



EMA5001 Lecture 3
Steady State &
Nonsteady State Diffusion -
Fick's 2nd Law & Solutions



Steady-State Diffusion

□ Steady State

- Steady State = Equilibrium? **No!**
 - Similarity: State function (e.g., μ , C) does NOT change with **time**
 - Difference: Net flux (or net reaction rate)
 - Zero (0) net flux for equilibrium state vs. non-zero net flux for steady state

□ Fick's 1st Law

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

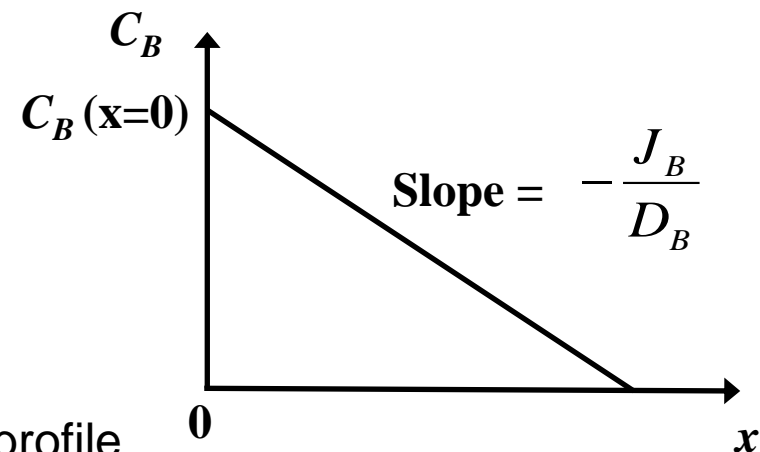
□ If steady state diffusion

- C_B does NOT change with time
- J_B does NOT change with time

For 1-D, **if D_B constant**, what is the concentration profile under steady state?

$$J_B = -D_B \frac{dC_B}{dx} \quad C_B(x) = \int -\frac{J_B}{D_B} dx$$

$$C_B(x) = C_B(x=0) - \frac{J_B}{D_B} x \quad \text{Linear concentration profile}$$





Nonsteady-State Diffusion

□ Nonsteady State

Concentration changes with both

- Location (x, y, z)
- Time (t)

Take a small slice at location x

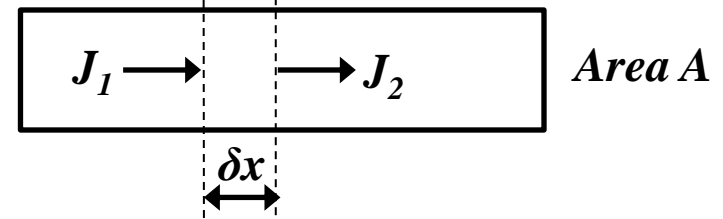
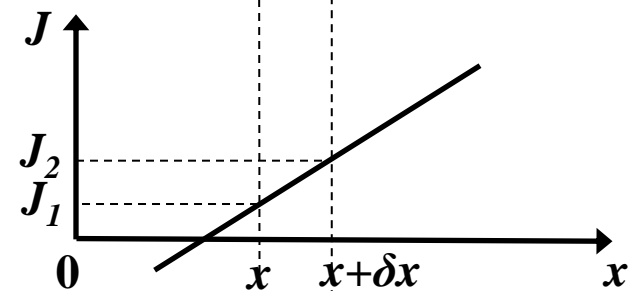
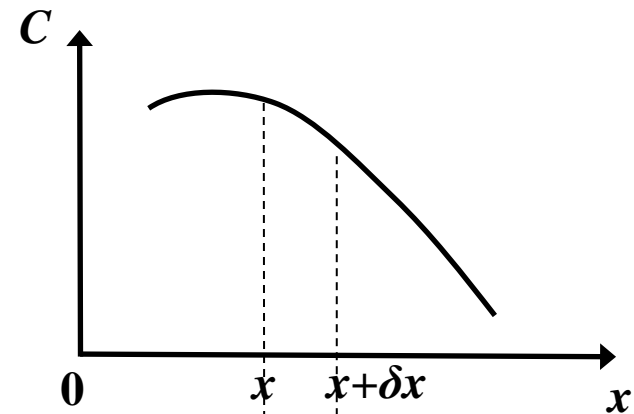
- δx : Thickness of the slice
- J_1 : Flux into the slice
- J_2 : Flux out from the slice

In small time period δt , the change of concentration in that slice

$$\delta C_B = \frac{J_1 A \delta t - J_2 A \delta t}{A \delta x}$$

We have

$$\frac{\delta C_B}{\delta t} = \frac{J_1 - J_2}{\delta x}$$





Fick's 2nd Law

Continued from p. 3

As δx and $\delta t \rightarrow 0$, we have
$$\frac{\partial C_B}{\partial t} = \frac{J_1 - J_2}{\delta x} = -\frac{\partial J_B}{\partial x}$$

Therefore
$$\frac{\partial C_B}{\partial t} = -\frac{\partial J_B}{\partial x}$$

Invoking Fick's 1st Law
$$J_B = -D_B \frac{\partial C_B}{\partial x}$$

We have
$$\frac{\partial C_B}{\partial t} = -\frac{\partial}{\partial x} \left(-D_B \frac{\partial C_B}{\partial x} \right) = \frac{\partial}{\partial x} \left(D_B \frac{\partial C_B}{\partial x} \right)$$

i.e.,

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left(D_B \frac{\partial C_B}{\partial x} \right)$$

Fick's 2nd Law

If D_B constant, simply to

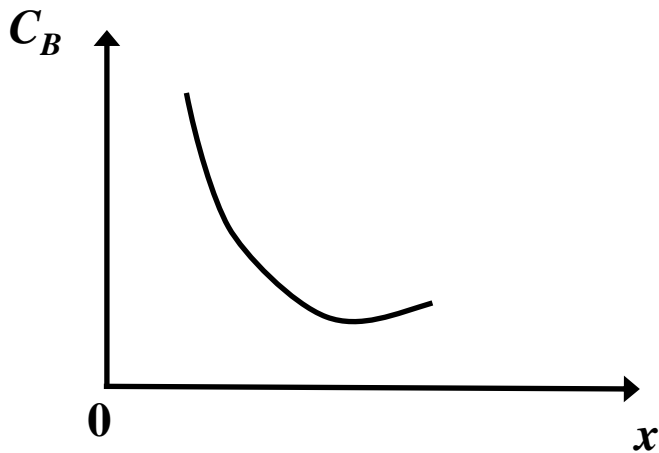
$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$



Implications of Fick's 2nd Law

□ Two concentration profiles

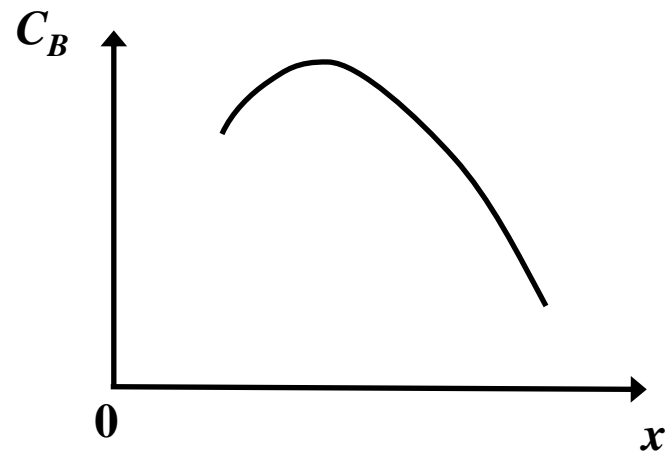
- Does the concentration in the specified region increase or decrease with time?



$$\frac{\partial^2 C_B}{\partial x^2} > 0$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} > 0$$

C_B **increases** with time



$$\frac{\partial^2 C_B}{\partial x^2} < 0$$

$$\frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} < 0$$

C_B **decreases** with time



Special Case – Homogenization

□ Diffusion to eliminate to local concentration variation

Simplest case: $t = 0$, C_B varies sinusoidally

$$C_B = \bar{C} + \beta_0 \sin \frac{\pi x}{l}$$

Assumption:

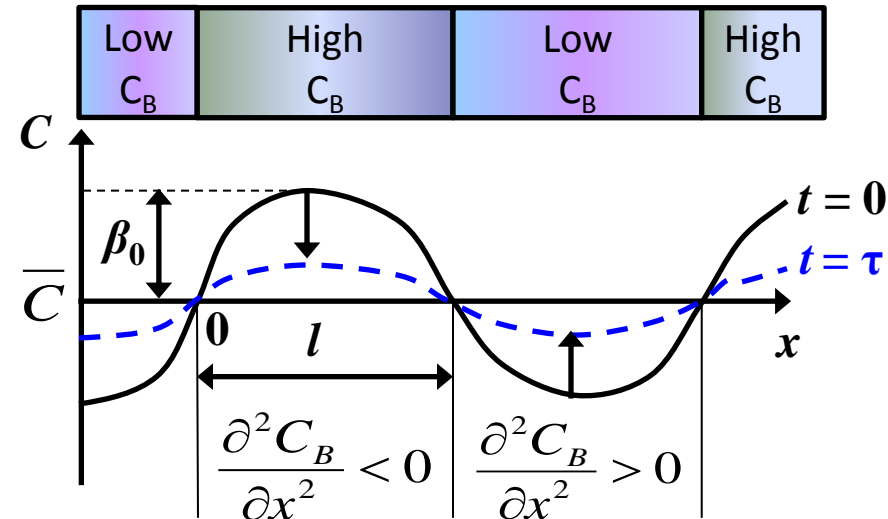
$$- D_B \text{ constant} \quad \frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2}$$

Solution to Fick's 2nd Law takes the form

$$C_B(x, t) = \bar{C} + \beta_0 \sin\left(\frac{\pi x}{l}\right) \exp\left(-\frac{t}{\tau}\right)$$

in which τ is **relaxation time** $\tau = \frac{l^2}{\pi^2 D_B}$

The amplitude of the variation $\beta = \beta_0 \exp\left(-\frac{t}{\tau}\right)$





Special Case – Spin-on Dopant for Silicon Wafer

□ Diffusion in Semi-Infinite Bar w/ Fixed Amount of Total Dopant

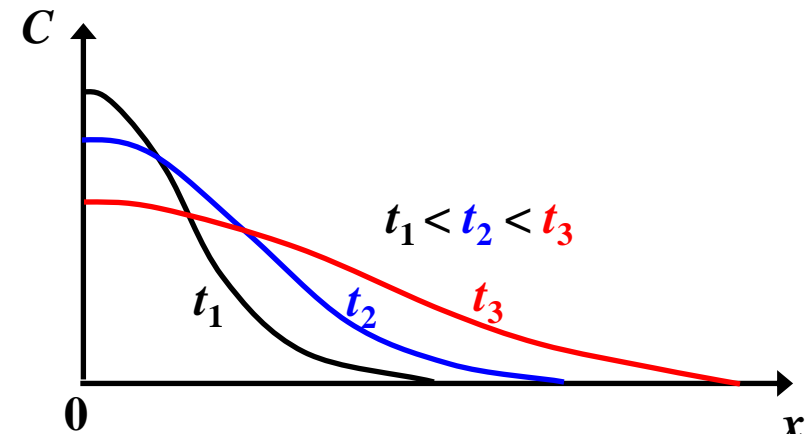
- Doping silicon surface with boron or phosphorous spin-on dopants and diffuse at 800-1000 °C

Fick's 2nd Law
$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left(D_B \frac{\partial C_B}{\partial x} \right)$$

Assumption:

- D_B constant
- Initial condition
 - $C_B(x=0, t=0) = \infty$; $C_B(x > 0, t=0) = 0$
- Boundary condition
 - Zero concentration far away from surface
 $C_B(x \rightarrow \infty) = 0$

If the total amount of dopant is fixed of N , then
$$C_B(x, t) = \frac{N}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$





Special Case – Infinite Diffusion Couple

□ Diffusion in Infinite Diffusion Couple

- Two dilute alloys of B in A welded together

Fick's 2nd Law

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left(D_B \frac{\partial C_B}{\partial x} \right)$$

Assumption:

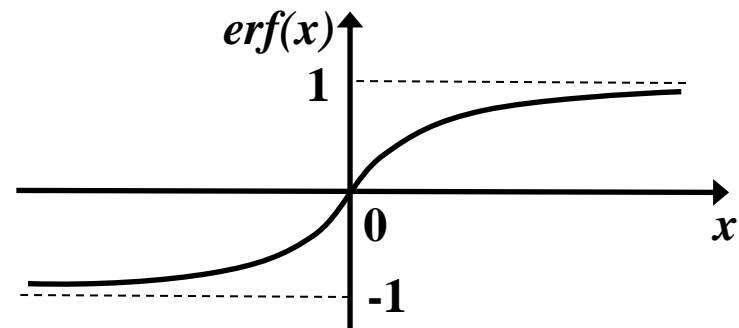
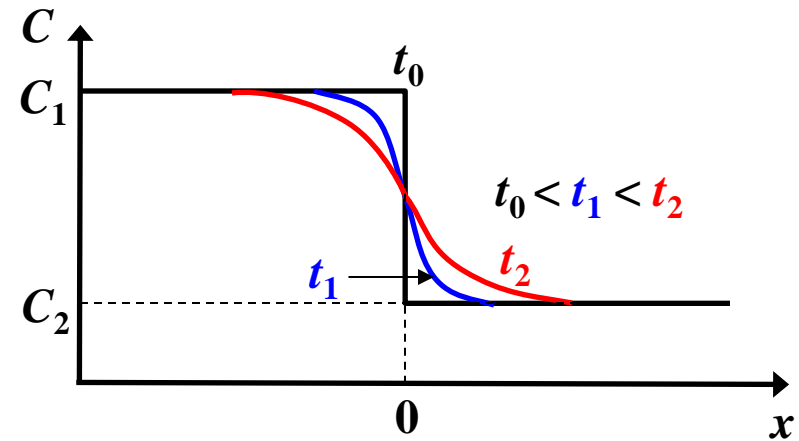
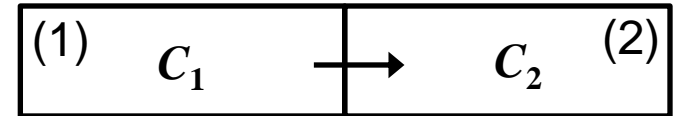
- D_B constant
- Initial condition
 - $C_B(x > 0, t = 0) = C_2$; $C_B(x < 0, t = 0) = C_1$
- Boundary condition:
 - $C_B(x \rightarrow \infty, t > 0) = C_2$; $C_B(x \rightarrow -\infty, t > 0) = C_1$

Solution is

$$C(x, t) = \frac{C_1 + C_2}{2} - \frac{C_1 - C_2}{2} \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

in which error function, erf is given by

$$\operatorname{erf}(z) = \frac{2}{\pi} \int_0^z \exp(-y^2) dy$$





Special Case – Carburization & Decarburization of Steel

□ Diffusion in Semi-Infinite Bar w/ Constant Surface Concentration

- Increase/decrease carbon concentration in surface
 - Carburization: CH₄/CO atmosphere at elevated temperature (for FCC γ -Fe)
 - Decarburization: vacuum at elevated temperature

Boundary/Initial conditions:

- Carburization:
 $C_B(x=0) = C_S$; $C_B(x \rightarrow \infty) = C_0$
- Decarburization:
 $C_B(x=0) = 0$; $C_B(x \rightarrow \infty) = C_0$

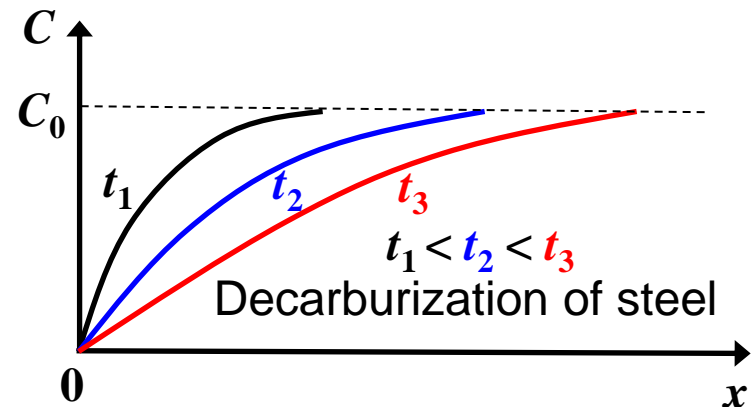
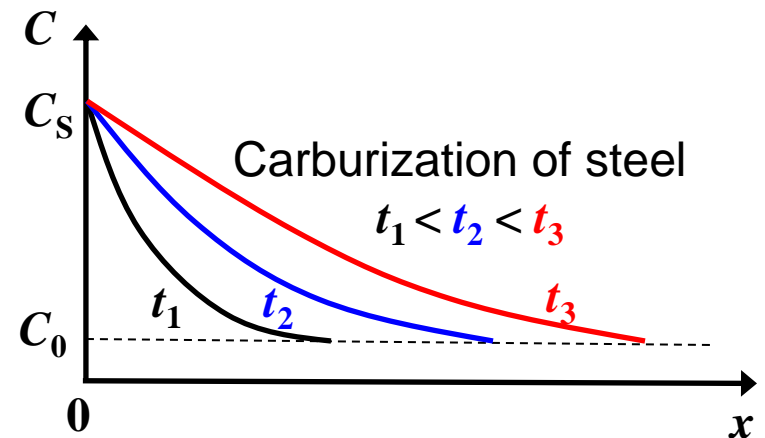
Solutions are

- Carburization

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

- Decarburization

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





Diffusion Length

Example: Carburization of steel

For error function, if $erf(z) = 0.5$, $z \approx 0.5$

Therefore, for concentration profile

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

When

$$erf\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5$$

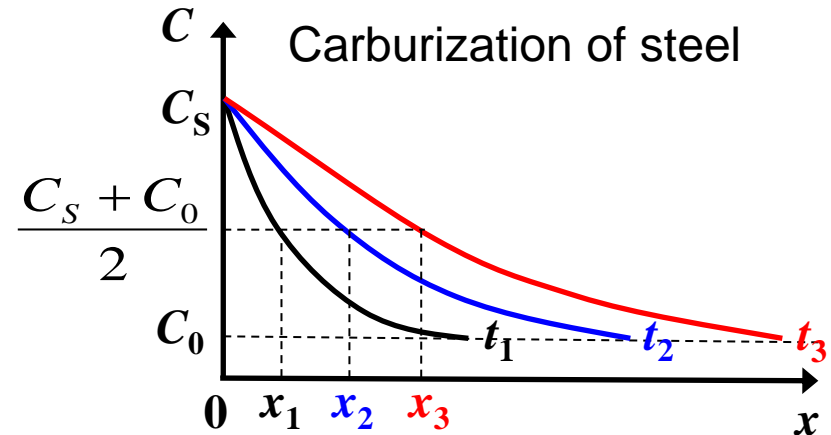
$$C(x, t) = \frac{C_s + C_0}{2}$$

Indicating

$$z = \frac{x}{2\sqrt{Dt}} \approx 0.5$$

Therefore,

$$x \approx \sqrt{Dt}$$



$$\text{If } x_1 = \frac{x_2}{2} = \frac{x_3}{3}$$

What is the relationship between t_1 , t_2 , and t_3 assuming D constant?

$$\sqrt{Dt_1} = \frac{\sqrt{Dt_2}}{2} = \frac{\sqrt{Dt_3}}{3}$$

$$t_1 = \frac{t_2}{2^2} = \frac{t_3}{3^2}$$

Diffusion Length - characteristic length in a material within which it experiences significant change due to diffusion



Microscopic View of Diffusion Length (1)

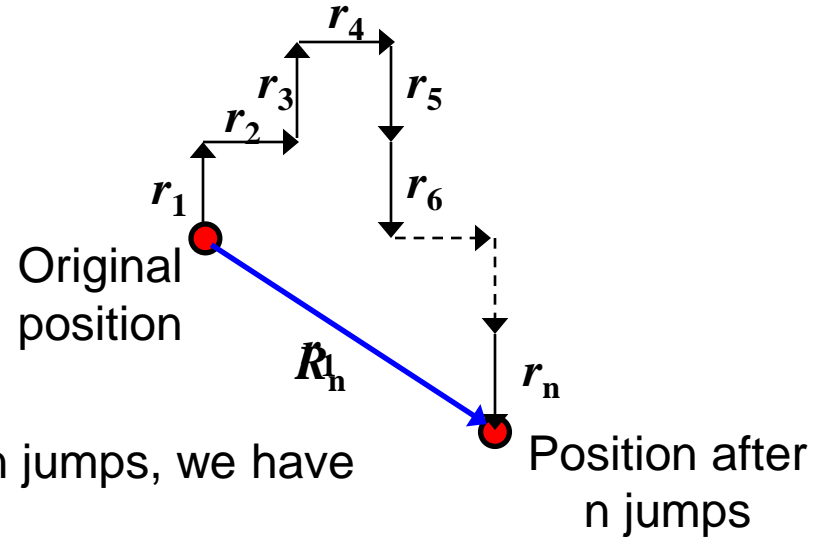
□ For an interstitial atom

Each random jump with displacement of \vec{r}_i
 After n jumps, total displacement vector is

$$\vec{R}_n = \vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \dots + \vec{r}_n = \sum_{i=1}^n \vec{r}_i$$

To obtain absolute displacement length after n jumps, we have

$$\begin{aligned} \vec{R}_n \cdot \vec{R}_n &= \sum_{i=1}^n \vec{r}_i \cdot \sum_{i=1}^n \vec{r}_i \\ &= \sum_{i=1}^n \vec{r}_i \cdot \vec{r}_i + 2 \sum_{i=1}^{n-1} \vec{r}_1 \cdot \vec{r}_{1+i} + 2 \sum_{i=1}^{n-2} \vec{r}_2 \cdot \vec{r}_{2+i} + \dots + 2 \sum_{i=1}^2 \vec{r}_{n-2} \cdot \vec{r}_{(n-2)+i} + 2 \sum_{i=1}^1 \vec{r}_{n-1} \cdot \vec{r}_{(n-1)+i} \\ &= \sum_{i=1}^n r_i^2 + 2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \vec{r}_j \cdot \vec{r}_{j+i} \end{aligned}$$





Microscopic View of Diffusion Length (2)

□ Continue from p. 11

$$\vec{R}_n \bullet \vec{R}_n = \sum_{i=1}^n r_i^2 + 2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \vec{r}_j \bullet \vec{r}_{j+i}$$

Successful jumping occurs only to the nearest neighbor, then for $i = 1, 2, \dots, n$, $|\vec{r}_i| = \alpha$ in which α is the jumping distance for an (interstitial) atom to its nearest neighbor.

Consider $\vec{r}_j \bullet \vec{r}_{j+i} = \alpha^2 \text{Cos} \theta_{j,j+i}$

in which $\theta_{j,j+i}$ is the angle between \vec{r}_j and \vec{r}_{j+i}

The displacement after n jumps will be

$$R_n^2 = n\alpha^2 + 2\alpha^2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \text{Cos} \theta_{j,j+i}$$

Now consider random jumping of a large amount of atoms:

Each atoms jumps for n times, and the “average” displacement among all atoms

$$\overline{R_n^2} = n\alpha^2 + 2\alpha^2 \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \text{Cos} \theta_{j,j+i}$$



Microscopic View of Diffusion Length (3)

Continued from p. 12

For average over a large amount of atoms, we have

$$\overline{\sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \text{Cos} \theta_{j,j+i}} = 0$$

Therefore,
$$\overline{R_n^2} = n\alpha^2 + 2\alpha^2 \overline{\sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \text{Cos} \theta_{j,j+i}} = n\alpha^2$$

If Γ is the successful jump frequency, and if the n jumps take time t , $n = \Gamma t$

$$\overline{R_n^2} = n\alpha^2 = (\Gamma t) \cdot \alpha^2 = \Gamma \alpha^2 t$$

From earlier derivation about diffusion of interstitial atoms, $D_B = \frac{1}{6} \Gamma_B \alpha^2 \rightarrow \Gamma_B \alpha^2 = 6D_B$

Therefore,
$$\overline{R_n^2} = (\Gamma \alpha^2) \cdot t = 6D_B t$$

The “average” (**root mean square**) displacement after time t for random walk is

$$\sqrt{\overline{R_n^2}} = 2.4 \sqrt{D_B t}$$



Homework

- Porter 3rd Ed, Exercise 2.1, 2.3, 2.6
- Due **Feb 3 class**