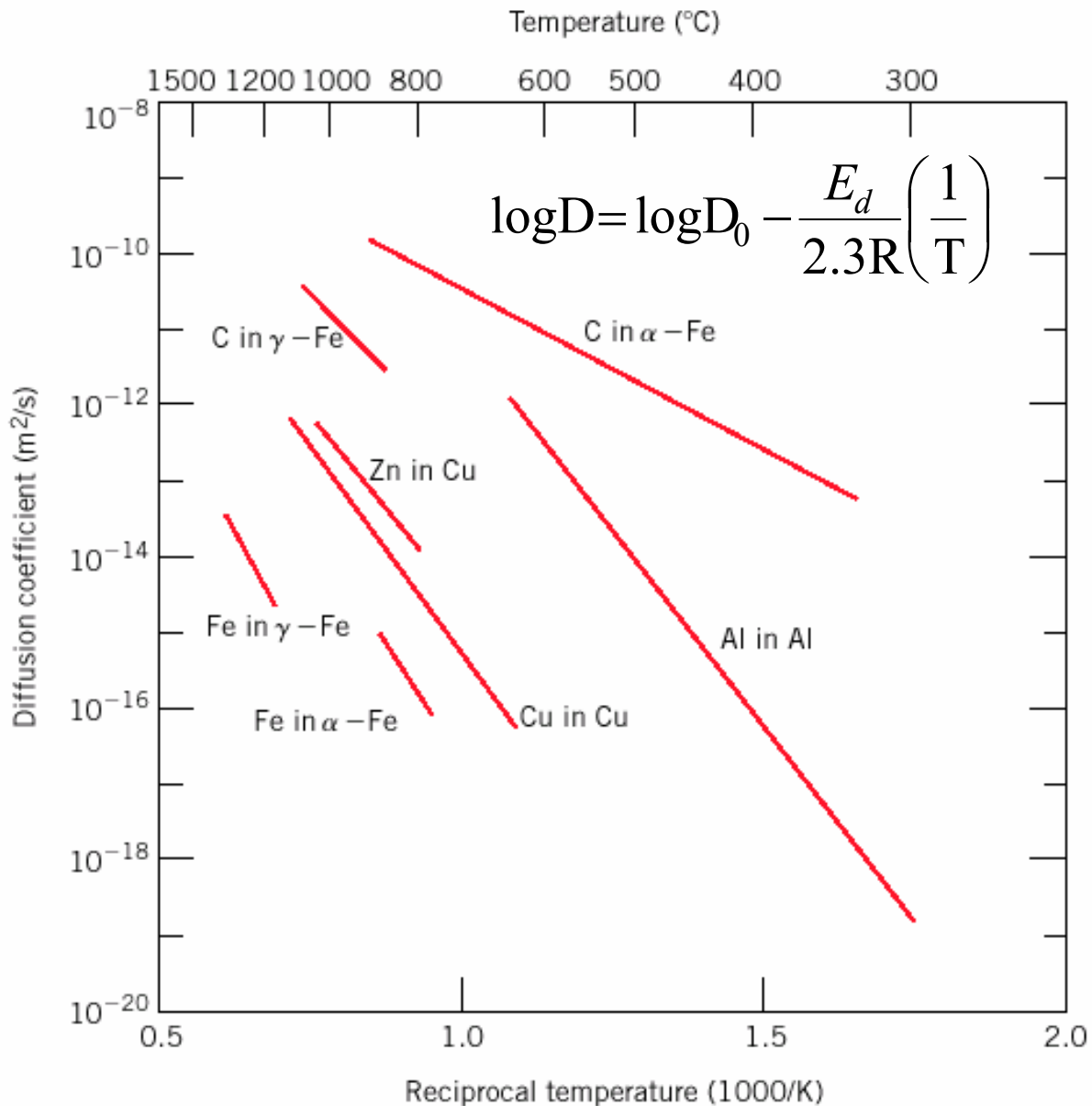
$$n_{\text{eq}}^i = N \exp\left(-\frac{\varepsilon_i^f}{k_B T}\right)$$

We can estimate that at room temperature in copper there is less than one interstitial per cm^3 , whereas just below the melting point there is one interstitial for every 10^{12} atoms – **there are virtually no “equilibrium” interstitials** in metals and most other elemental crystals.

In Si, however, intrinsic interstitials play an important role in diffusion and formation of defect structures.

Non-equilibrium self-interstitials in most materials are very mobile (they can move through formation of intermediate low-energy configurations, e.g. dumbbells, when two atoms share the space of one), $\varepsilon_i^m \approx 0.5\varepsilon_v^m$ for metals. They quickly diffuse out of the bulk of the crystal after being formed.

Diffusion of interstitial impurities



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

Diffusion of interstitial impurities

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

Impurity	$D_0, \text{mm}^2/\text{s}^{-1}$	$\epsilon_i^m, \text{kJ/mol}$
C in FCC Fe	23.4	148
C in BCC Fe	2	84.1
N in FCC Fe	91	168.6
N in BCC Fe	0.3	76.1
H in FCC Fe	0.63	43
H in BCC Fe	0.1	13.4

from Porter and Easterling textbook & Smithells Metals Reference Book

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

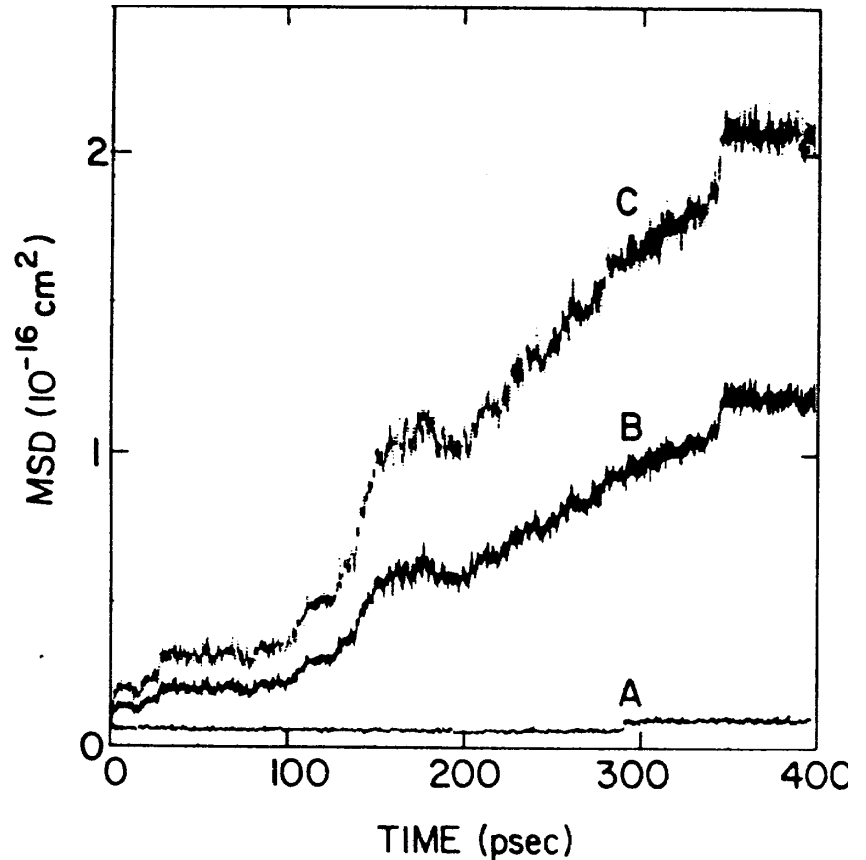
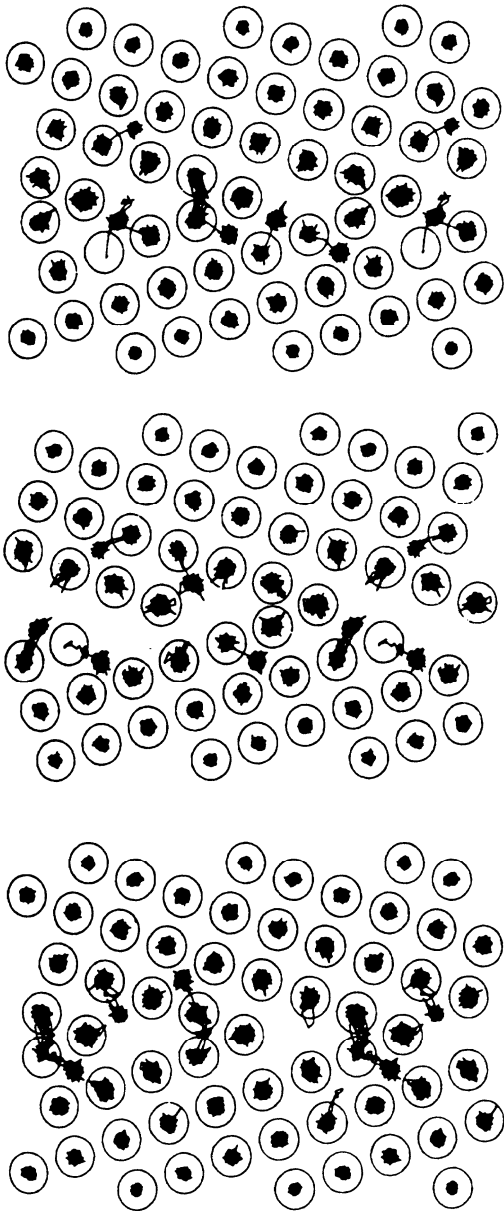
vacancy
mechanism -

*from Smithells
Metals Reference
Book*

	$D_0, \text{mm}^2/\text{s}^{-1}$	$E_d, \text{kJ/mol}$
Fe in γ -Fe	49	284
Fe in α -Fe	276	250.6
Fe in δ -Fe	201	240.7
Fe in Cr	47	332
Au in Ag	85	202.1
Si in Si	146000	484.4

Fast diffusion paths (I)

More open atomic structure at defects (grain boundaries, dislocations) can result in a significantly higher atomic mobility along the defects.



Mean-square displacement of all atoms in the system (B), atoms in the grain boundary region (C), and bulk region of the system (A).

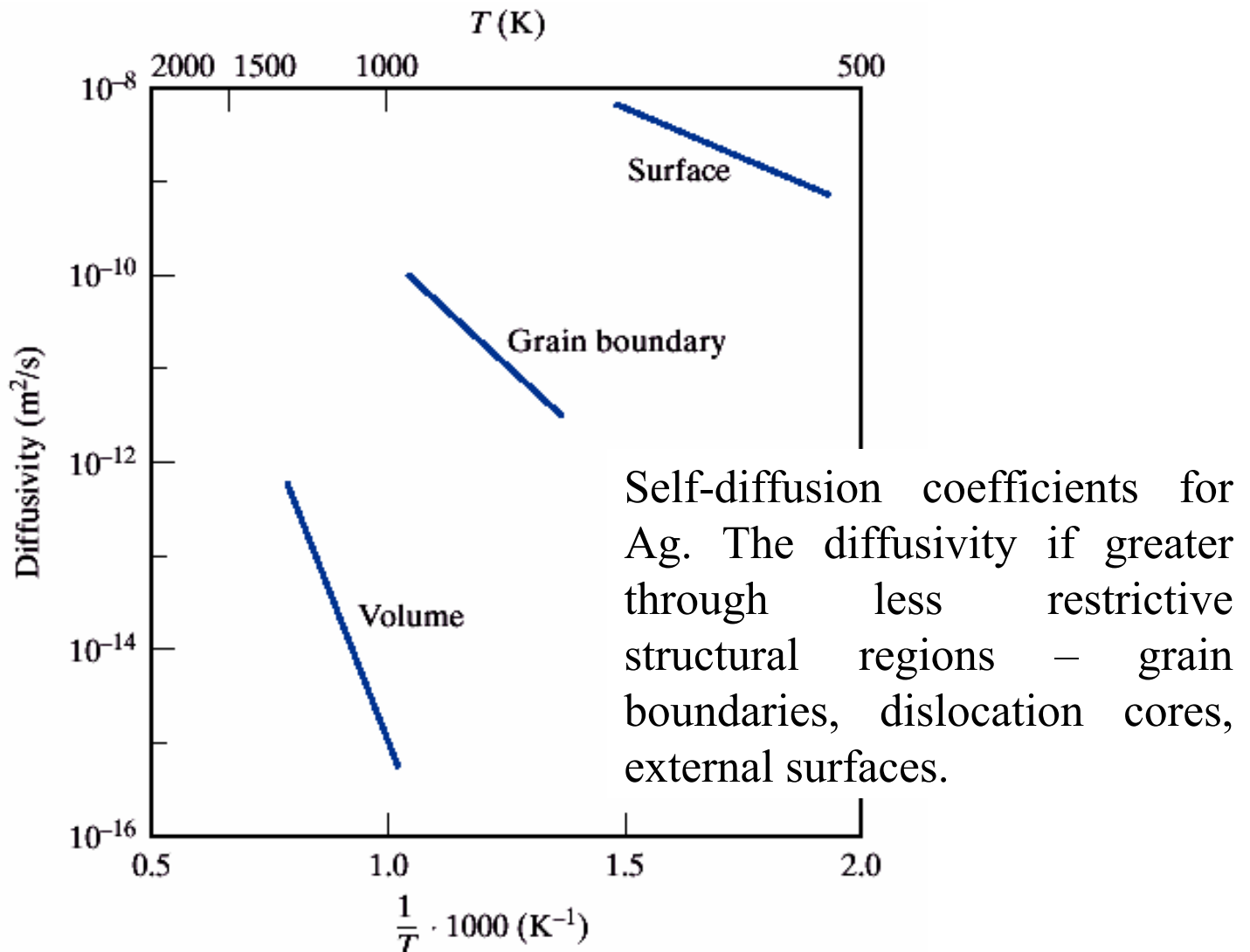
The plots are from the computer simulation by T. Kwok, P. S. Ho, and S. Yip. Initial atomic positions are shown by the circles, trajectories of atoms are shown by lines. We can see the difference between atomic mobility in the bulk crystal and in the grain boundary region.

Fast diffusion paths (II)

Diffusion coefficient along a defect (e.g. grain boundary) can be also described by an Arrhenius equation,

$$D^{\text{G.B.}} = D_0^{\text{G.B.}} \exp\left(-\frac{\epsilon_{\text{G.B.}}^{\text{m}}}{k_{\text{B}} T}\right)$$

with the activation energy for grain boundary diffusion significantly lower than the one for the bulk. However, the effective cross-sectional area of the boundaries is only a small fraction of the total area of the bulk (an effective thickness of a grain boundary is ~ 0.5 nm). The grain boundary diffusion is less sensitive to the temperature change – becomes important at low T.



Diffusion in nanocrystalline materials: Examples

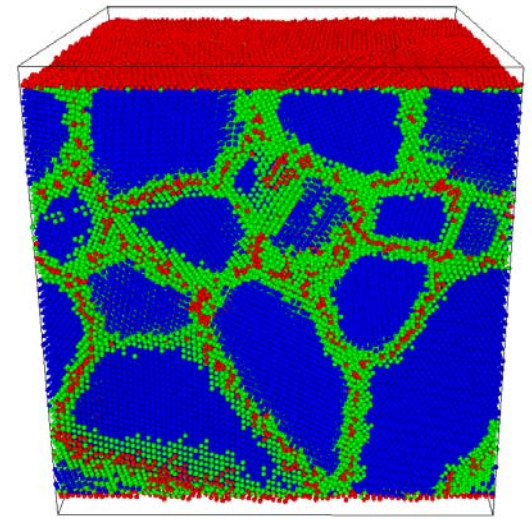
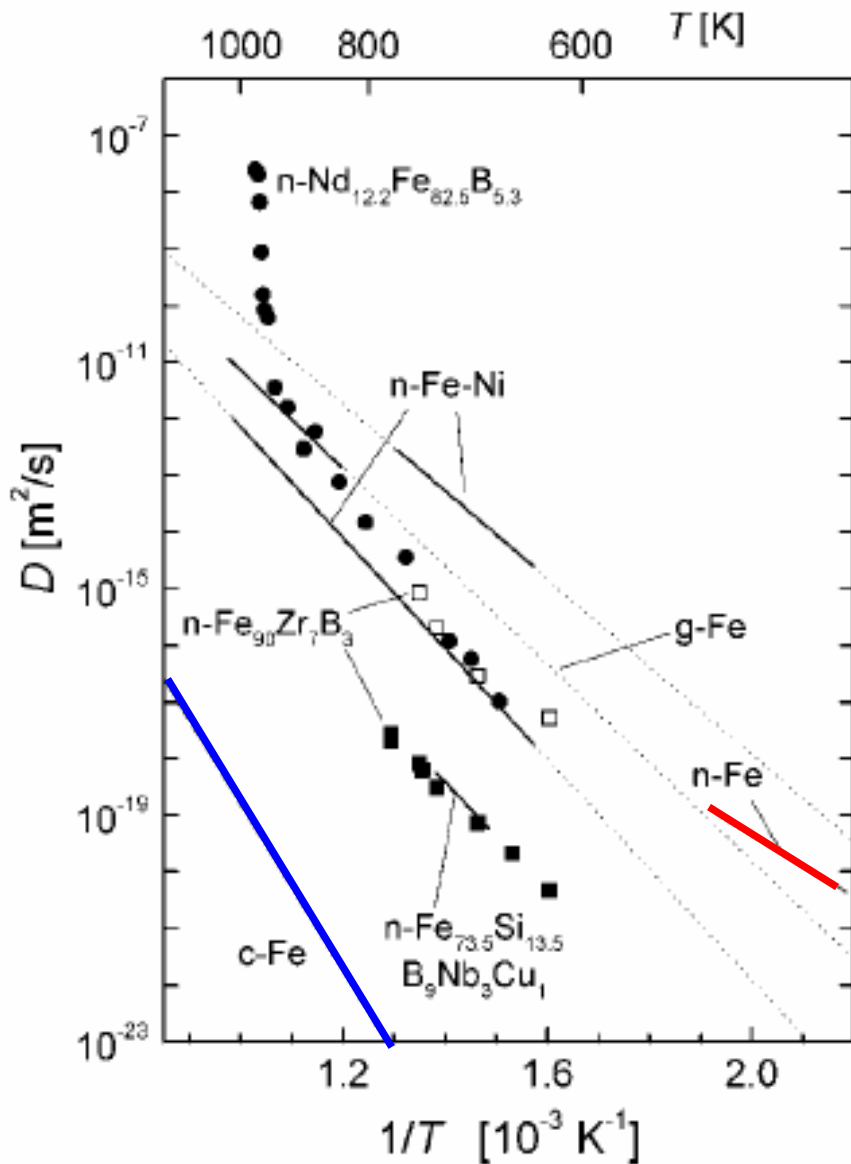
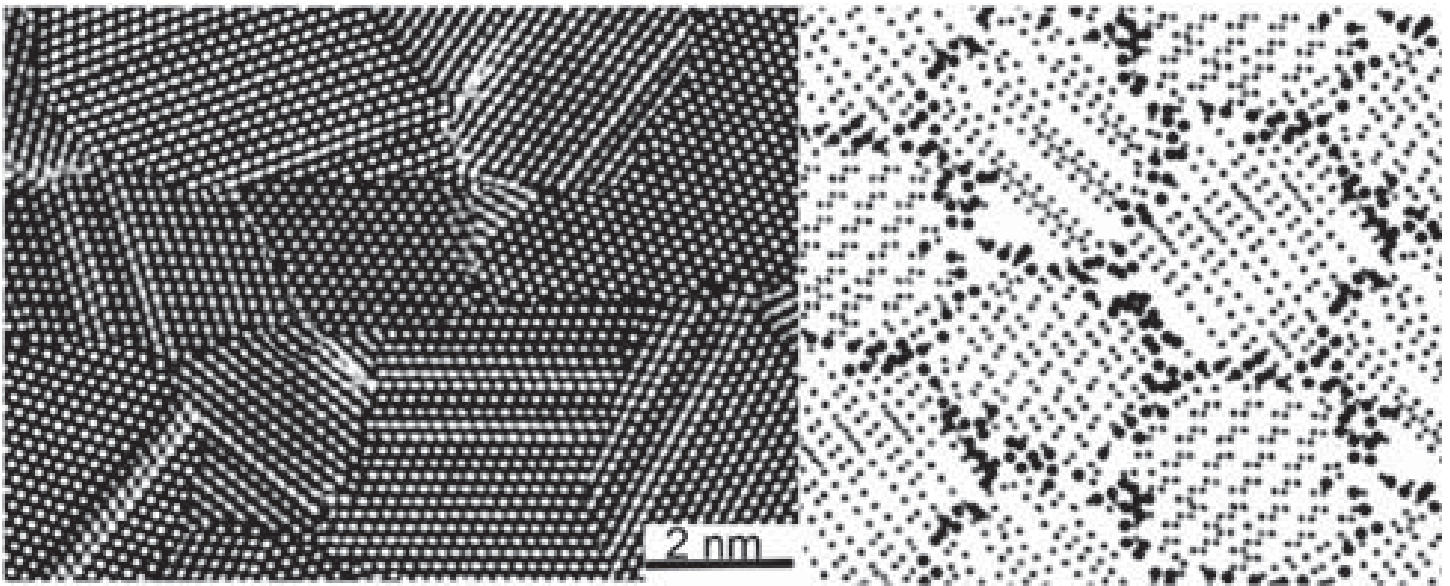


image by Zhibin Lin et al.
J. Phys. Chem. C 114, 5686, 2010

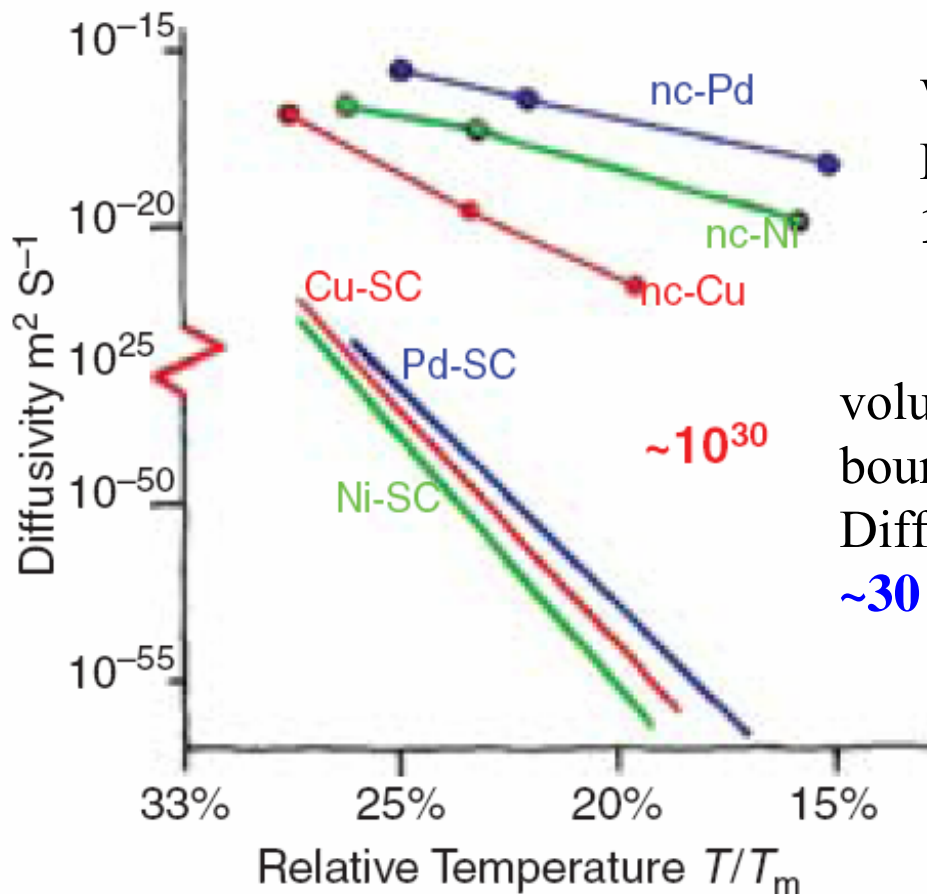
Arrhenius plots for ^{59}Fe diffusivities in nanocrystalline Fe and other alloys compared to the crystalline Fe (ferrite).

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

Diffusion in nanocrystalline materials: Examples



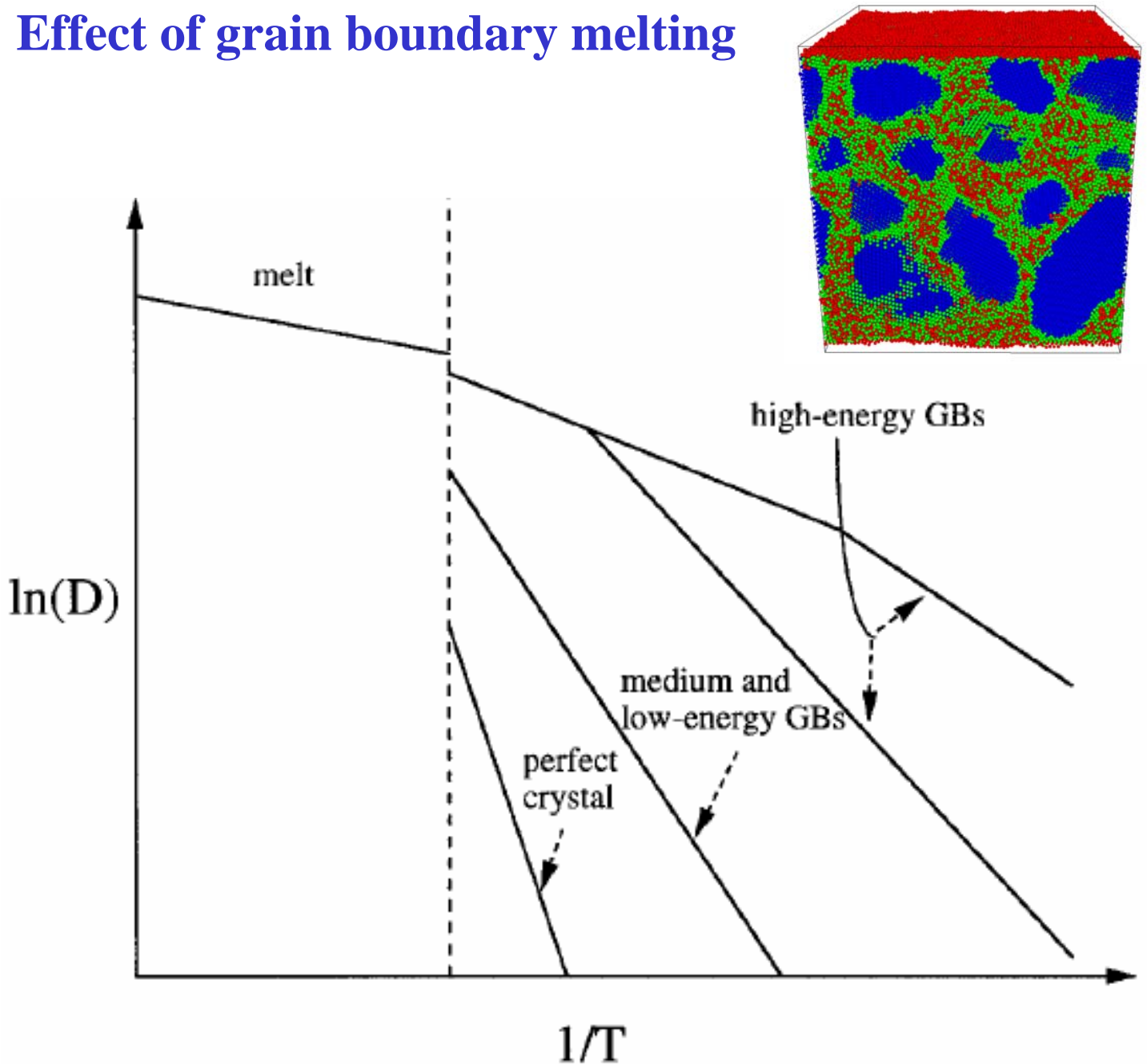
High-resolution electron micrograph (left, [Acta Mater. **56**, 5857, 2008]) and computed atomic structure (right, [Acta Mater. **45**, 987, 1997]) of nanocrystalline Si.



Wurschum et al.,
Defect Diffus. Forum
143-147, 1463, 1997]

volume fraction of grain boundary regions: $\sim 50\%$.
Diffusivity is enhanced by **~ 30 orders of magnitude.**

Effect of grain boundary melting



Schematic diagram for self-diffusion in high-angle GBs in fcc metals obtained in MD simulations [Phil. Mag. A **79**, 2735, 1999]

Experiments: [Herth et al., Phys. Rev. Lett. **92**, 095901, 2004]
 ^{59}Fe tracer diffusion in nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ at temperatures close to the intergranular melting transition: the diffusion coefficient in the intergranular liquid layers is lower than in bulk melts indicating a hampered atomic mobility due to confinement.

Summary on the Diffusion Mechanisms

Make sure you understand language and concepts:

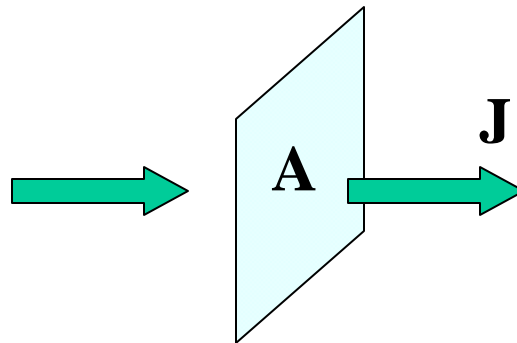
- Mobility of atoms and diffusion
- Activation energy
- High diffusivity path
- Arrhenius equation
- Interstitial diffusion
- Self-diffusion
- Vacancy diffusion

Factors that Influence Diffusion:

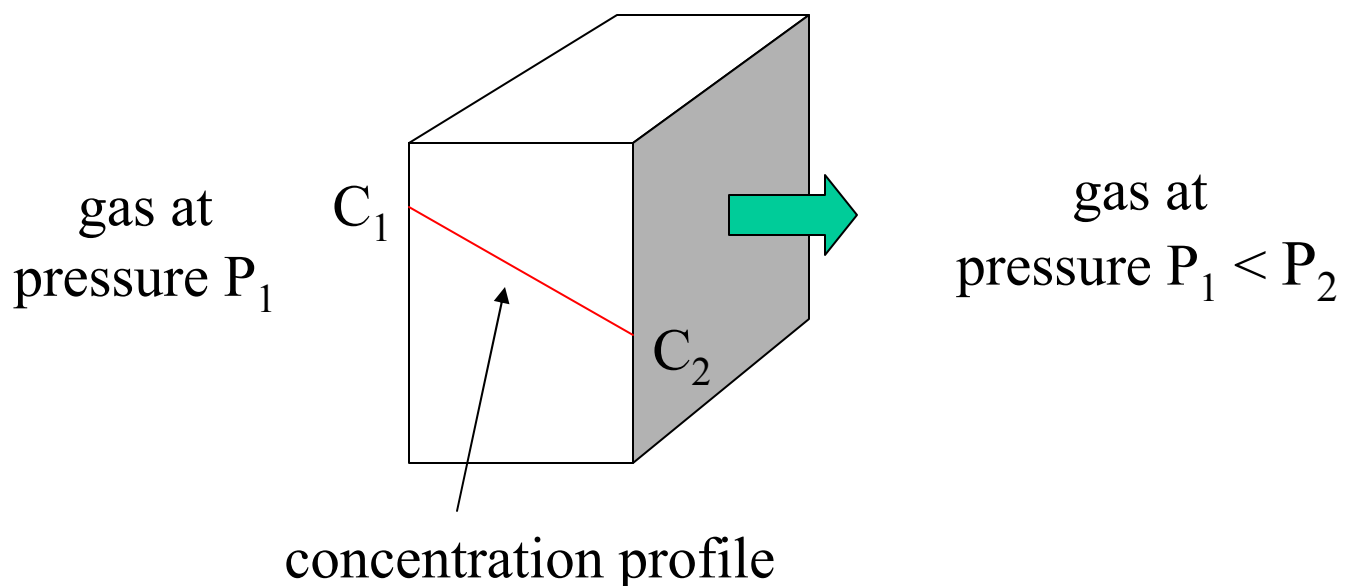
- Temperature - diffusion rate increases very rapidly with increasing temperature (Arrhenius dependence)
- Diffusion mechanism - interstitial is usually faster than vacancy
- Diffusing and host species - D_o , E_d is different for every solute - solvent pair
- Microstructure – low-temperature diffusion is faster in polycrystalline vs. single crystal materials because of the accelerated diffusion along grain boundaries and dislocation cores.

Phenomenological description of diffusion: diffusion flux

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



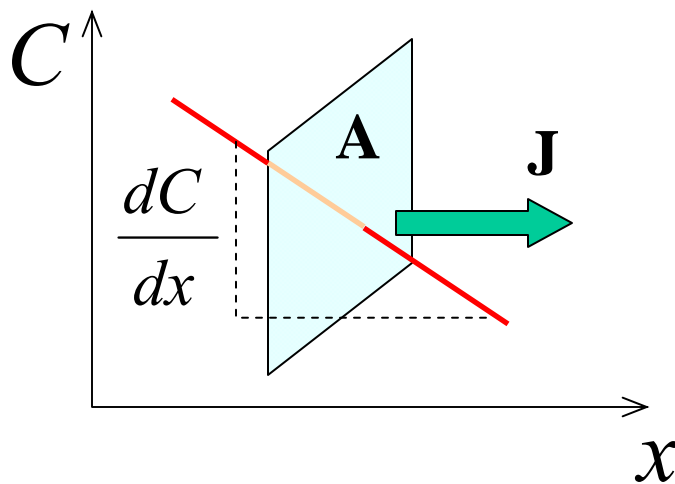
Let's consider **steady state diffusion** - the diffusion flux does not change with time. Example: diffusion of gas molecules through a thin metal plate.



Steady-State Diffusion: Fick's first law

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

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



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

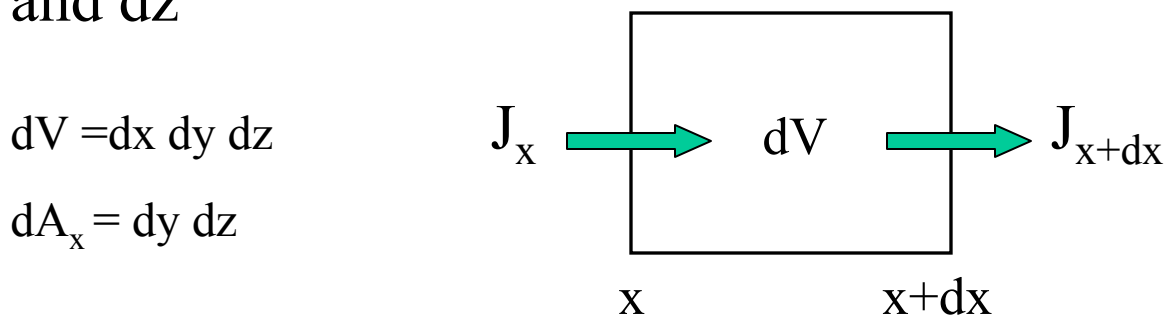
The minus sign in the equation means that diffusion is down the concentration gradient.

Fick's first law applies to steady state flux in a uniform concentration gradient.

Nonsteady-State Diffusion: Fick's second law (I)

In most practical cases steady-state conditions are not established, i.e. concentration gradient is not uniform and varies with both distance and time. Let's derive the equation that describes nonsteady-state diffusion along the direction x .

Consider an element of material with dimensions dx , dy , and dz



$$J_x = -D \frac{\partial C(x, t)}{\partial x} \qquad J_{x+dx} = J_x + \frac{\partial J_x}{\partial x} dx$$

The number of particles that diffuse into the volume dV during time dt is $J_x dA_x dt$ from the left and $-J_{x+dx} dA_x dt$ from the right.

From the balance of coming and going particles:

$$(J_x - J_{x+dx}) dA_x dt = dC(x, t) dV \qquad \frac{\partial C(x, t)}{\partial t} dx = J_x - J_{x+dx}$$

And using expressions for J_x and J_{x+dx} we have

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

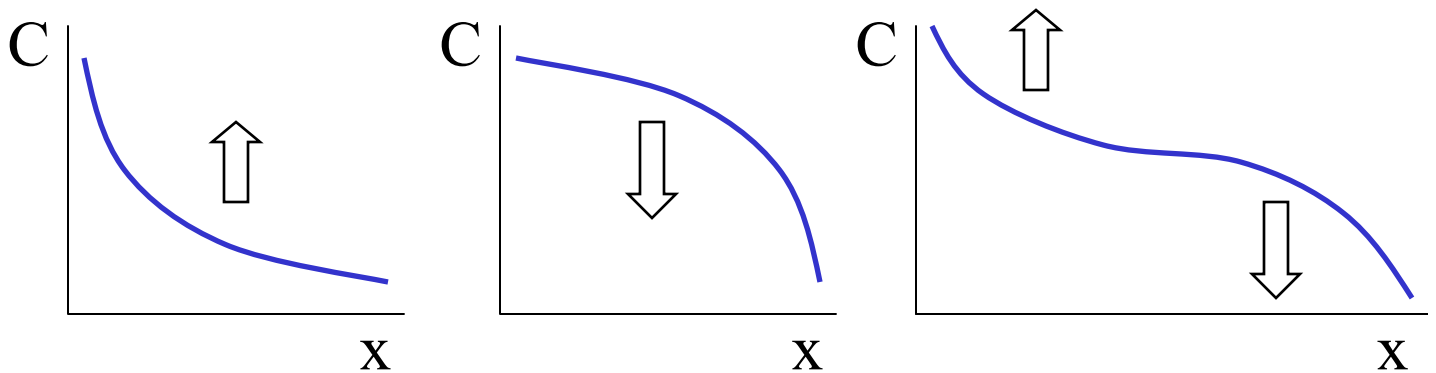
Nonsteady-State Diffusion: Fick's second law (II)

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

If dependence of D on x (and C !) is ignored,

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \quad [m^{-3}t^{-1}] = [m^2t^{-1}] \times [m^{-3}m^{-2}]$$

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

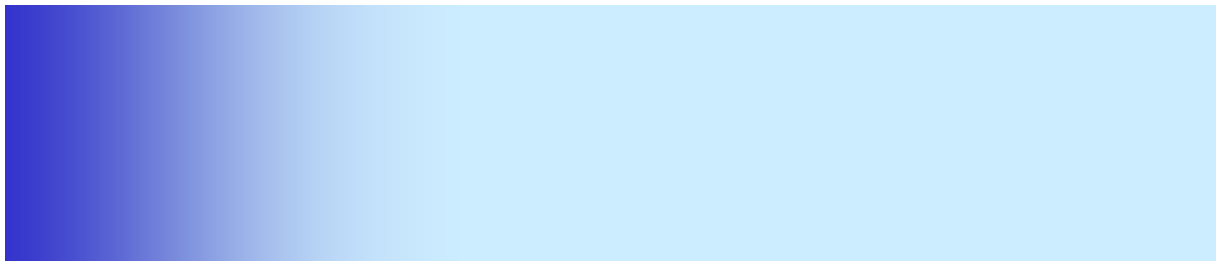


Concentration increases with time in those parts of the system where concentration profile has a positive curvature. And decreases where curvature is negative.

Driving force for diffusion

In general, it is common for atoms to diffuse from regions of high concentration towards the regions of low concentration. Thus, the phenomenological Fick's laws describe the diffusion in terms of the relationships between the diffusion flux and concentration gradient.

E.g., consider ideal solution:



↑
Atoms here jump
randomly both right
and left

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

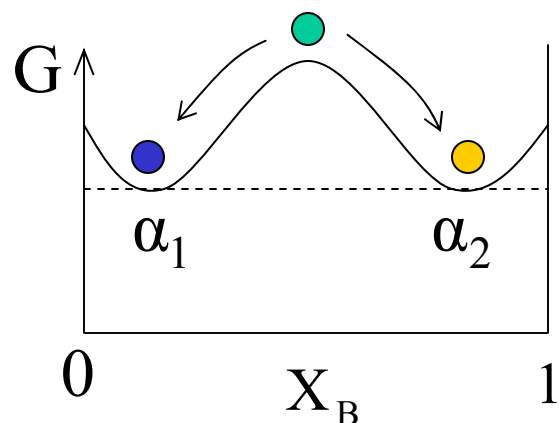
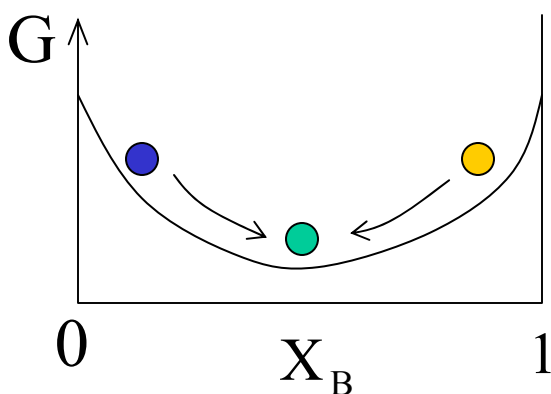
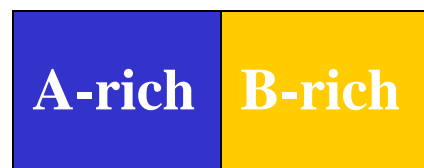
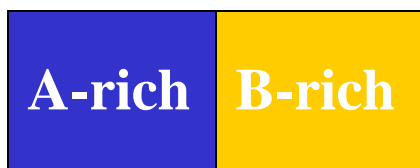
As a result there is a net flux of atoms from left to right.

The thermodynamic properties of solid solutions, however, play an important role in diffusion and, under certain conditions, may even induce the diffusion against the concentration gradient ($D < 0$)!

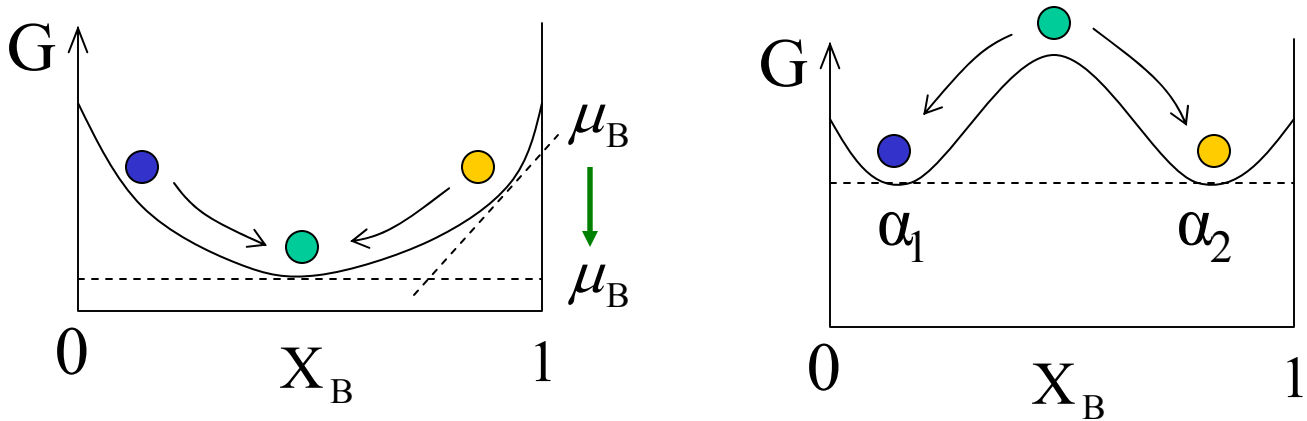
Driving force for diffusion (I)

The *empirical* Fick's first law assumes proportionality between the diffusion flux and the concentration gradient. But thermodynamics tells us that any spontaneous process should go in the direction of **minimization of the free energy**.

As we can see from the examples below, atoms can diffuse from regions of high concentration towards the regions of low concentration – down the concentration gradient (left) as well as from the regions of low concentration towards the regions of high concentration – **up the concentration gradient?** (right)



Driving force for diffusion (II)



Diffusion occurs so that the free energy is minimized and is therefore driven by the gradient of free energy.

The chemical potential of atoms of type A can be defined as the free energy per mole of A atoms. $G = \mu_A X_A + \mu_B X_B$

Therefore, the free energy gradient can be expressed through the chemical potential gradient:

$$J_x = -M_A C_A \frac{\partial \mu_A}{\partial X} \quad \text{where } M_A \text{ is the atomic mobility of A atoms.}$$

In both cases the A and B atoms are diffusing from the regions where chemical potential is high to the regions where chemical potential is lower. **The driving force for diffusion is gradient of chemical potential.**

Atoms migrate so as to remove differences in chemical potential. Diffusion ceases at equilibrium, when

$$\mu_B^{\alpha_1} = \mu_B^{\alpha_2} \quad \text{and} \quad \mu_A^{\alpha_1} = \mu_A^{\alpha_2}$$

Driving force for diffusion (III)

Chemical potential gradient is the driving force for diffusion:

$$J_x = -M_B C_B \frac{\partial \mu_B}{\partial X} \quad \text{where } M_B \text{ is mobility of B atoms}$$

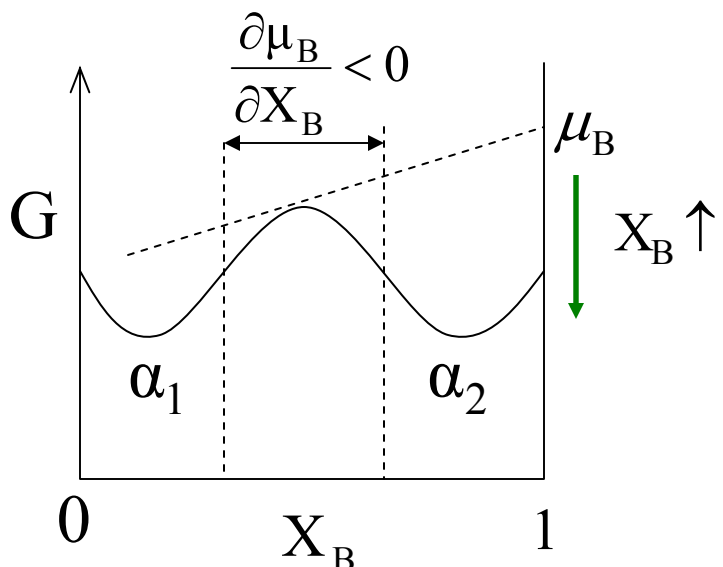
$$J_x = -D_B \frac{\partial C_B}{\partial X} \implies D_B = M_B C_B \frac{\partial \mu_B}{\partial C_B} = M_B X_B \frac{\partial \mu_B}{\partial X_B}$$

if $\frac{\partial \mu_B}{\partial X_B} > 0$, then $D_B > 0$ - gradient of chemical potential is in the same direction as the concentration gradient.

if $\frac{\partial \mu_B}{\partial X_B} < 0$, then $D_B < 0$ - diffusion occurs against the concentration gradient!

For example, we can identify regions with negative $\partial \mu / \partial X_B$ in a system with miscibility gap:

We will discuss the behavior of homogeneous solution cooled within the miscibility gap later, after deriving equations for diffusion flux in ideal and regular solutions.



Driving force for diffusion (IV)

Lets consider diffusion driven by the chemical potential gradient for ideal and regular solutions.

$$J_x = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

For an ideal solution: $\mu_B = G_B + RT \ln X_B$

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial \mu_B}{\partial X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{C_B} \frac{\partial C_B}{\partial x}$$

$$J_B = -M_B RT \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x} \quad D_B = M_B RT$$

For a regular solution: $\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B$

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial \mu_B}{\partial X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{X_B} \left(1 - \frac{2\Omega(1 - X_B)X_B}{RT} \right) \frac{\partial X_B}{\partial x} =$$

$$= \frac{RT}{C_B} \left(1 - \frac{2\Omega X_A X_B}{RT} \right) \frac{\partial C_B}{\partial x} \quad D_B = M_B RTF$$

F

The factor in brackets is termed *the thermodynamic factor F*. It defines how inter-atomic interaction affects the diffusion of the atoms in the presence of concentration gradient.

Driving force for diffusion (V)

As shown below, the thermodynamic factor is the same for both species A and B at a given composition and *is related to the curvature of the free energy curve*.

$$G^{\text{reg}} = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$
$$= (1 - X_B)G_A + X_B G_B + \Omega(1 - X_B)X_B + RT[(1 - X_B)\ln(1 - X_B) + X_B \ln X_B]$$

$$\frac{\partial G}{\partial X_B} = -G_A + G_B + \Omega - 2\Omega X_B + RT\left[-\ln(1 - X_B) - \frac{(1 - X_B)}{(1 - X_B)} + \ln X_B + \frac{X_B}{X_B}\right] =$$

$$= -G_A + G_B + \Omega - 2\Omega X_B + RT[-\ln(1 - X_B) + \ln X_B] =$$

$$= G_B - G_A + \Omega(1 - 2X_B) + RT \ln\left(\frac{X_B}{1 - X_B}\right)$$

$$\frac{\partial^2 G}{\partial X_B^2} = -2\Omega + RT\left[\frac{1}{1 - X_B} + \frac{1}{X_B}\right] = -2\Omega + \frac{RT}{X_A X_B}$$

$$\frac{\partial \mu_B}{\partial X} = \frac{RT}{C_B} \left(1 - \frac{2\Omega X_A X_B}{RT}\right) \frac{\partial C_B}{\partial X} = \frac{RT}{C_B} F \frac{\partial C_B}{\partial X}$$

$$F = \left(1 - \frac{2\Omega X_A X_B}{RT}\right) = \frac{X_A X_B}{RT} \frac{\partial^2 G}{\partial X_B^2}$$

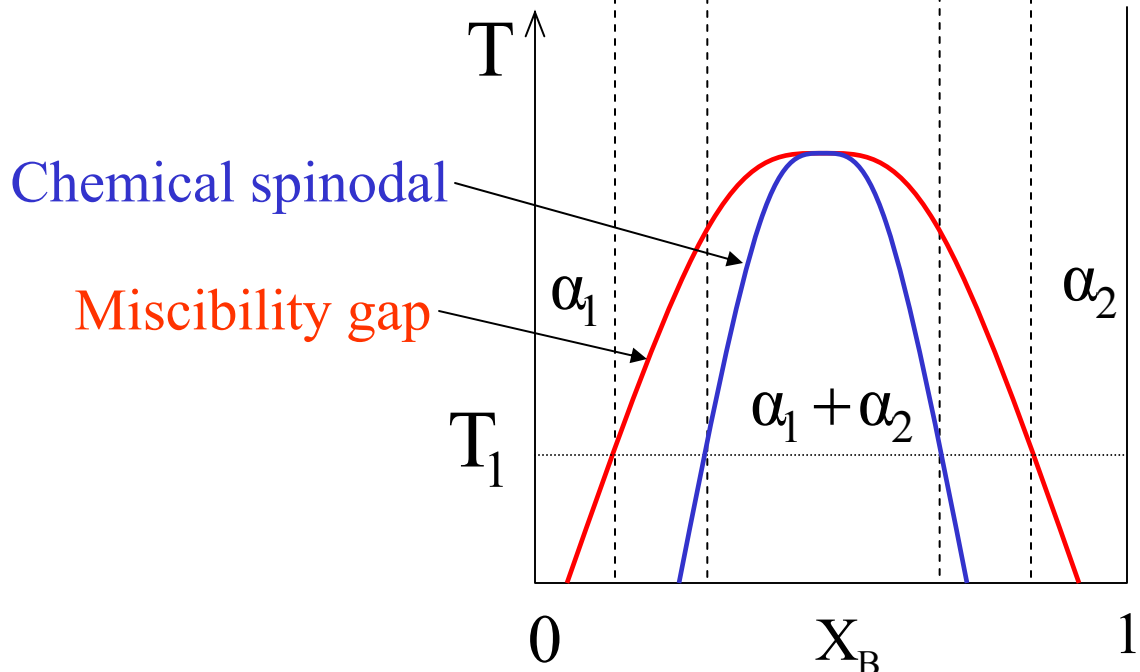
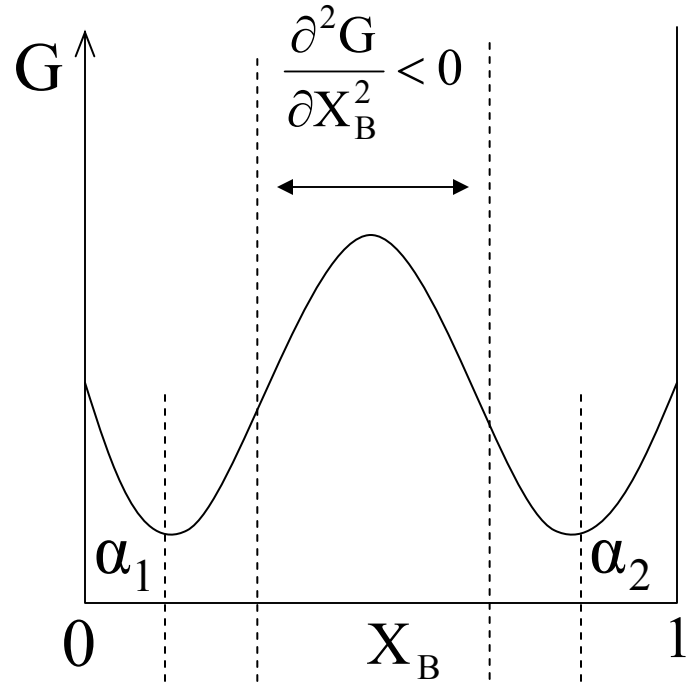
Diffusion against the concentration gradient: Spinodal Decomposition

When the free energy curvature is negative, the thermodynamic factor F is negative, and the diffusion is directed against the concentration gradient:

$$\frac{\partial^2 G}{\partial X_B^2} < 0 \implies F < 0$$

$$D_B = M_B R T F < 0$$

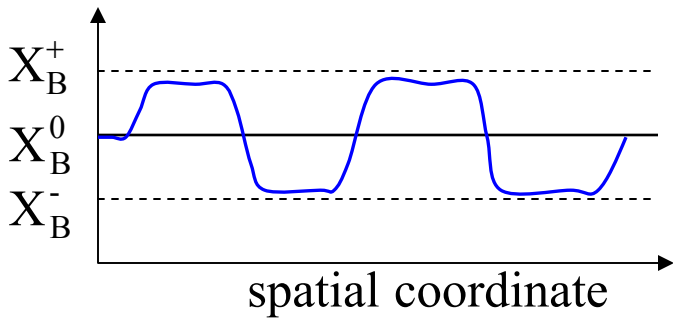
$$J_B = -D_B \frac{\partial C_B}{\partial X}$$



Spinodal Decomposition

Homogeneous solution cooled into the miscibility gap will decompose into α_1 and α_2 so that the total free energy of the system decreases.

The mechanism of decomposition into α_1 and α_2 is different within the chemical spinodal region and outside (in the nucleation regions). Let's consider small fluctuations around the average composition X_B^0 :



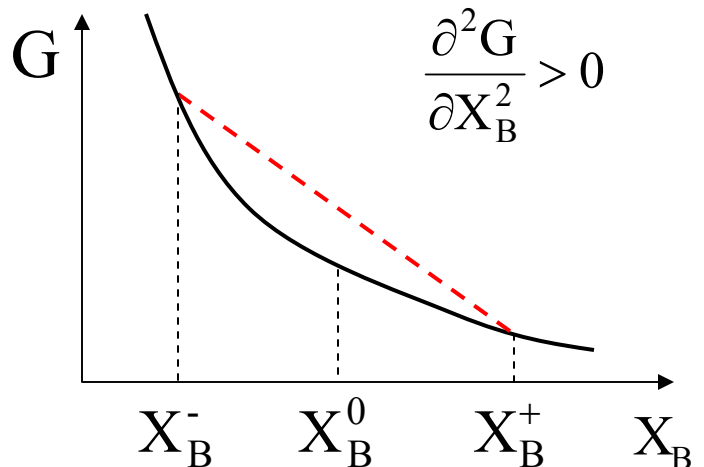
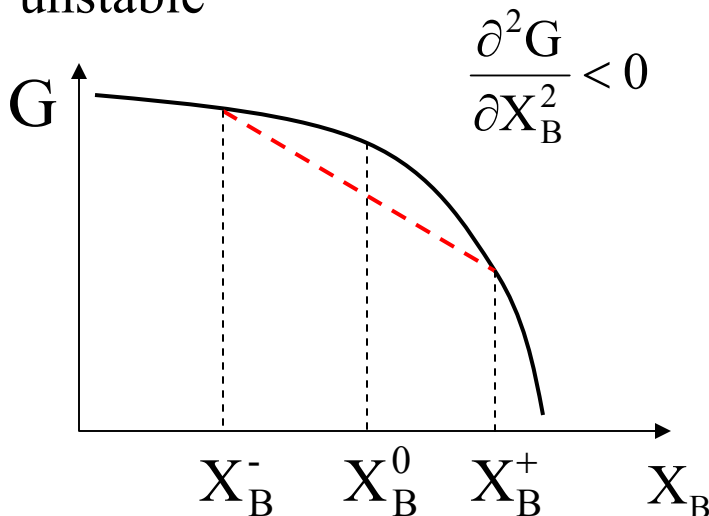
$$X_B^+ \ll \alpha_2 \quad X_B^+ \approx X_B^- \approx X_B^0$$

(fluctuations are small)

$$X_B^- \gg \alpha_1$$

Free energy decreases as a result of an arbitrary infinitesimal fluctuation in composition – the system is unstable

Free energy increases as a result of an infinitesimal fluctuation in composition – the system is stable with respect to small fluctuations

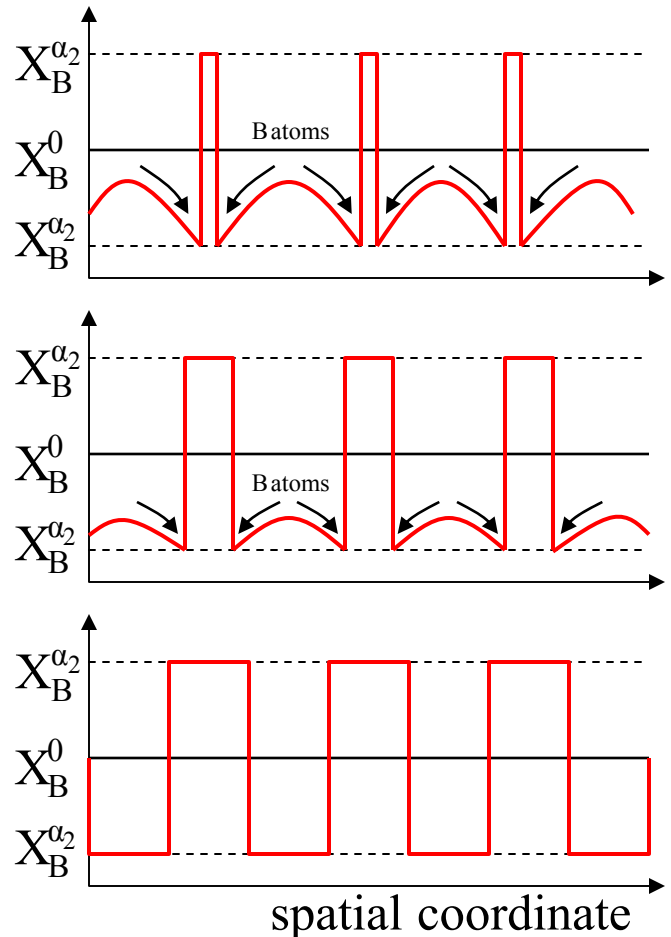
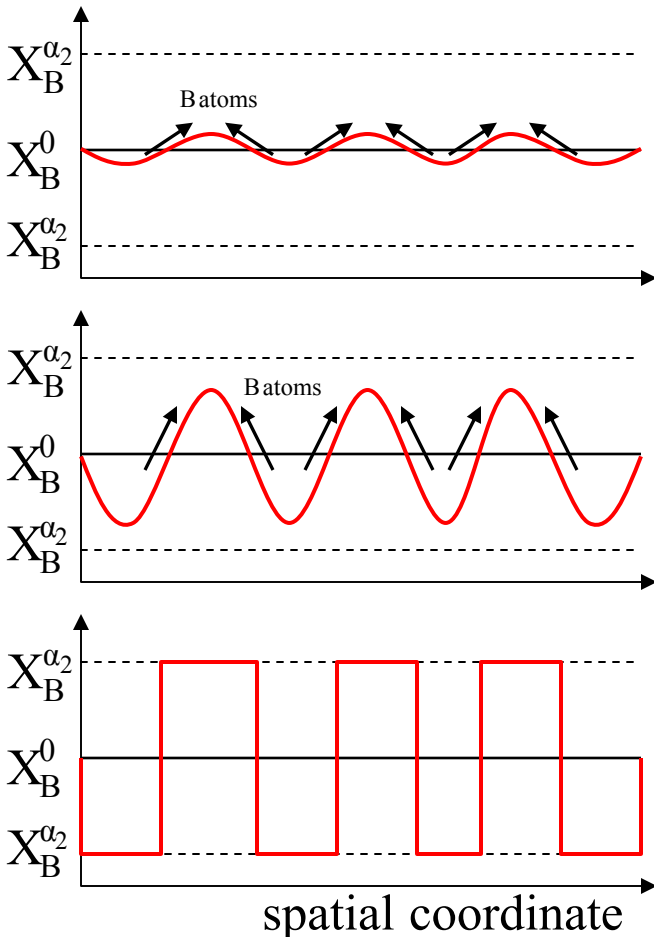


Spinodal Decomposition

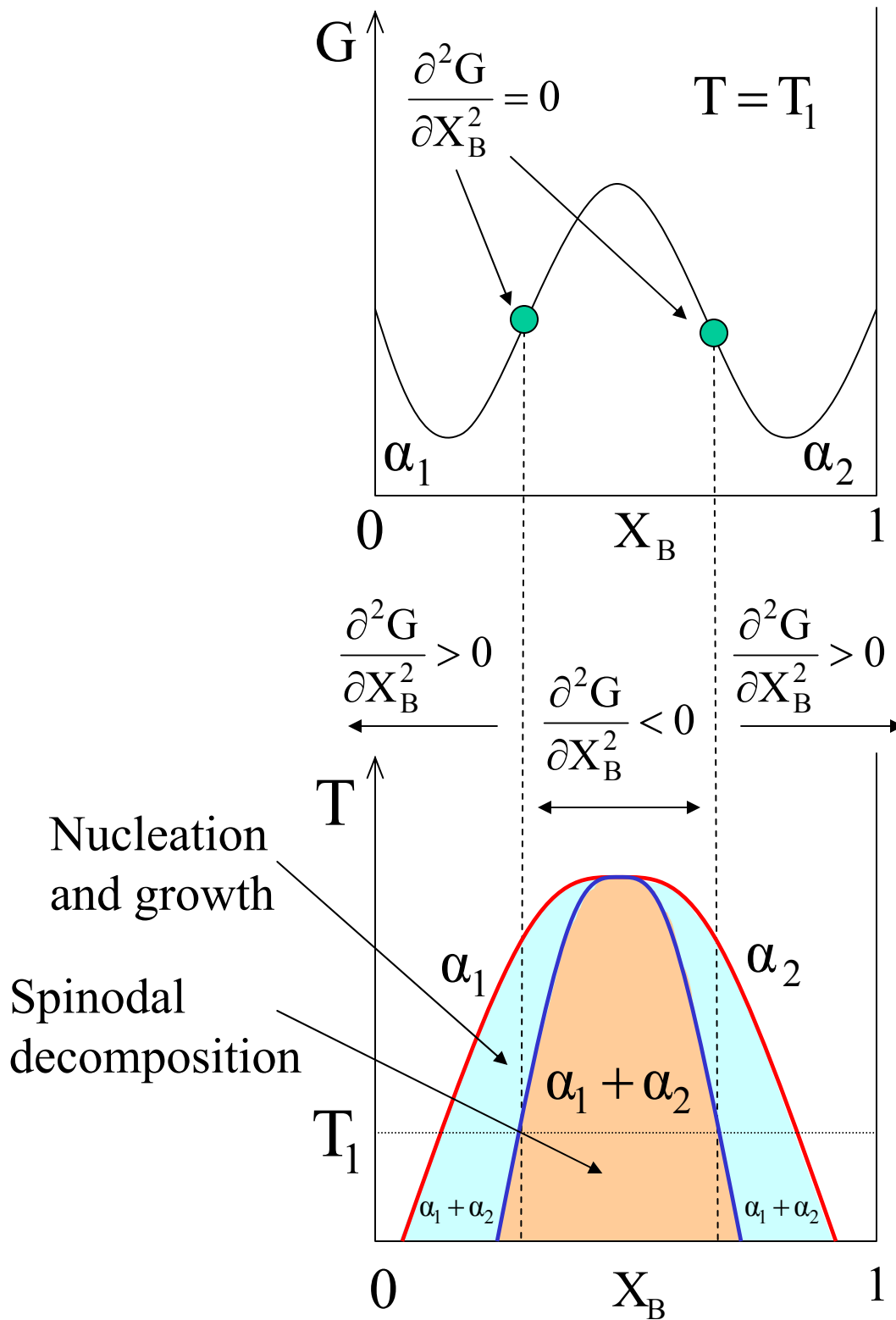
Although the system within the miscibility gap but outside the spinodal region is stable (metastable) with respect to small fluctuations, it is unstable to the separation into α_1 and α_2 determined by the common tangent construction. There is large difference in composition between α_1 and α_2 and large composition fluctuations are required in order to decrease the free energy. A process of formation of a large composition fluctuation is called **nucleation**. The phase separation is occurring in this case by **nucleation and growth** (will be discussed later).

Spinodal decomposition

Nucleation and growth



Region of spinodal decomposition on a phase diagram with a miscibility gap



Solutions to the diffusion equation

Numerical integration

- finite difference method
- spatial and time discretization
- initial and boundary conditions
- stability

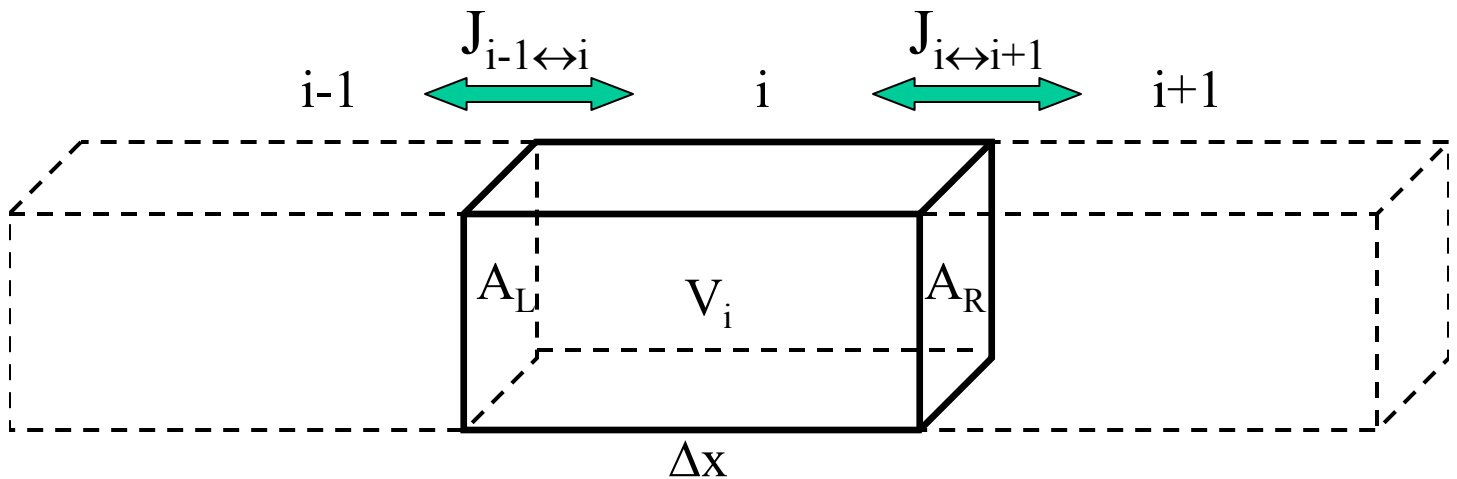
Analytical solution for special cases

- plane source
- thin film on a semi-infinite substrate
- diffusion pair
- constant surface composition

Numerical integration of the diffusion equation (I)

Finite difference method. Spatial Discretization. Internal nodes.

For 1D thermal conduction let's "discretize" the 1D spatial domain into N small finite spans, $i = 1, N$:



Balance of particles for an *internal* ($i = 2 \div N-1$) volume V_i (change in concentration during Δt due to the particle exchange with adjacent cells):

$$\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} V_i = J_{i-1 \rightarrow i} A_L - J_{i \rightarrow i+1} A_R$$

First Fick's law: $J_{i-1 \rightarrow i} = -D \frac{C_i^t - C_{i-1}^t}{\Delta x}$

$$J_{i \rightarrow i+1} = -D \frac{C_{i+1}^t - C_i^t}{\Delta x}$$

$$\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} V_i = -D \frac{C_i^t - C_{i-1}^t}{\Delta x} A_L - (-D) \frac{C_{i+1}^t - C_i^t}{\Delta x} A_R$$

$$V_i = \Delta x \Delta y \Delta z, A_L = A_R = \Delta y \Delta z \quad \frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2}$$

Numerical integration of the diffusion equation (II)

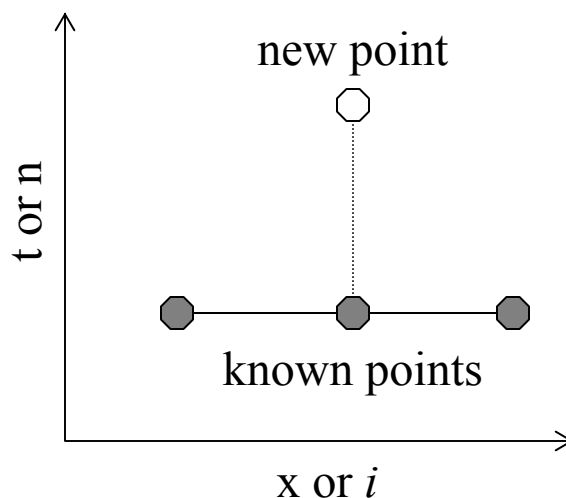
Finite difference method. Spatial Discretization. Internal nodes.

$$\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2}$$

$$C_i^{t+\Delta t} = C_i^t + \Delta t \cdot D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2}$$

Using this equation we can calculate unknown concentration at time $t+\Delta t$ if we know concentrations at previous timestep t .

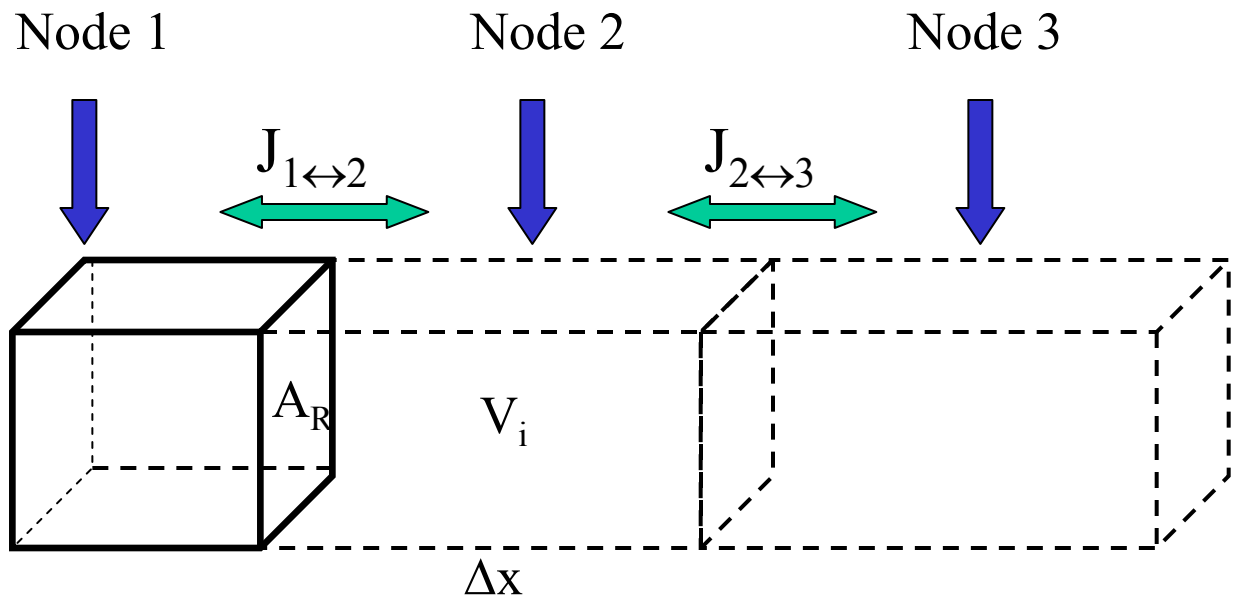
The finite difference scheme that we discussed is called the **explicit Forward Time Centered Space (FTCS)** method, since the unknown temperature at node i is given explicitly in terms of only known temperatures computed at the previous timestep.



Numerical integration of the diffusion equation (III)

Finite difference method. Spatial Discretization. **End nodes.**

Let's consider the first node, $i = 1$ and let's place the node at the surface.



Balance of particles for volume V_1 that is represented by the end node:

$$\frac{C_1^{t+\Delta t} - C_1^t}{\Delta t} V_1 = -J_{1 \rightarrow 2} A_R$$

First Fick's law: $J_{1 \rightarrow 2} = -D \frac{C_2^t - C_1^t}{\Delta x} A_R$

$$\frac{C_1^{t+\Delta t} - C_1^t}{\Delta t} V_1 = D \frac{C_2^t - C_1^t}{\Delta x} A_R$$

$$V_1 = V_N = V_{i=2 \div N-1} / 2, \quad \Delta x A_R = \Delta x \Delta y \Delta z = V_{i=2 \div N-1} = 2V_1$$

$$\frac{C_1^{t+\Delta t} - C_1^t}{\Delta t} = 2D \frac{C_2^t - C_1^t}{\Delta x^2}$$

Numerical integration of the diffusion equation (IV)

Finite difference method. Spatial Discretization. **End nodes.**

$$\frac{C_1^{t+\Delta t} - C_1^t}{\Delta t} = 2D \frac{C_2^t - C_1^t}{\Delta x^2}$$

$$C_1^{t+\Delta t} = C_1^t + \Delta t \cdot 2D \frac{C_2^t - C_1^t}{\Delta x^2}$$

Similarly, for another end node N, one can derive:

$$C_N^{t+\Delta t} = C_N^t - \Delta t \cdot 2D \frac{C_N^t - C_{N-1}^t}{\Delta x^2}$$

If an initial concentration profile at time $t=0$ is given, we can use the derived equations for all nodes, from 1 to N, to calculate concentration profile at time Δt , $2\Delta t$, $3\Delta t$, etc. up to the time that we are interested in.

Stability criterion

Assuming that the coefficients of the differential equation are constant (or so slowly varying as to be considered constant) the stability criterion for

$$C_i^{t+\Delta t} = C_i^t + \Delta t \cdot D \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{\Delta x^2}$$

is
$$\frac{2D\Delta t}{\Delta x^2} \leq 1$$

This condition is referred to as the Von Neumann stability condition.

Physical interpretation: the maximum timestep is, up to a numerical factor, the diffusion time across a cell of width Δx (remember Einstein relation $D = s^2/2dt$).

Position (C, T,...) dependent D(x,t)

For a position-dependent diffusion coefficient, it should be evaluated at the interfaces between the volumes V_i in order to preserve the conservation of the total number of particles

$$\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = \frac{D_{i+1/2} (C_{i+1}^t - C_i^t) - D_{i-1/2} (C_i^t - C_{i-1}^t)}{\Delta x^2}$$

e.g., for sample with non-uniform T distribution

$$D_{i+1/2} = \frac{1}{2} [D(T_{i+1}^t) + D(T_i^t)]$$

Simple boundary conditions

No mass transfer through the boundary:

$$\left. \frac{\partial C}{\partial x} \right|_{x=L} = 0$$

Constant concentration at the boundary $C_L = C_f$ and we can use the following boundary condition:

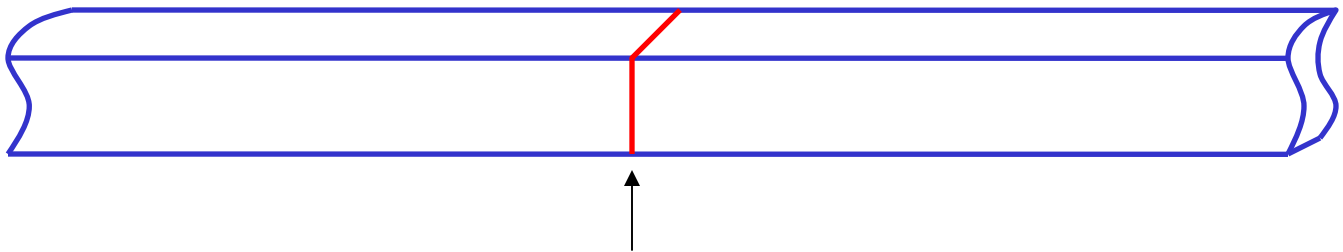
$$C \Big|_{x=L} = C_f$$

Analytical Solutions of the Diffusion Equation

While the numerical method described above can be applied to solve the diffusion equation for any initial and boundary conditions, in many special cases it is possible to derive analytic solutions as well. The advantage of analytical solution – does not involve long computations, gives clear picture of the dependence of the solution on different parameters in the whole range of x and t .

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

Let's consider the simple case of solute atoms initially inserted into the middle of an infinite one-dimensional system (plane source).



All solute is in one plane initially

With time the solute atoms will diffuse from the plane. The redistribution of the atoms can be described by the following solution of the diffusion equation:

$$C(x, t) = \frac{A}{\sqrt{t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Analytical solution for plane source

We can show by differentiation that for the plane source in an infinite system

$$C(x, t) = \frac{A}{\sqrt{t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is the solution of the diffusion equation

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

Analytical solution for plane source

Coefficient A we can find from the condition that the total quantity of solute per unit cross-section area S is

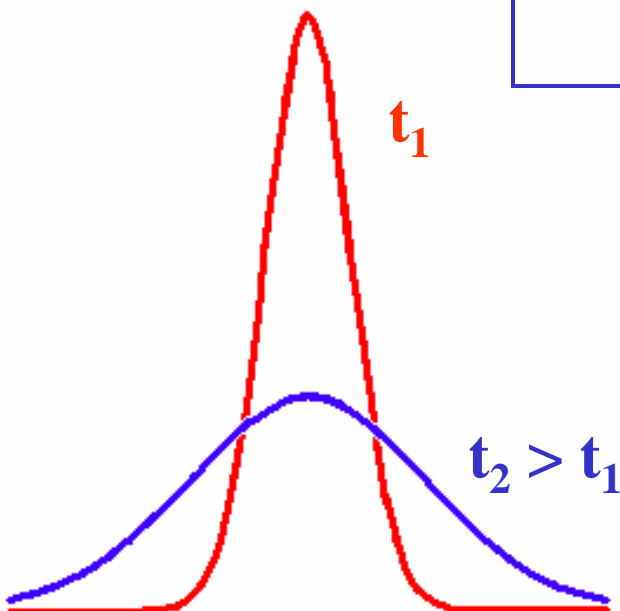
$$M = S \int_{-\infty}^{+\infty} C(x, t) dx = S \int_{-\infty}^{+\infty} \frac{A}{\sqrt{t}} \exp\left(-\frac{x^2}{4Dt}\right) dx$$

Using substitution of variable $y = \frac{x}{\sqrt{4Dt}}$ $dx = \sqrt{4Dt} dy$

$$M = \frac{AS \sqrt{4Dt}}{\sqrt{t}} \int_{-\infty}^{+\infty} \exp(-y^2) dy = AS \sqrt{4D} \times \sqrt{\pi}$$

$$A = \frac{M}{S \sqrt{4\pi D}}$$

$$C(x, t) = \frac{M}{S 2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$



The solution is a Gaussian concentration profile whose width increases with time

Thin film deposited on a semi-infinite piece of material

$$\left. \frac{\partial C}{\partial x} \right|_{x=0} = 0$$


Using the same solution we have a different condition for coefficient A:

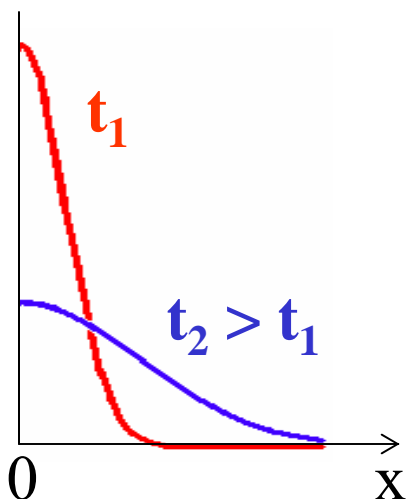
$$M = S \int_0^{+\infty} \frac{A}{\sqrt{t}} \exp\left(-\frac{x^2}{4Dt}\right) dx$$

Using substitution of variable $y = \frac{x}{\sqrt{4Dt}}$ $dx = \sqrt{4Dt} dy$

$$M = \frac{AS \sqrt{4Dt}}{\sqrt{t}} \int_0^{+\infty} \exp(-y^2) dy = AS \sqrt{4D} \times \frac{\sqrt{\pi}}{2}$$

$$A = \frac{M}{S \sqrt{\pi D}}$$

$$C(x, t) = \frac{M}{S \sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

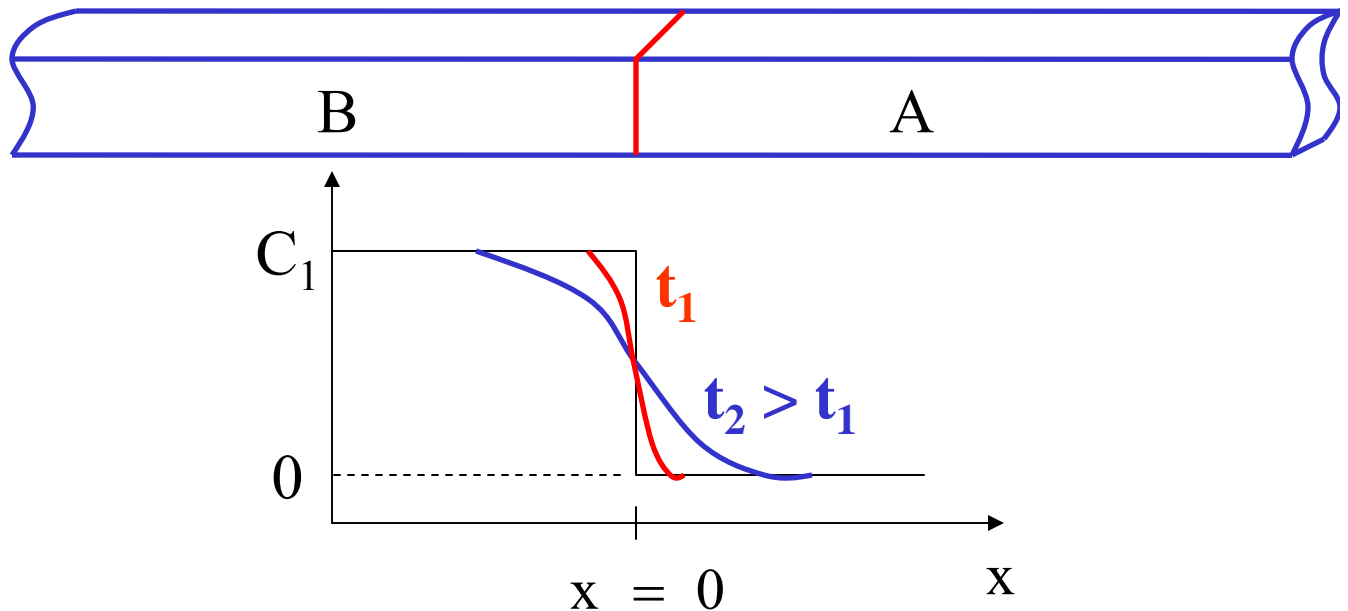


The solution is a half of a Gaussian concentration profile.

At the surface, the boundary condition

$$\left. \frac{\partial C}{\partial x} \right|_{x=0} = 0 \quad \text{is satisfied}$$

Analytical solutions: Pair of Semi-infinite Solids (I)

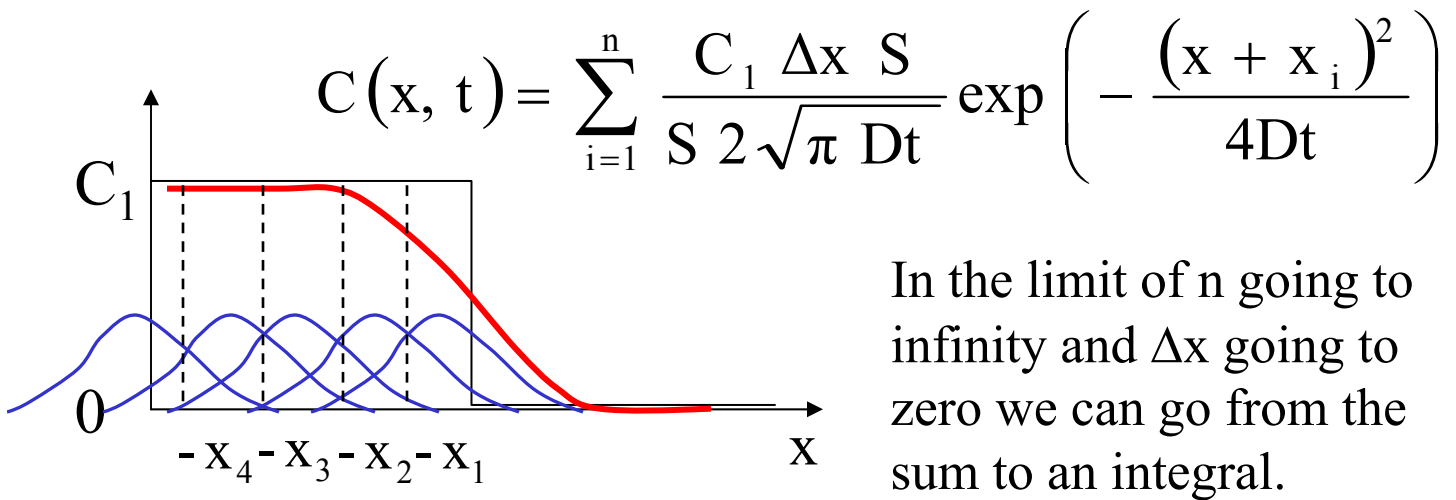


Think of the block of B as being made up of many thin layers of thickness Δx and cross-sectional area S . Each layer initially contains $C_1 \Delta x$ of B atoms. We know that if the areas surrounding a layer are initially B-free, the distribution of solute atoms that originate from a thin layer can be described by the Gaussian profile. Assuming that the presence of other solutes (atoms of type B) do not affect the diffusion of atoms that originate from the layer, the overall solution can be found as superposition of the Gaussian profiles from the layers.

$$C(x, t) = \sum_{i=1}^n \frac{C_1 \Delta x S}{S 2 \sqrt{\pi Dt}} \exp \left(- \frac{(x + x_i)^2}{4Dt} \right)$$

The diagram below the equation shows a graph of concentration C_1 versus position x . The graph shows a red curve representing the overall solution and several blue curves representing individual Gaussian profiles. The x-axis is labeled x and has tick marks at $-x_4, -x_3, -x_2, -x_1$. A dashed oval around the coefficient in the equation is labeled M .

Analytical solutions: Pair of Semi-infinite Solids (II)



$$C(x, t) = \frac{C_1}{2\sqrt{\pi} Dt} \int_0^{\infty} \exp\left(-\frac{(x + w)^2}{4Dt}\right) dw$$

Substituting $\frac{x + w}{2\sqrt{Dt}} = u$ we can rewrite the integral:

$$C(x, t) = \frac{C_1}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^{\infty} e^{-u^2} du = \frac{C_1}{\sqrt{\pi}} \left(\int_{\frac{x}{2\sqrt{Dt}}}^0 e^{-u^2} du + \int_0^{\infty} e^{-u^2} du \right)$$

Using definition of the error function: $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy$

and taking into account that $\operatorname{erf}(\infty) = 1$ and $\operatorname{erf}(-z) = -\operatorname{erf}(z)$

$$C(x, t) = \frac{C_1}{2} \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \right]$$

Analytical solutions: Constant surface composition (I)

$$C|_{x=0} = C_s \quad \text{---} \quad C|_{x=\infty} = C_0$$

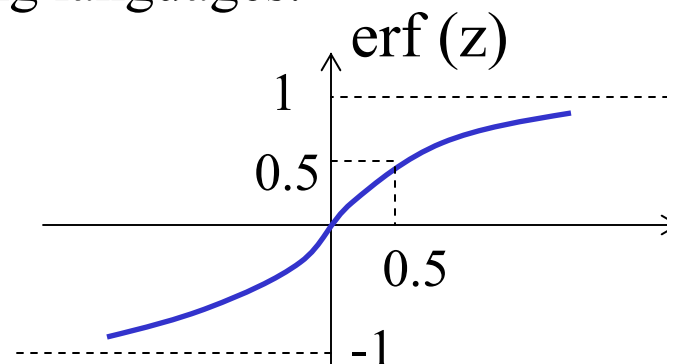

A similar solution of the diffusion equation can be derived for a constant surface concentration. If the initial concentration of solute atoms in the specimen is C_0 and concentration at the surface is C_s , the analytical solution of the Fick's second law is

$$C = C_s - (C_s - C_0) \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

where erf is the error function that is an indefinite integral defined by the equation: $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy$

The error function is tabulated in books of standard mathematical functions and is defined as an internal function in some of programming languages.

$$\begin{aligned} \operatorname{erf}(z) &= 1 && \text{for } z = \infty \\ \operatorname{erf}(z) &= 0 && \text{for } z = 0 \\ \operatorname{erf}(z) &= 0.5 && \text{for } z = 0.5 \end{aligned}$$



Summary

Make sure you understand language and concepts:

- Activation free energy barrier
- Arrhenius rate equation
- Driving force for diffusion
- Diffusion in ideal and real solutions
- Thermodynamic factor
- Diffusion against the concentration gradient
- Spinodal decomposition
- Diffusion against the concentration gradient
- Flux
- Steady-state diffusion
- Fick's first law
- Diffusion coefficient
- Nonsteady-state diffusion
- Fick's second law
- Numerical integration of the diffusion equation
 - Finite difference method
 - Spatial and time discretization
 - Initial and boundary conditions
 - Stability criterion
- Analytical solutions for special cases
 - plane source
 - thin film on a semi-infinite substrate
 - diffusion pair
 - constant surface composition