Diffusion

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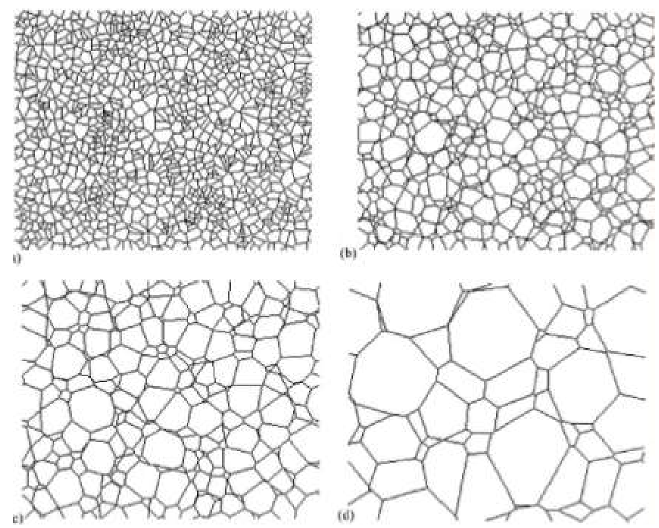
Diffusion

- Movement of matter from one region to another
- Generally from region of higher concentration to lower concentration
- Pizza in a seminar room
- Colour drop in water
- Solid state diffusion
- Irreversible process
- Entropy increases, Gibbs free energy decreases

- Steel gears must be hard at teeth to avoid wear but tough to bear shock

- More carbon at surface than at the center

- Doping of silicon to make
  p or n type extrinsic semi-conductor



- Grain growth

- Precipitate growth

- Mass transfer

Fick's first law

- Adolf Fick proposed that the flux (of atomic species) is proportional to the negative of the concentration gradient in 1855.

$$J \propto -\frac{dC}{dx}$$

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

J ($mole/m^2s$) is flux
D (m^2/s) is diffusion coefficient
C ($mole/m^3$) = concentration of species like atoms, ions, etc.
x (m) position
dC/dx = concentration gradient

$$\vec{J} = -D\,\nabla C$$

Generalized form in terms of gradient

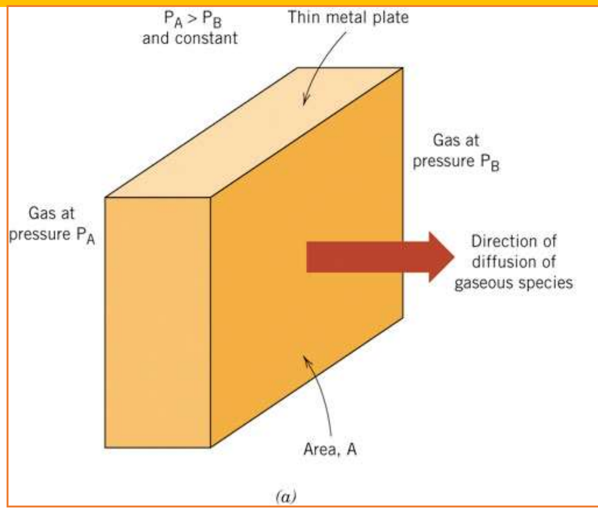
Steady state diffusion

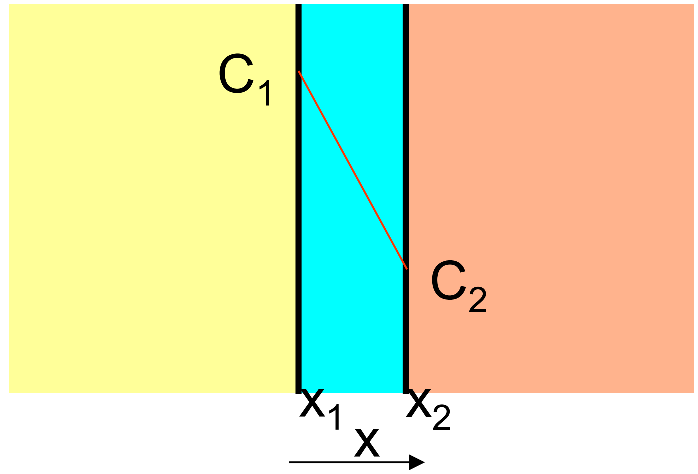
1. Diffusion along only one direction
2. Diffusivity independent of concentration
3. Diffusion in isotropic medium

$$J_x = -D\left[\frac{\partial C(x,t)}{\partial x}\right]_{x=x',t=t'}$$

On top of the above simplification if there is one more simplification of **Steady State**

$$J_x = -D\left[\frac{d\,C(x)}{dx}\right]_{x=\text{at any location in the medium}}$$





Fick's first law of diffusion

Rate of diffusion independent of time

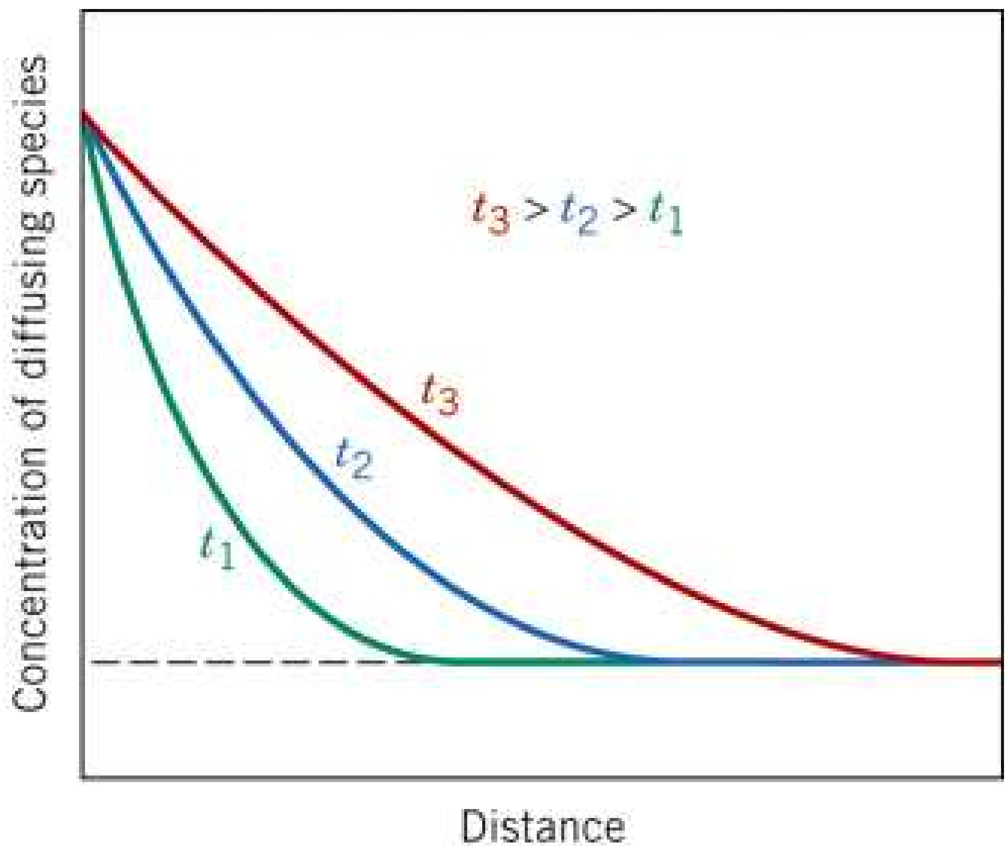
$$J = -D\frac{dC}{dx}$$

D ≡ diffusion coefficient

$$\frac{dC}{dx} \cong \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1} \longrightarrow J = -D\frac{C_2 - C_1}{x_2 - x_1}$$

Adopted from Callister

Non-Steady-State Diffusion



Fick's second law

- Fick's first law provides flux in an isotropic medium if concentration is known at two points
- Real life situation is different
- Need to account for steady as well as as non-steady state diffusion
- We want to predict composition at a point as a function of time
- Diffusivity can be a function of time

- Continuity condition for the Fick's first law is the second law

- Notice the change from simple derivative to partial derivative

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

- Generalized form has a Laplacian

$$\frac{\partial C}{\partial t} = -\nabla \bullet \vec{J} \qquad \vec{J} = -D\,\nabla C$$

$$\frac{\partial C}{\partial t} = \nabla \bullet (D\,\nabla C) \qquad \frac{\partial C}{\partial t} = D\,(\nabla \bullet \nabla C) \;\Rightarrow\; \frac{\partial C}{\partial t} = D\,\nabla^2 C$$

Analytical solution

Analytical solution of the linear diffusion equation that is Fick's second law where diffusivity is independent of concentration that is **Steady state condition**

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

$$0 = D\,\frac{d^2 C(x)}{dx^2}$$

$$C(x) = a\,x + \mathrm{b}$$

General form of the concentration profile

Analytical solution as a function of distance x for different time during diffusion is a Gaussian

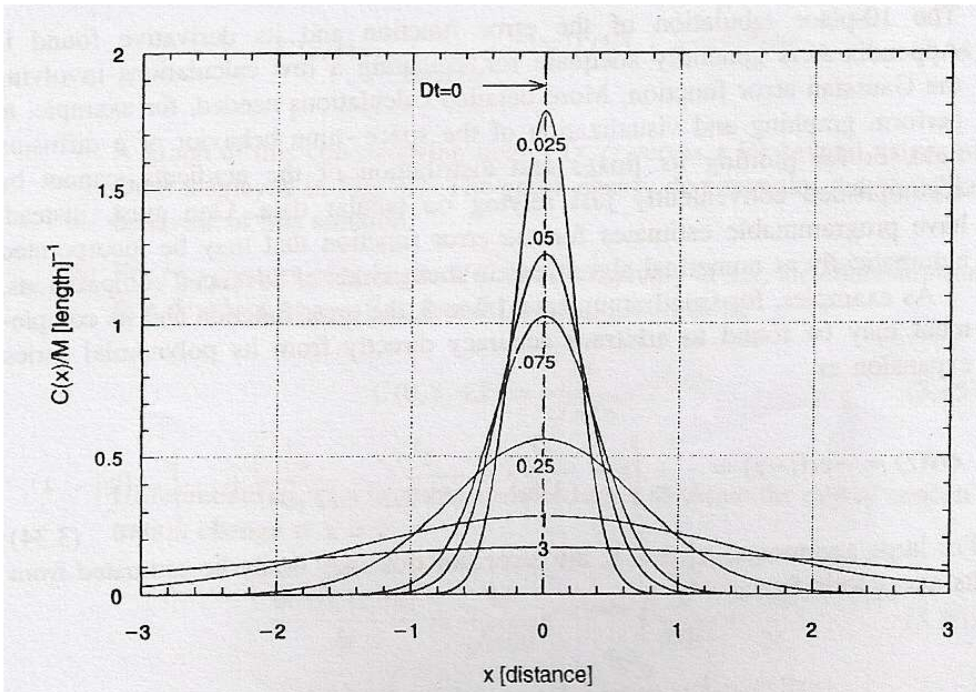


FIGURE 3.6 Normalized plot of eq. (3.31). The area under each curve is unity.

Boundary condition

- Second order differential equation

- Two conditions, boundary or initial, are required

  Initial condition: $C(x, t=0) = 0$ for $x \neq 0$
  Boundary condition: $C(x = \pm\infty, t) = 0$ for all t

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

- **Infinite medium**

- Solve PDE using Laplace Transform method, to obtain the final solution

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

- Actual condition is to consider a **semi-infinite medium**
- Fixed concentration at t = 0, x = 0 Thin film configuration
- Fixed concentration at x = 0 and all t: Carburizing configuration

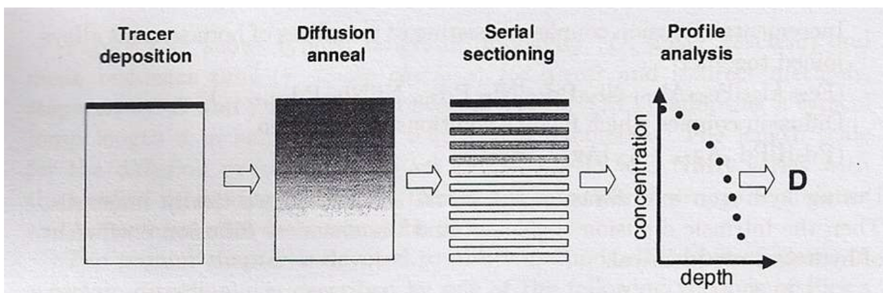


Fig. 13.3. Schematic illustration of the tracer method: The major steps – deposition of the tracer, diffusion anneal, serial sectioning, and evaluation of the penetration profile – are indicated

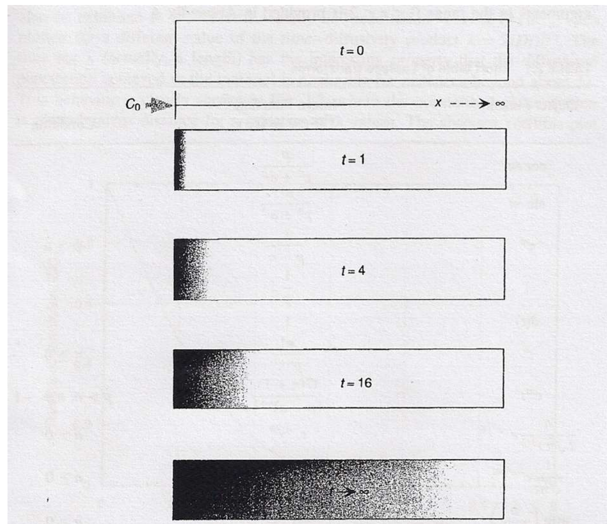


FIGURE 3.1 One-dimensional diffusion into a semi-infinite medium. The concentration at $x = 0$ is maintained for all time at a fixed value C_0 while diffusant spreads toward the right

- C (x=0, t = 0) = M (cm^{-2}), and after that there is no more supply of diffusant during the diffusion process

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

- The supply of diffusant is maintained on one end of the medium for t > 0, such that C (x=0, t > 0) = C_o

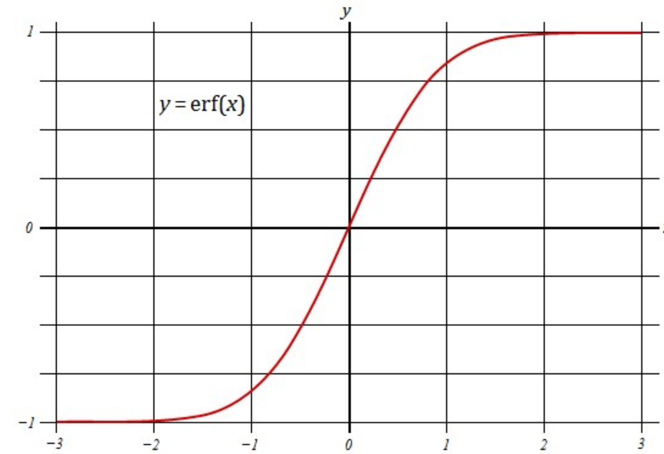
Initial condition: C(x > 0, t = 0) = 0

Boundary condition : C(x = 0, t > 0) = C_o

$$C(x,t)=C_o erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

The term **erf(x)** stands of error-function, and **erfc(x)** stands for complimentary error-function, that it **erfc(x) = 1 – erf(x)**

$$\text{definition}: \; erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta$$



http://www.had2know.com/academics/error-function-calculator-erf.htr

$$C(x,t) = C_o erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

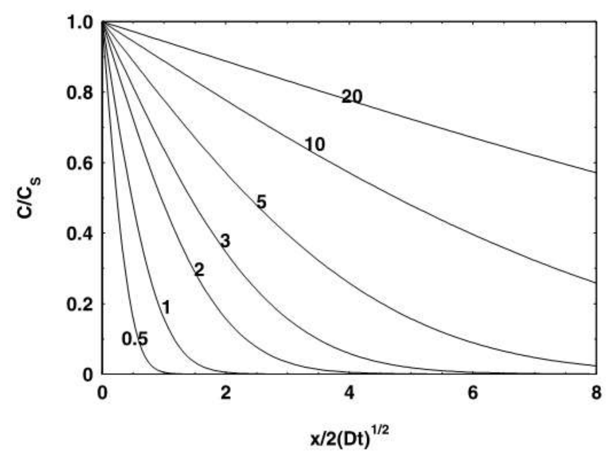


Fig. 3.3. Solution of the diffusion equation for constant surface concentration C_s and for various values of the diffusion length $2\sqrt{Dt}$

Mehrer

Characteristic Diffusion length

Used for quick estimation of the distance the diffusion atoms have moved into the material $\sqrt{Dt}$

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

Atomistic diffusion mechanisms

- Fluctuation in thermal energy distribution

- The dominant mechanism depends on a number of factors, including:
  - the crystal structure
  - nature of the bonding in the host crystal
  - relative differences of size and electrical charge between the host and the diffusing species
  - the type of site preferred by the diffusing species (e.g., anion or cation, substitutional or interstitial)

- Vacancy mechanism on metals and solid solutions, metalloids, ionic solids

- Interstitialcy mechanism

(Indirect interstitial mechanism)

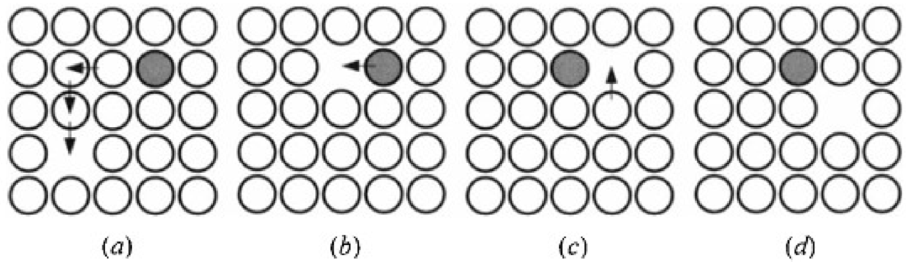


Figure 8.2: Vacancy mechanism for diffusion of substitutional atoms.

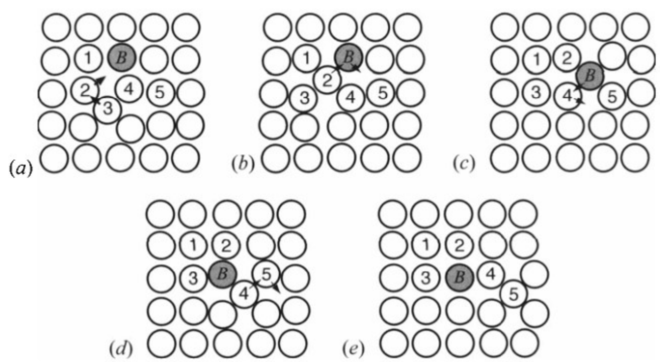


Figure 8.4: Substitutional diffusion by the interstitialcy mechanism. **(a)** The interstitial defect corresponding to the interstitial atom (3) is separated from a particular substitutional atom B (shaded). **(b)** The interstitial defect moved adjacent to B when the previously interstitial atom (3) replaced the substitutional atom (2). (2) then became the interstitial atom. **(c)** Atom (2) has replaced B, and B has become the interstitial atom. **(d)** B has replaced atom (4), which has become the interstitial atom. **(e)** The interstitial defect has migrated away from B. As a result, B has completed one nearest-neighbor jump and the interstitial defect has moved at least four times.

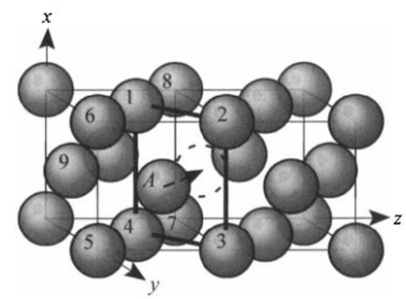


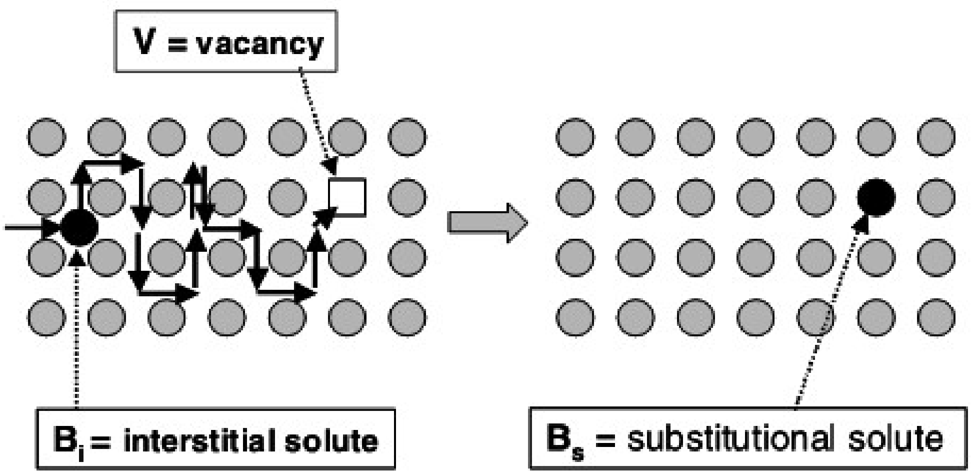
Figure 8.3: Atom-vacancy exchange in f.c.c. crystal. Atom initially at A jumps into a nearest-neighbor vacancy (dashed circle). The four nearest-neighbor atoms common to A and the vacant site (joined by the bold rectangle) form a "window" 1234 through which the A atom must pass. The A atom is centered in unit-cell face 2356. The vacancy is centered in unit-cell face 2378.

- Interstitial mechanism: C, H, N in metal

- Interstitial-substitutional exchange

mechanisms of foreign atom diffusion

Cu in Ge



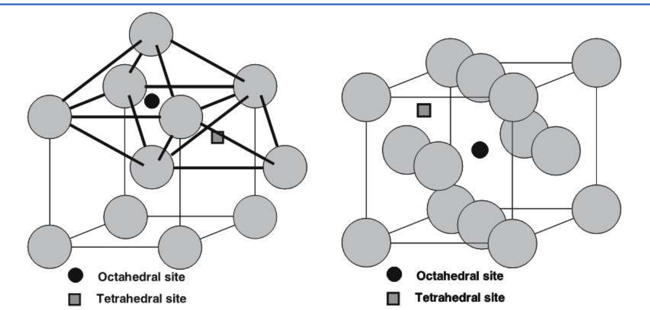
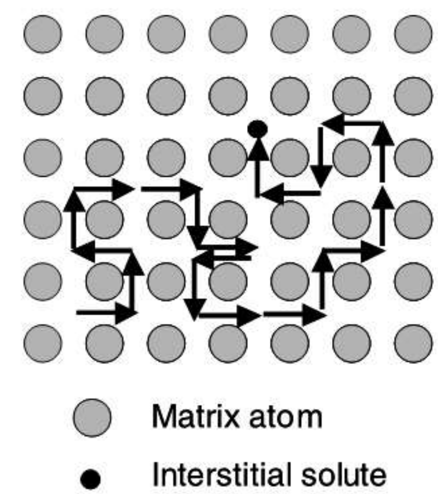


Fig. 6.1. Octahedral and tetrahedral interstitial sites in the bcc (*left*) and fcc (*right*) lattice

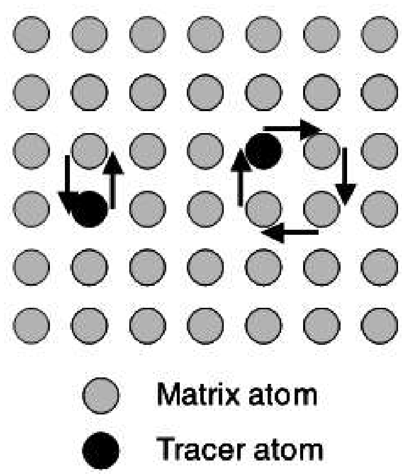


. Direct interstitial mechanism of diffusion

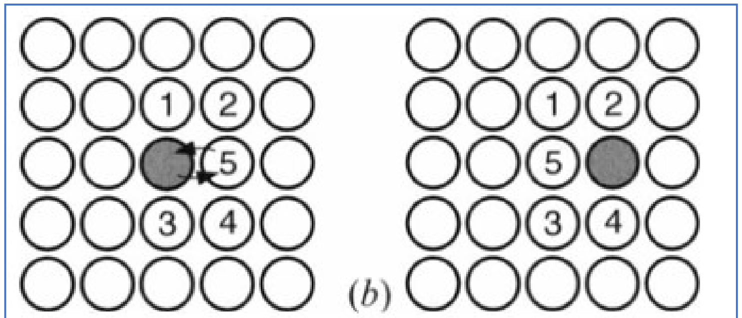
➢ Direct exchange and Ring Mechanism

➢ Direct exchange and ring mechanisms have in common that the **lattice defects are not involved.**

➢ Debatable



Direct exchange and ring diffusion mechanism

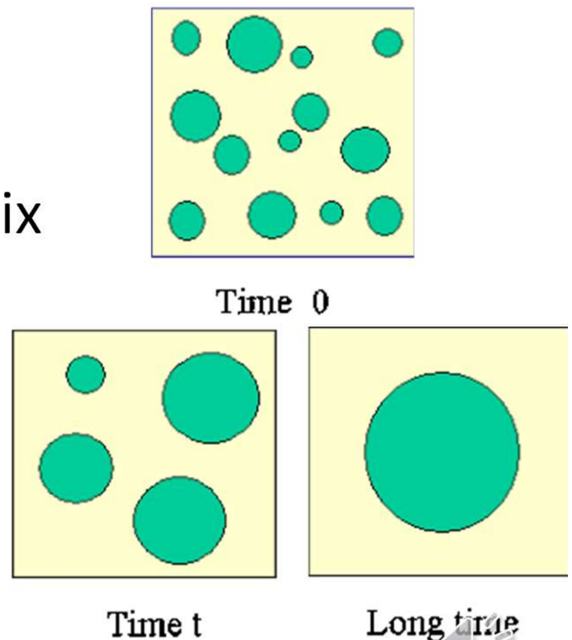


Ring mechanism for diffusion of substitutional a

- Uphill vs downhill diffusion

http://www-personal.umich.edu/~weilu/research/nanophase/model/model_coarsening.html

- Diffusion occurs from higher chemical to lower chemical potential
- Precipitate coarsening: larger precipitates grow at the expense of smaller



- Against composition gradient through the matrix
- Minimize energy by reducing surface area
- Thermodynamics of diffusion is important

- Defects play an important role in different materials processes like phase transformation, oxidation, thermomechanical processing and creep

- Grain boundary diffusivity or diffusion coefficient higher than lattice diffusion

- Dislocation core enhances diffusivity: Pipe diffusion

- High point defect concentration may aid diffusion

- Tremendous technological importance in electronic, ceramic and metal industry