# MLL 100

# Introduction to Materials Science and Engineering

***Lecture-20 (February 25, 2022)***

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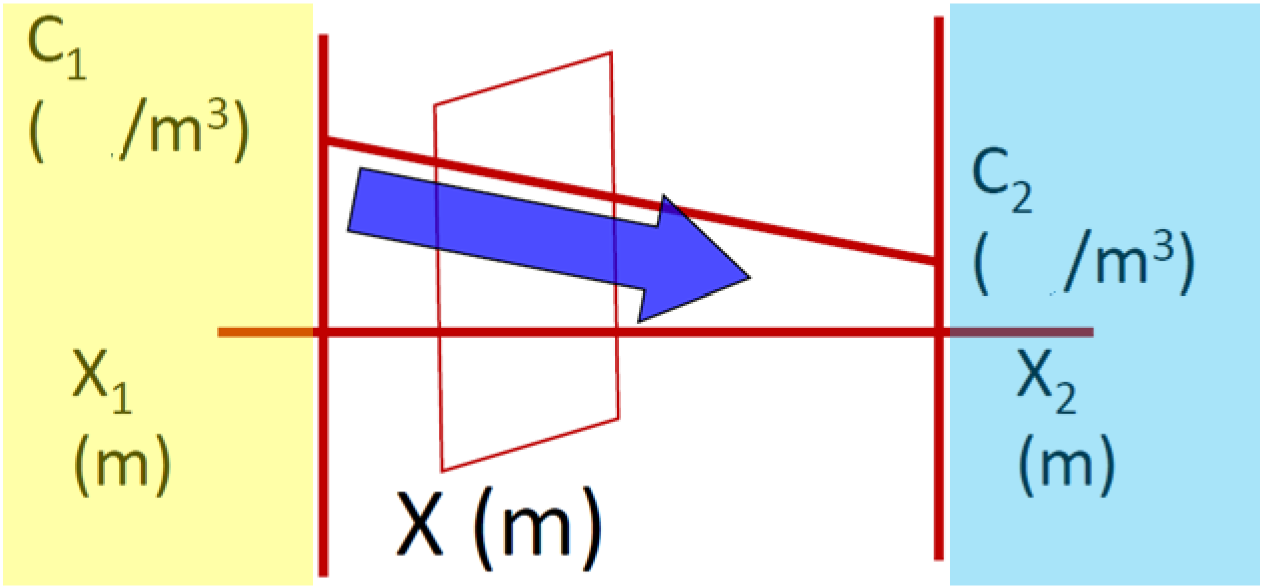
# What have we learnt in Lecture-19?

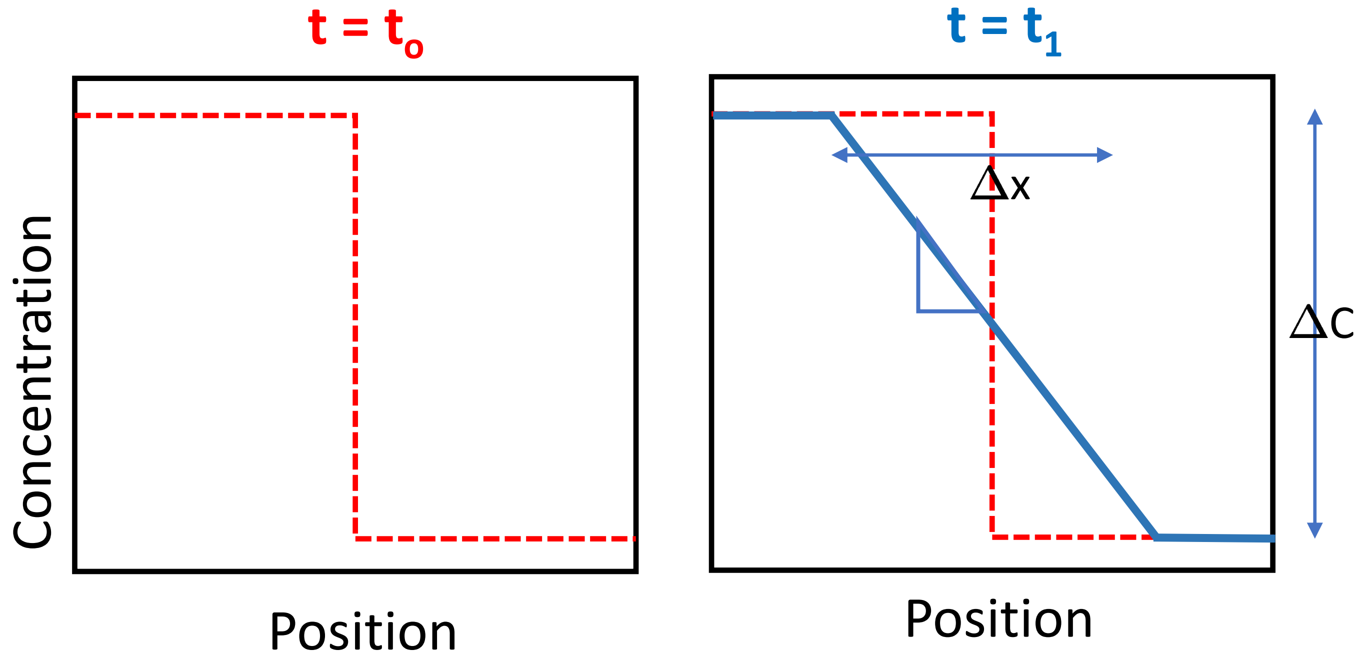
- Diffusion
- Driving force of diffusion: chemical potential gradient

Gradient →
- Concentration / Chemical potential
- Electric
- Magnetic
- Stress
- Pressure

- Analogy to Fick's first law

# Fick's first law of diffusion




*For one-dimensional:*

*Flux of atoms per unit area per unit time*

*(-ve) sign implies flow of atoms down the concentration gradient*

$$J_i = -D\left(\frac{dC_i}{dx}\right)$$

*Material property*

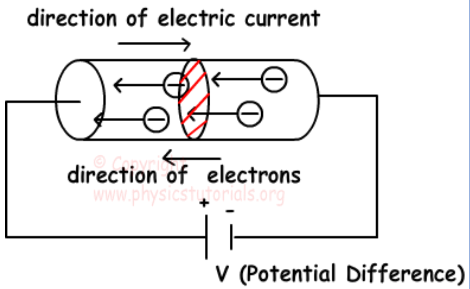
*Gradient*

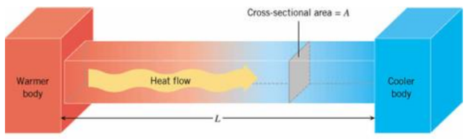
*How the composition of a material varies with the distance?*

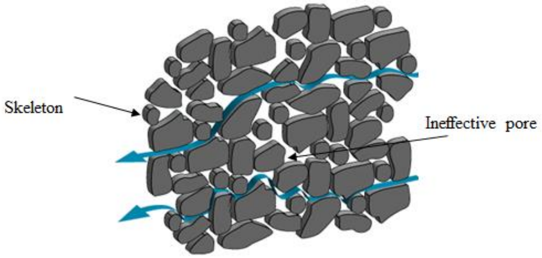
**What is the unit of diffusion coefficient (D)?**

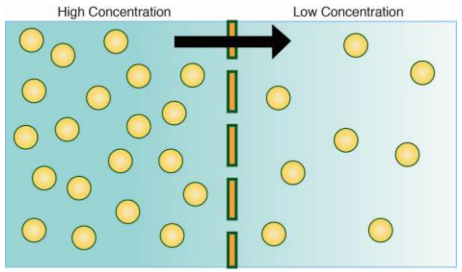
$$\overset{atoms/m^2.s}{J} = -\overset{m^2/s}{D}\,\frac{(C_2 - C_1)_{atoms/m^3}}{(x_2 - x_1)_{m}}$$

| | Charge flow (electrical conduction) | Phonon flow (thermal conduction) | Fluid flow in porous medium | Atomic flow (diffusion) |
|---|---|---|---|---|
| What quantity flows? | Electrons | phonons | fluid | atoms |



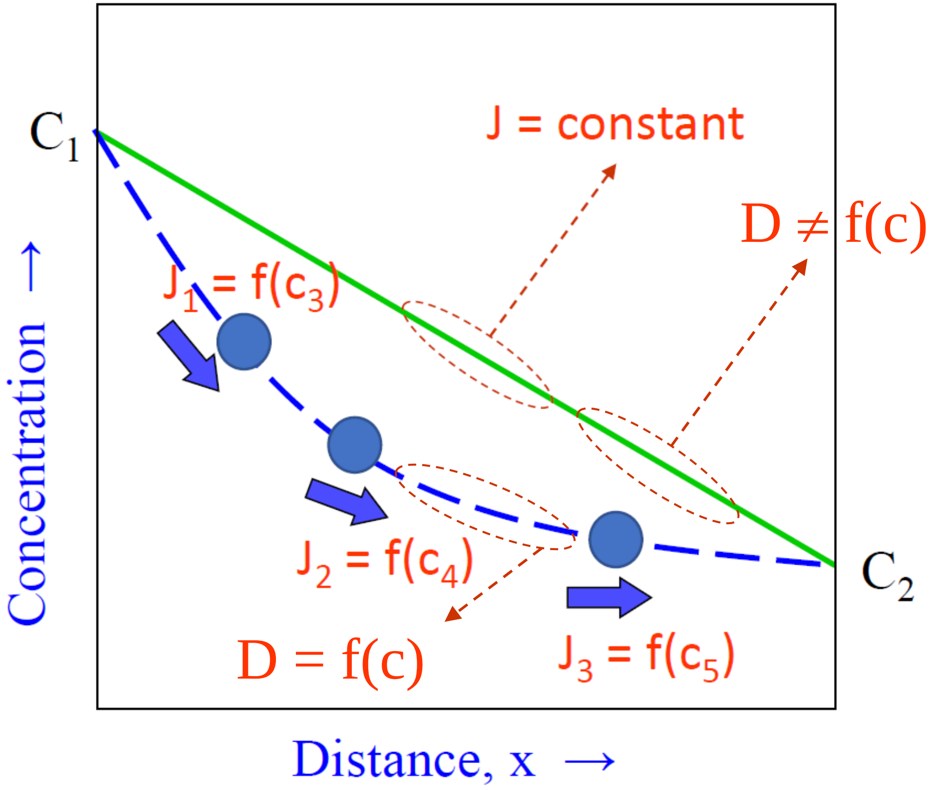

| | Charge flow (electrical conduction) | Phonon flow (thermal conduction) | Fluid flow in porous medium | Atomic flow (diffusion) |
|---|---|---|---|---|
| What is the gradient? | Potential drop $j_e \propto -\frac{dV}{dx}$ | Temperature difference $j_q \propto -\frac{dT}{dx}$ | Pressure difference $j_f \propto -\frac{dP}{dx}$ | Concentration difference $J \propto -\frac{dC}{dx}$ |
| What material property gets represented? | Electrical conductivity $j_e = -\boldsymbol{\sigma}\frac{dV}{dx}$ | Thermal conductivity $j_q = -\boldsymbol{\kappa}\frac{dT}{dx}$ | Hydraulic permeability $j_f = -\boldsymbol{K}\frac{dP}{dx}$ | Diffusivity $J = -\boldsymbol{D}\frac{dC}{dx}$ |
| What is the law describing this behaviour? | Ohm's law | Fourier's law | Darcy's law | Fick's law |

# Steady-state of diffusion

In steady state diffusion there is neither accumulation nor depletion of the diffusing species anywhere in the medium at any time and Fick's first law is easily applicable

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

Constant



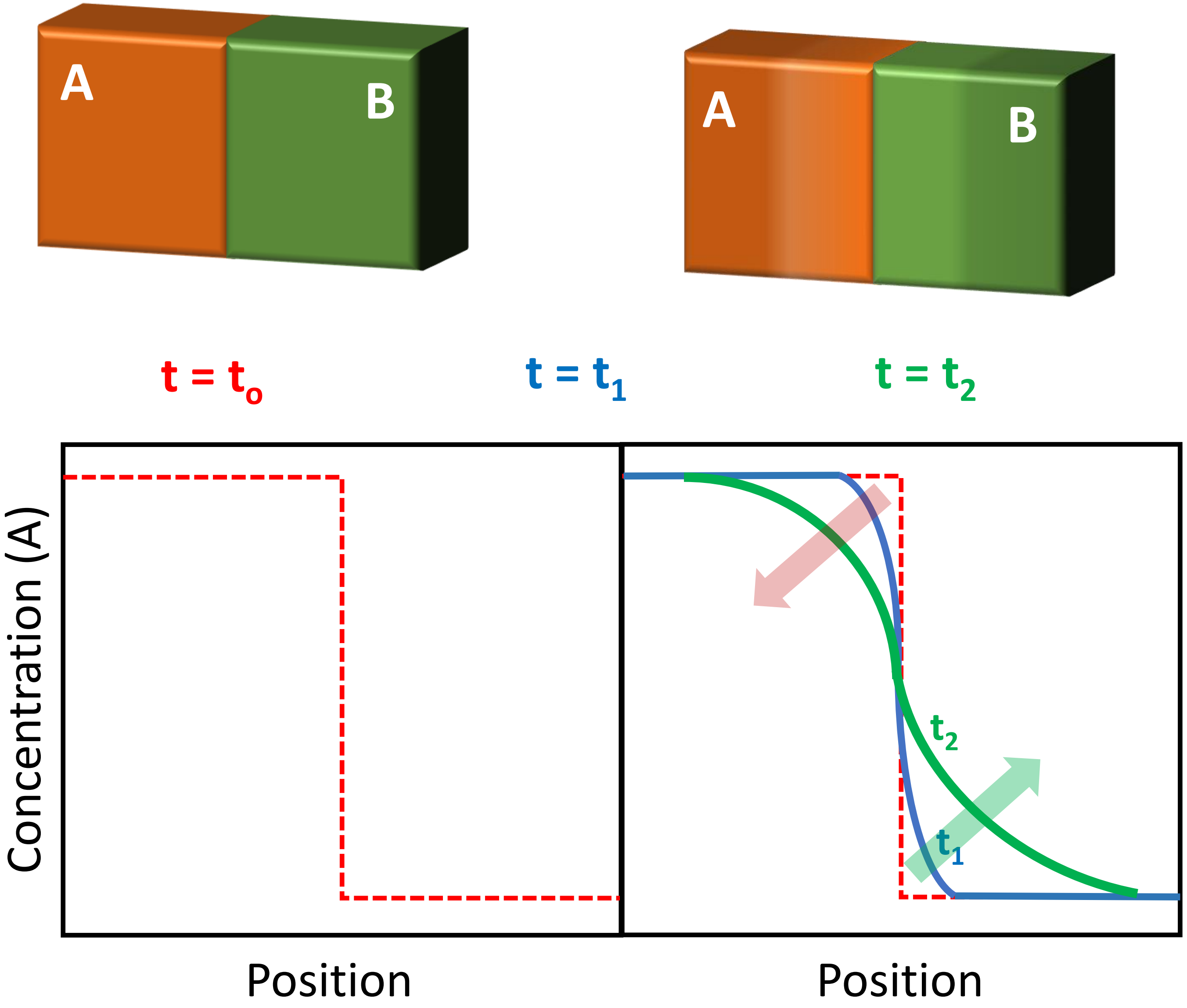

## Steady-state

$$Concentration \neq f\ (time, t)$$

$$\frac{dC}{dx} = constant; \quad \frac{dC}{dt} = 0$$

$J \neq f(x,t)$ *(No accumulation of matter)*

# Fick's second law: *for non-steady state*



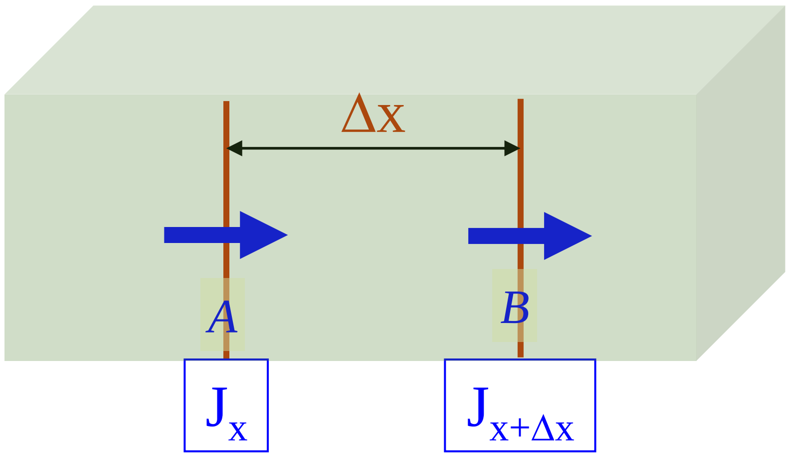

$$Concentration = f\ (position, time)$$

$$\frac{dC}{dx} \neq constant; \quad \frac{dC}{dt} \neq 0$$

$$\frac{dc}{dt} = D\,\frac{d^2c}{dx^2}$$

# Fick's second law

$J_x$ is the flux arriving at plane A and $J_{x+\Delta x}$ is the flux leaving plane B. Then the Accumulation of matter is given by: $(J_x - J_{x+\Delta x})$.




- How many atoms got accumulated in Δx in time Δt?
- (Atoms crossing plane A)-(Atoms crossing plane B) $= (N_x)-(N_{x+\Delta x})$
- Flux, $J = (\text{No. of atoms})/(A.t)$ $= (J_x.A.t)-(J_{x+\Delta x}.A.t)$

$$\left[\left(\frac{Atoms}{m^3}\frac{1}{s}\right).m\right] = \left[\frac{Atoms}{m^2 s}\right] \equiv [J]$$

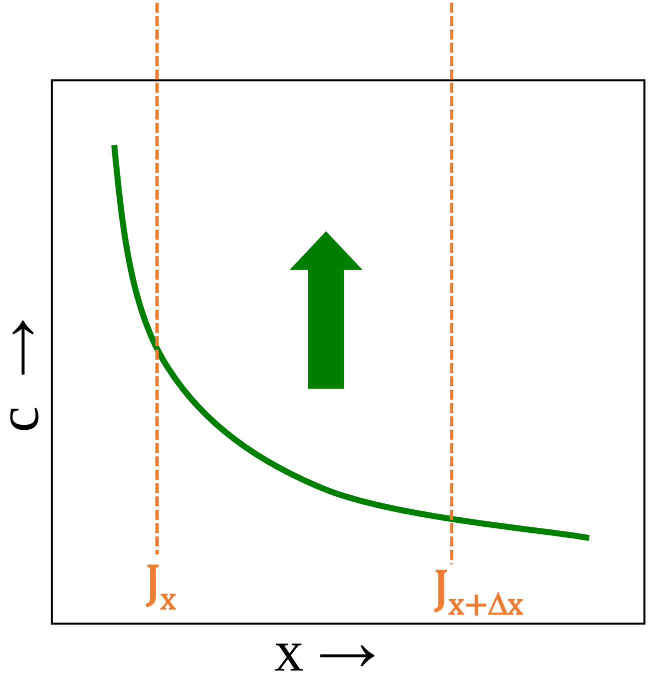
$$(N_x)-(N_{x+\Delta x}) = (J_x-J_{x+\Delta x})\ .A.t$$

$$(\Delta N_x) = (\Delta J_x)\ .A.\Delta t$$

- Concentration, $C = (\text{No. of atoms})/(V)$

$$(\Delta C_x).\ V = (\Delta J_x)\ .A.\ \Delta t$$

$$(\Delta C_x).\ A.\ \Delta\ x = (\Delta J_x)\ .A.\ \Delta t$$



- Rearrangement of terms:

$$\left(\frac{\Delta \mathrm{c_x}}{\Delta \mathrm{t}}\right) = -\frac{\Delta \mathrm{J_x}}{\Delta x}$$

- Applying limits on both the sides of the equation:

$$\lim_{t \to 0}\left(\frac{\Delta \mathrm{c_x}}{\Delta \mathrm{t}}\right) = \lim_{x \to 0}\left(-\frac{\Delta \mathrm{J_x}}{\Delta x}\right)$$

$$\left(\frac{dc}{dt}\right) = -\frac{dJ}{dx}$$

- On substituting the Fick's first law:

$$\left(\frac{\partial c}{\partial t}\right) = -\frac{\partial}{\partial x}\left(-D\frac{\partial c}{\partial x}\right)$$

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

- Assuming that the diffusion coefficient *D* is not a function of location *x* and the concentration (*c*) of diffusing species, a simplified version of Fick's second law as:

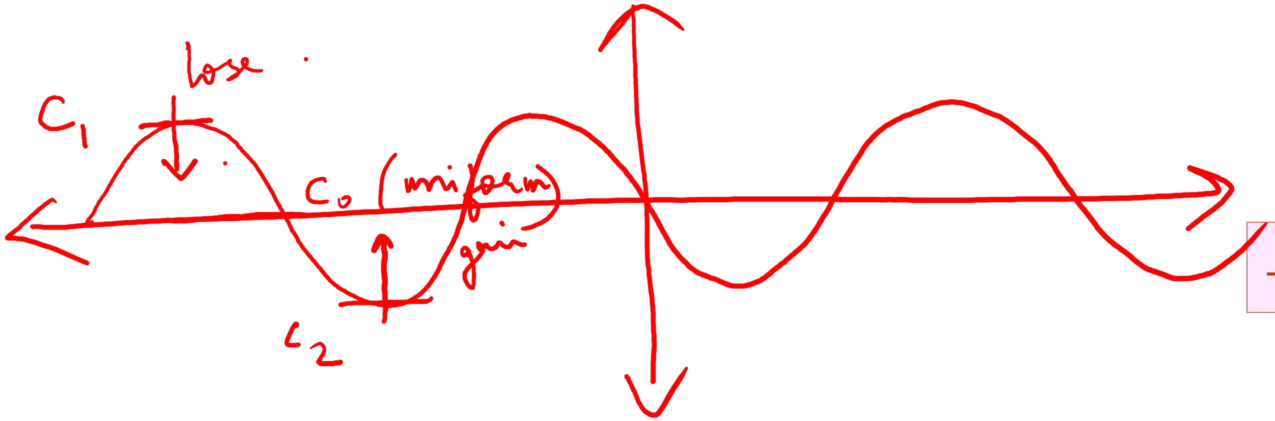
$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

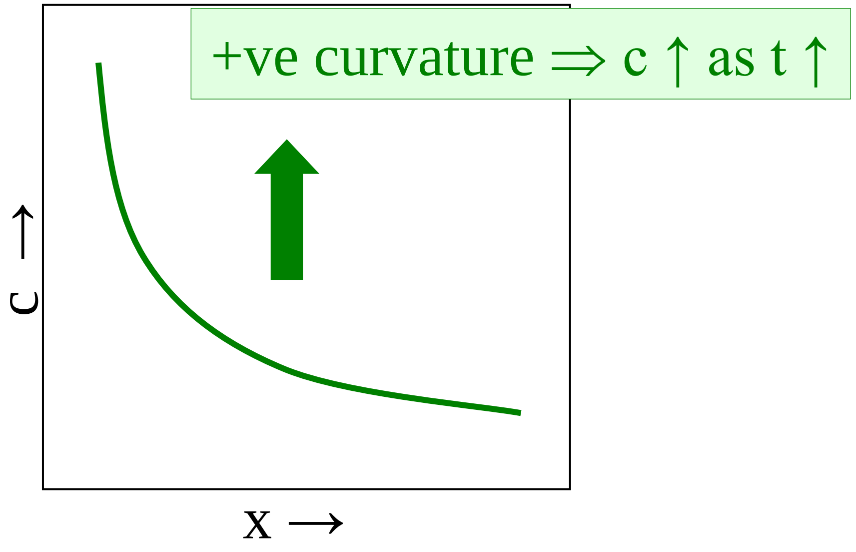
# Homogenization

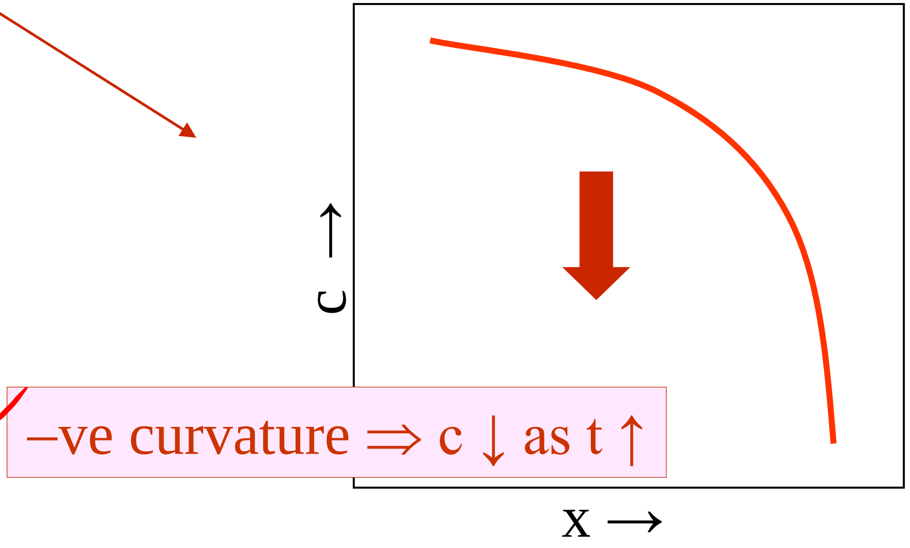
***RHS: Curvature of the c vs x curve***

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

*LHS: change is concentration with time*



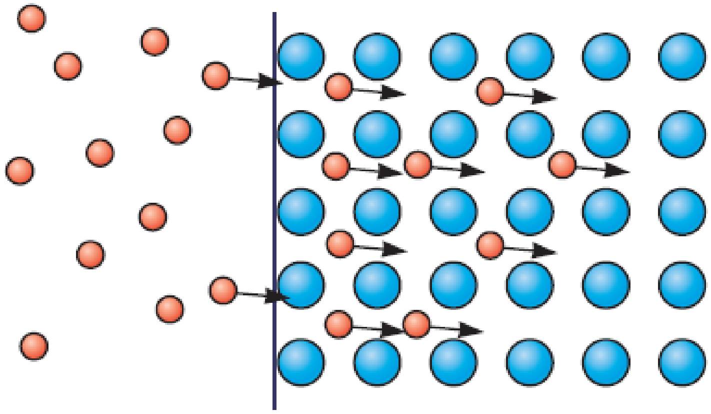
$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2} \rightarrow c(x,t) = A - B\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

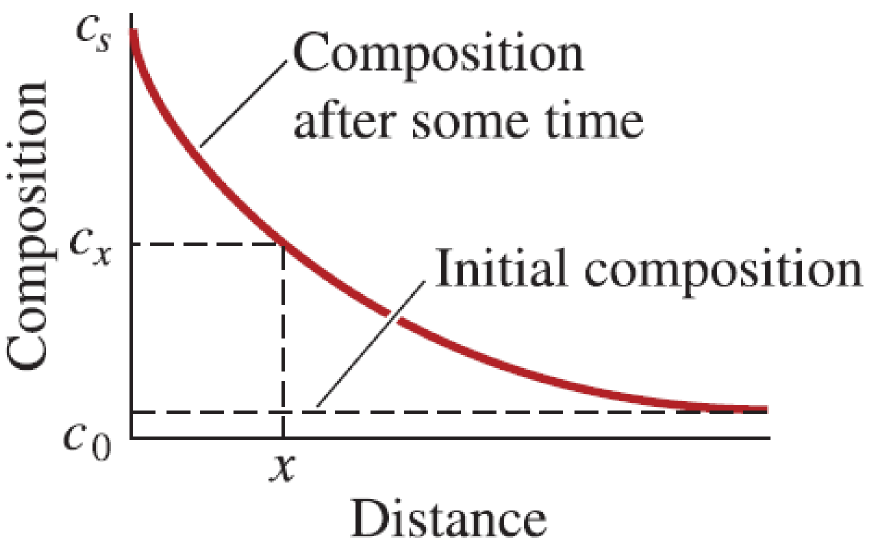
*Solution with 2 constants*
*determined from Boundary Conditions and Initial Condition*

**Tabulation of Error Function Values**

| $z$ | $erf(z)$ | $z$ | $erf(z)$ | $z$ | $erf(z)$ |
|---|---|---|---|---|---|
| 0 | 0 | 0.55 | 0.5633 | 1.3 | 0.9340 |
| 0.025 | 0.0282 | 0.60 | 0.6039 | 1.4 | 0.9523 |
| 0.05 | 0.0564 | 0.65 | 0.6420 | 1.5 | 0.9661 |
| 0.10 | 0.1125 | 0.70 | 0.6778 | 1.6 | 0.9763 |
| 0.15 | 0.1680 | 0.75 | 0.7112 | 1.7 | 0.9838 |
| 0.20 | 0.2227 | 0.80 | 0.7421 | 1.8 | 0.9891 |
| 0.25 | 0.2763 | 0.85 | 0.7707 | 1.9 | 0.9928 |
| 0.30 | 0.3286 | 0.90 | 0.7970 | 2.0 | 0.9953 |
| 0.35 | 0.3794 | 0.95 | 0.8209 | 2.2 | 0.9981 |
| 0.40 | 0.4284 | 1.0 | 0.8427 | 2.4 | 0.9993 |
| 0.45 | 0.4755 | 1.1 | 0.8802 | 2.6 | 0.9998 |
| 0.50 | 0.5205 | 1.2 | 0.9103 | 2.8 | 0.9999 |

- $erf(\infty) = 1$
- $erf(-\infty) = -1$
- $erf(0) = 0$
- $erf(-x) = -erf(x)$



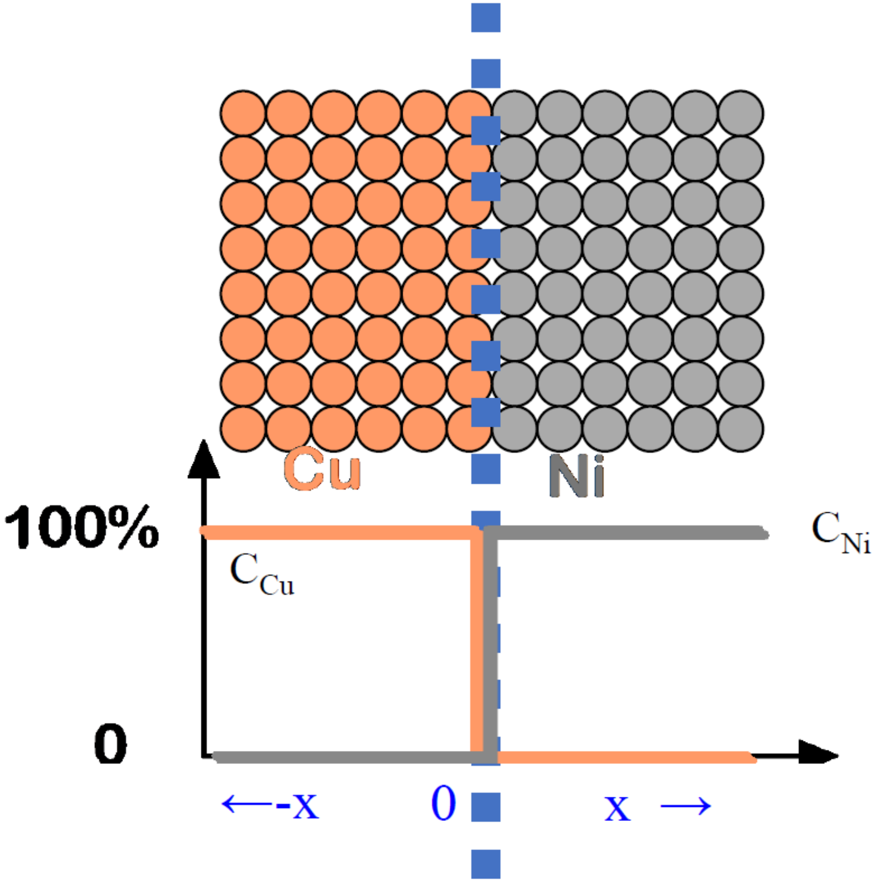



- Solution to the equation depends on the boundary conditions for a particular situation

$$\frac{c_s - c_x}{c_s - c_0} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$c_s$: a constant concentration of the diffusing atoms at the surface of the material,
$c_0$: initial uniform concentration of the diffusing atoms in the material
$c_x$: concentration of the diffusing atom at location $x$ below the surface after time $t$.

# Calculating values of A and B




- $c(+x, t=0) = C_{Ni}$
- $c(-x, t=0) = C_{Cu}$

- *$Erf(\infty) = 1$*
- *$Erf(-\infty) = -1$*
- *$Erf(0) = 0$*
- *$Erf(-\gamma) = -Erf(\gamma)$*

$$c(x,t) = A - B\ erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

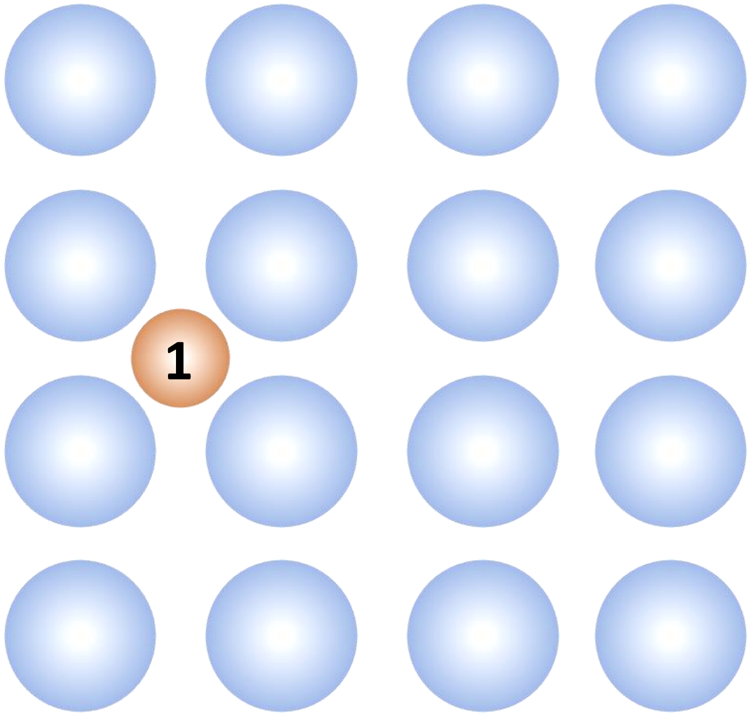
- *Substituting these values and erf values*

- $C_{Ni} = A - B\ erf(\infty) = A\text{-}B$

- $C_{Cu} = A - B\ erf(-\infty) = A+B$

$A = (C_{Ni} + C_{Cu})/2$
$B = (C_{Cu} - C_{Ni})/2$

# How does ‘temperature’ influence atomic movement?




Highly Temperature Dependent

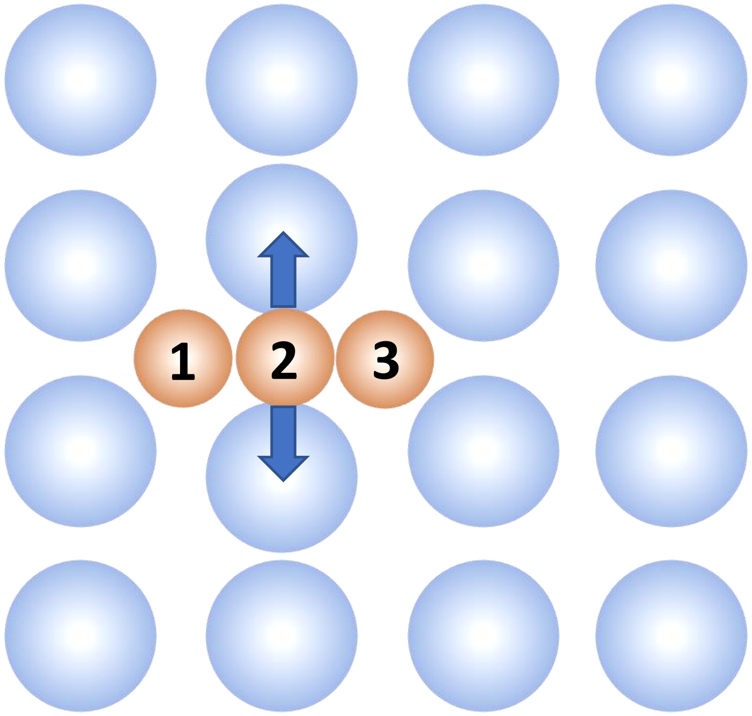
$$D = D_0 exp\left(-\frac{Q}{RT}\right)$$

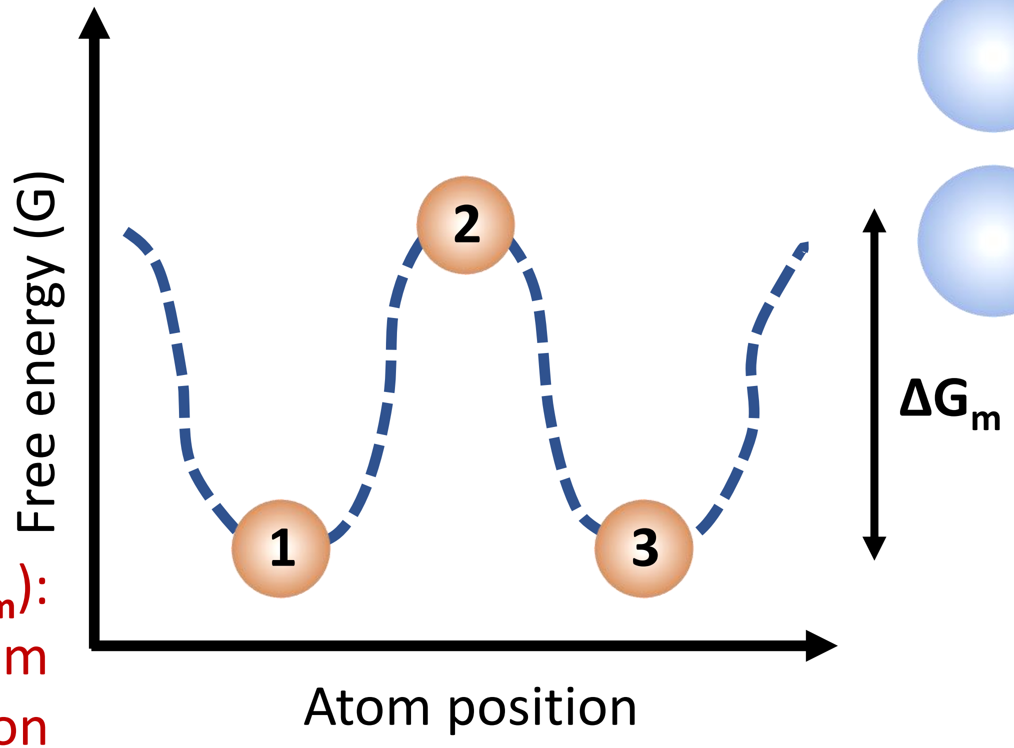
Activation Energy

Pre-exponential Factor

Gas constant

Absolute temperature




Activation energy barrier ($\Delta G_m$): Difference in energy of the atom before its jump and at its position halfway.

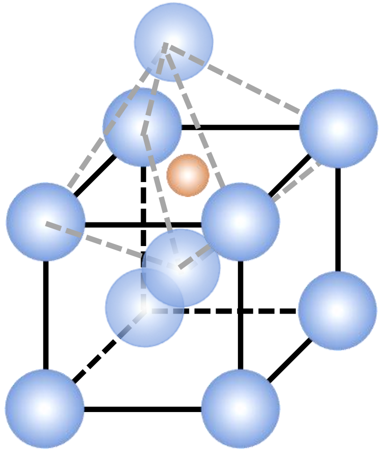
# How does an atom diffuse in a solid?

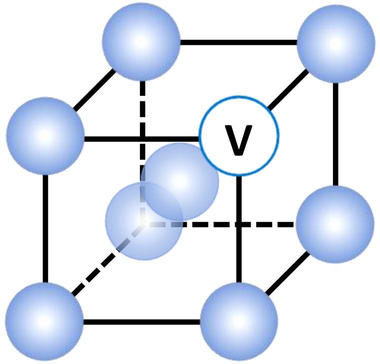
**Crystal structure**

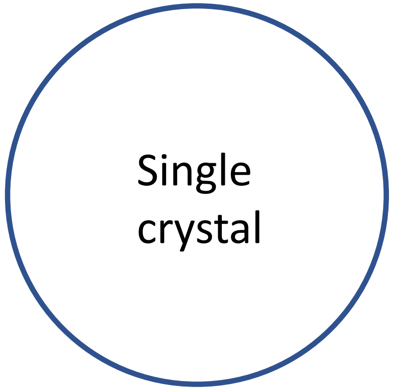
- Interstitial
- Substitutional
  - ➲ Vacancy

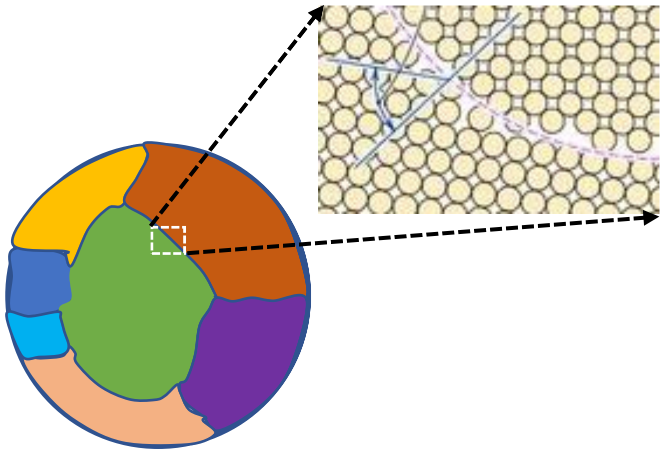
**Grain structure**

- Lattice
- Grain boundary





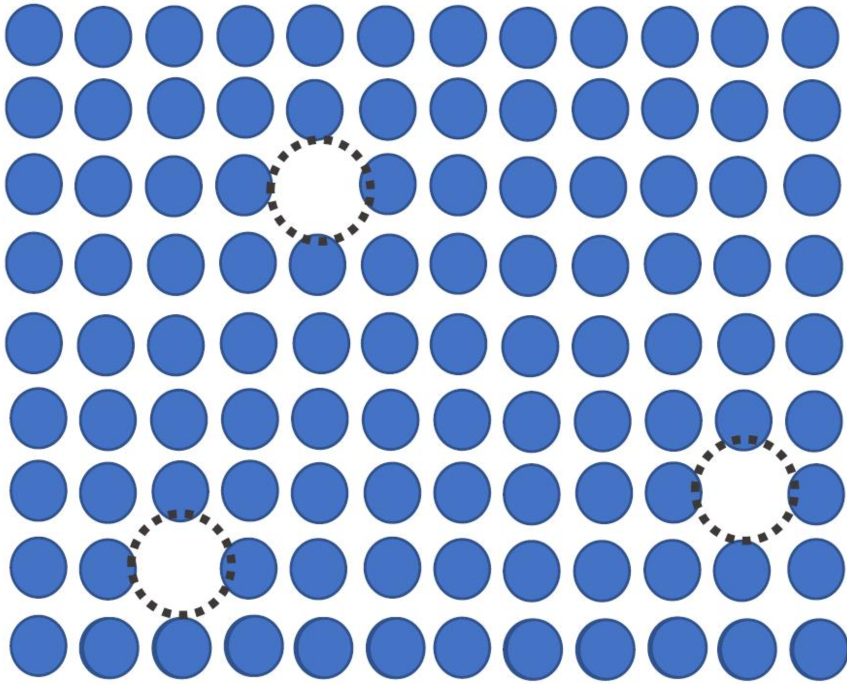



# Vacancy diffusion requires high content of vacancies

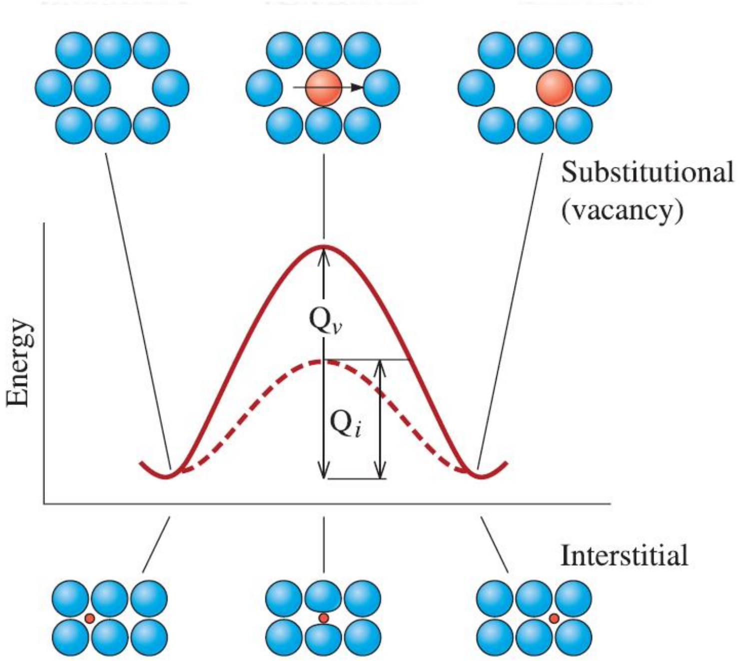
*Probability for an atomic jump* $\propto$

*(probability that the atom has sufficient energy)*

$\times$*(probability that the nearby site is vacant)*



$$D_{sub} = p\delta^2\vartheta \boxed{exp\left(-\frac{\Delta H_m}{RT}\right)} \boxed{exp\left(-\frac{\Delta H_f}{RT}\right)}$$




$$Q_{vacancy} = \Delta H_m + \Delta H_f$$

$$Q_{interstitial} = \Delta H_m$$

$$Q_{vacancy} > Q_{interstitia}$$