MLL 100

Introduction to Materials Science and Engineering

Lecture-19 (February 23, 2022)

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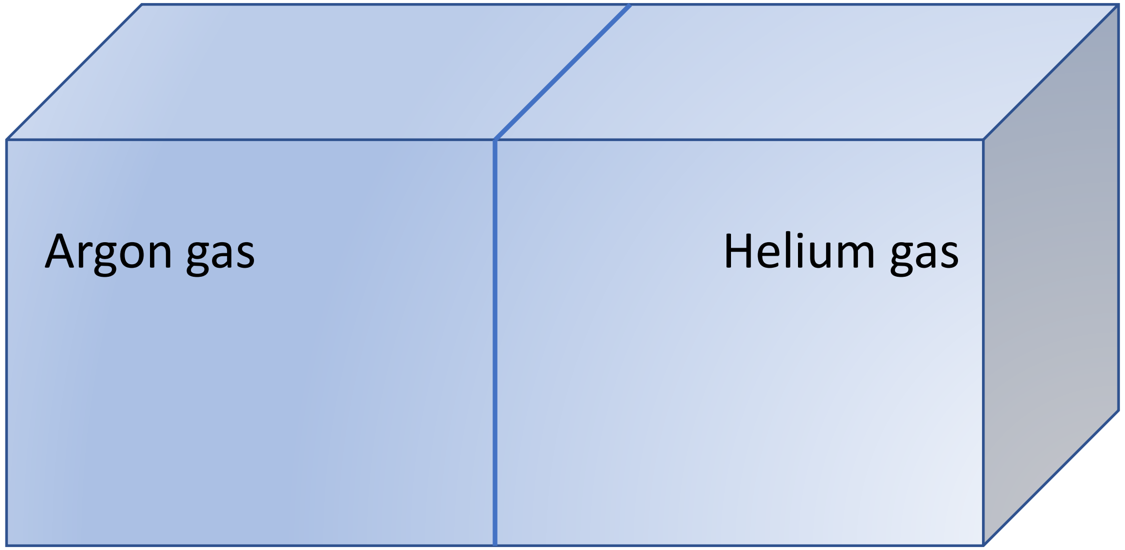
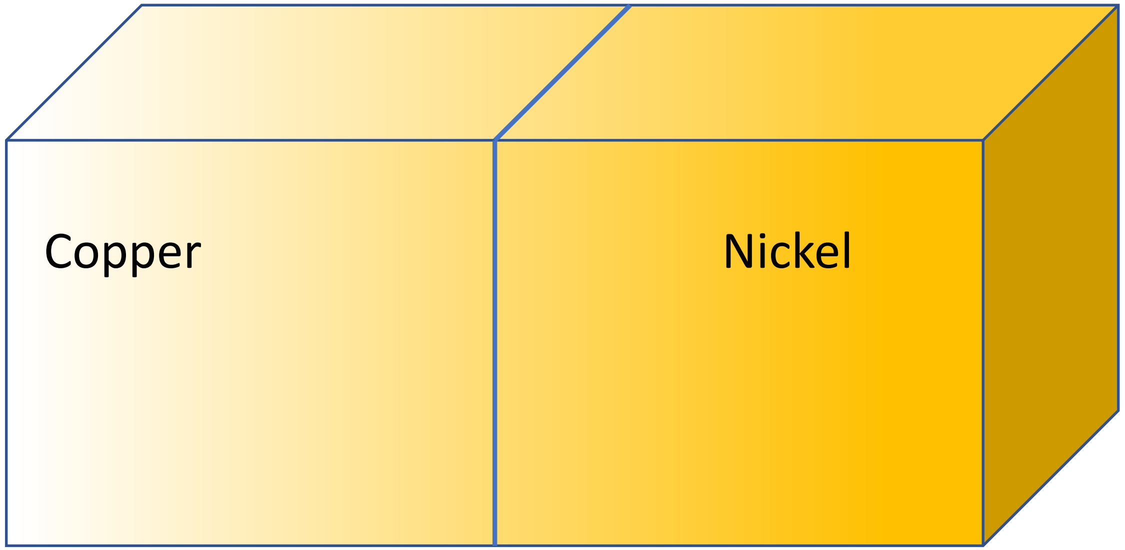
What have we learnt in Lecture-18?

- TTT diagram (Transformation-temperature-time)
- Avrami equation
- Bainite, Martensite
- Different kinds of cooling rates: Annealing, Normalizing, Austempering, Quenching

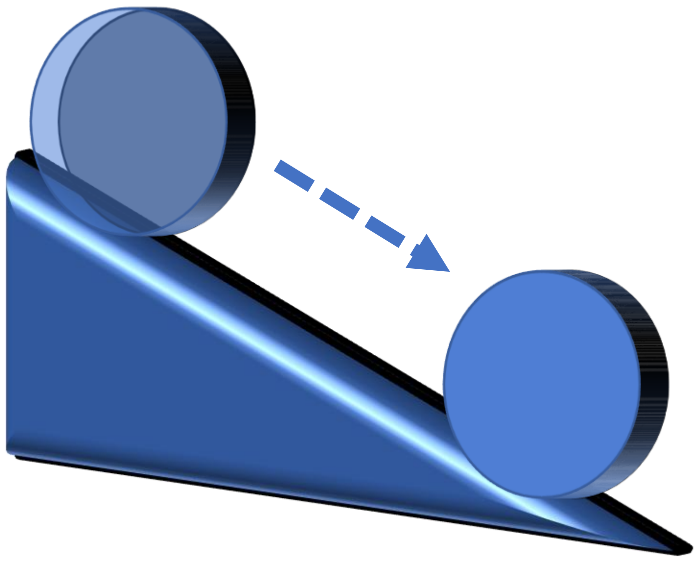
Imagine a chamber with a partition in the middle. Either side of the partition contains two different gases, Argon and Helium. What happens if the partition gets removed?

In the second case, consider two single solid crystals, copper and nickel. What happens after the removal of partition?

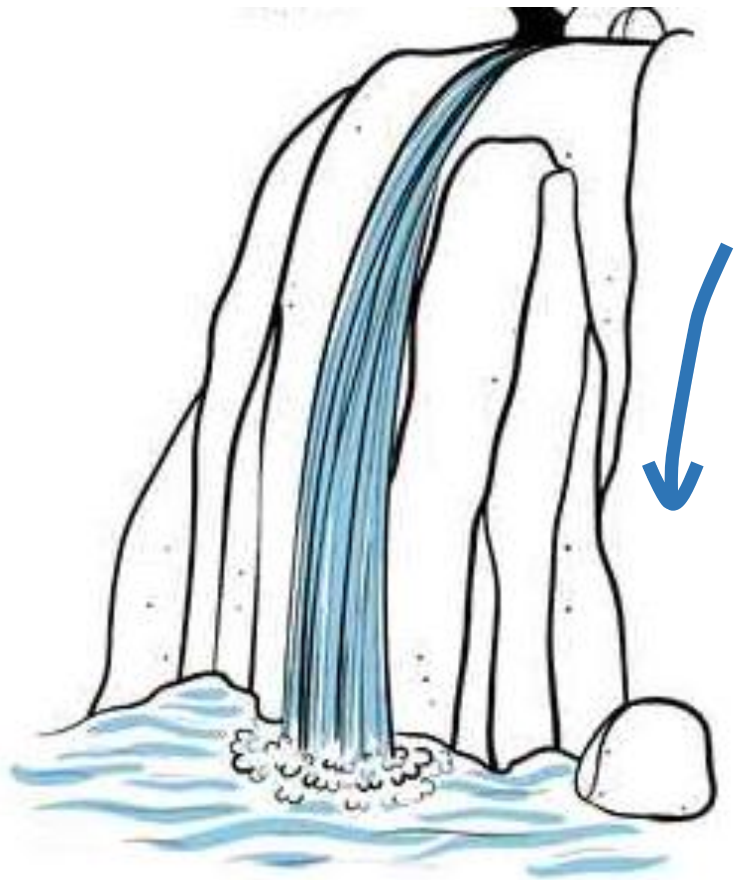




Diffusion



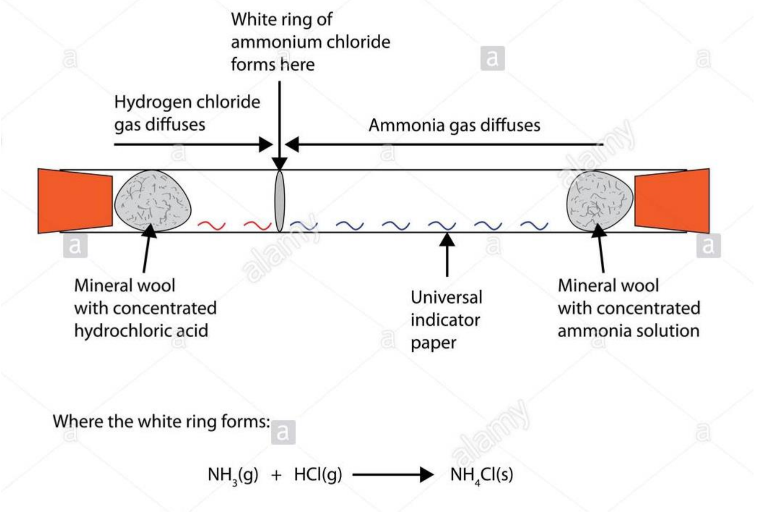
Disc rolling down the slope

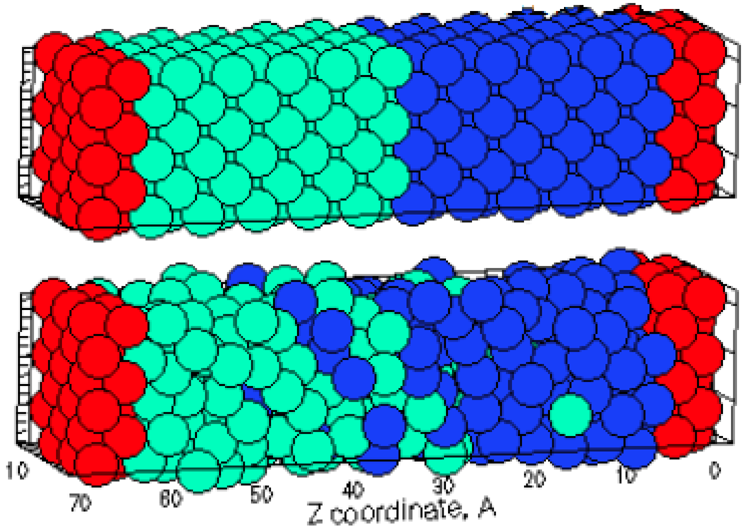


Water falling down the hill slope

What is diffusion?

- Flow of atoms under the influence of a gradient, i.e. from a higher potential region to a lower potential region.





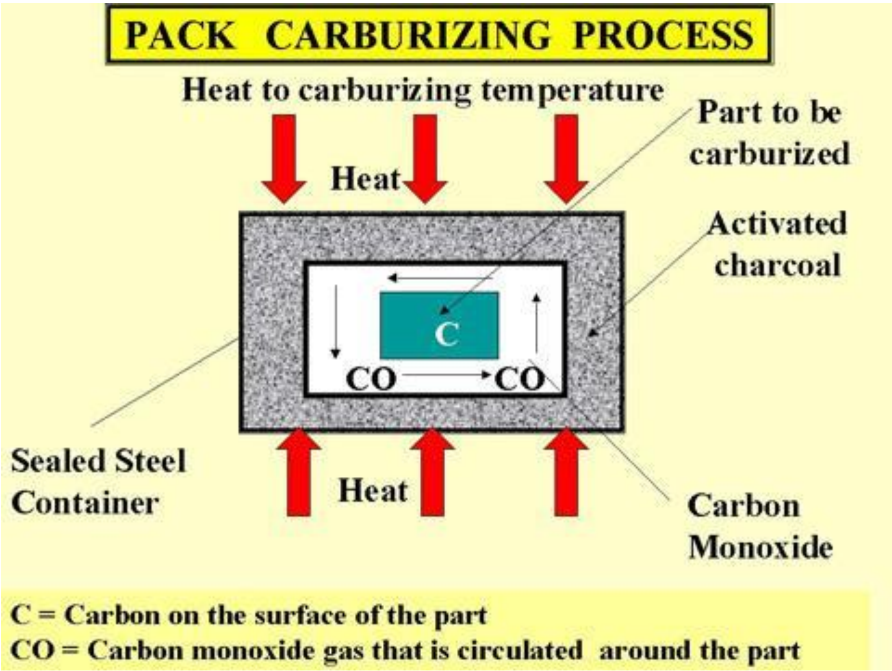
Gas: Diffusion of ammonia

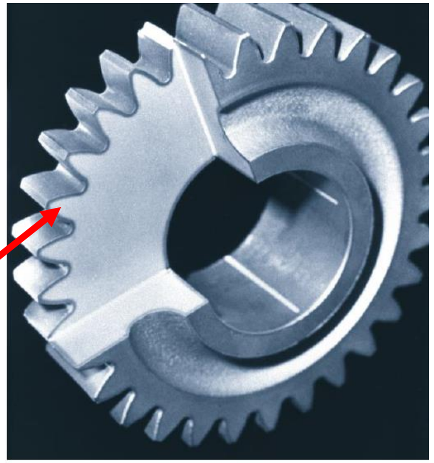
Liquid: Diffusion of ink in water

Solid: Diffusion of atoms in copper and brass

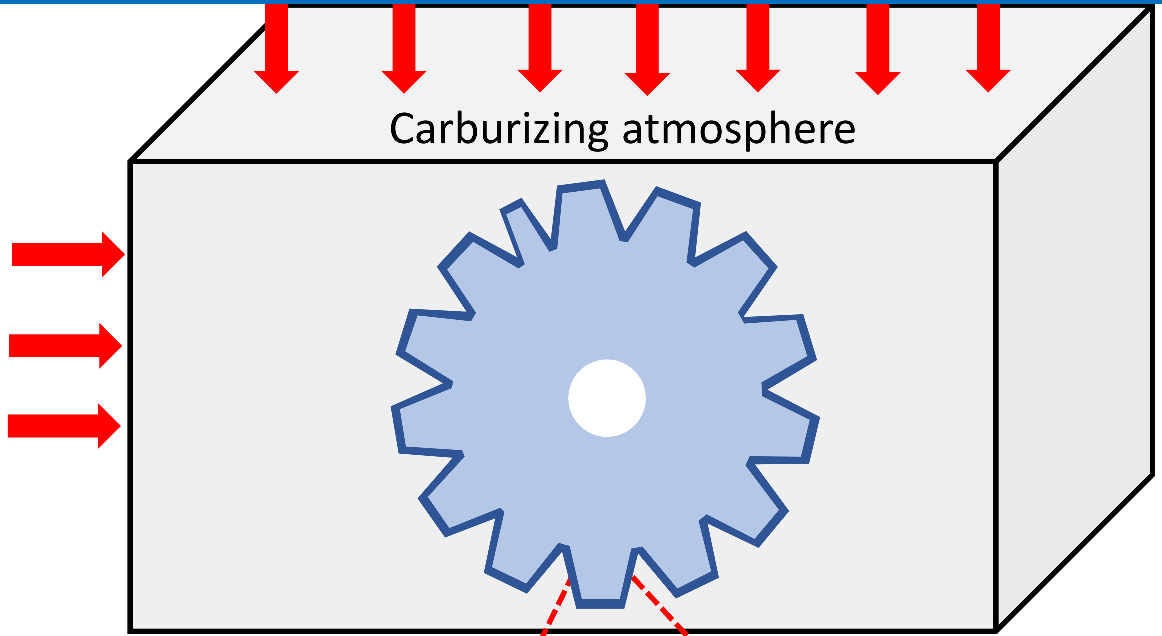
Diffusion in solids occur very slowly compared to those in liquids and gases, and also, is very restricted.

How was diffusion exploited to engineer gears?

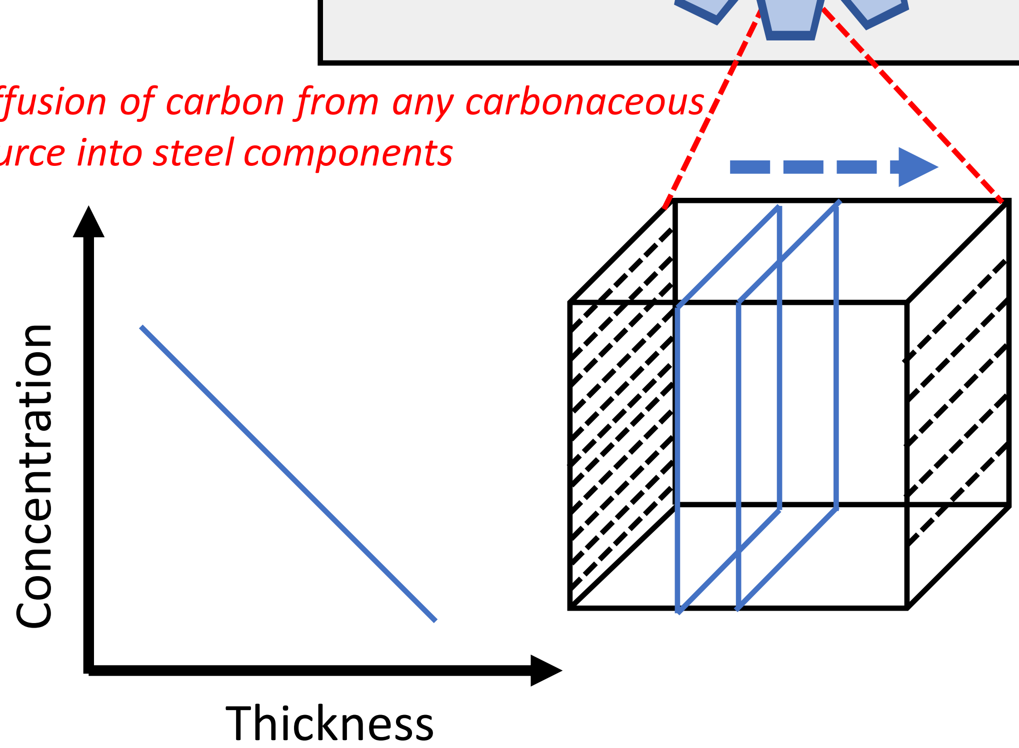




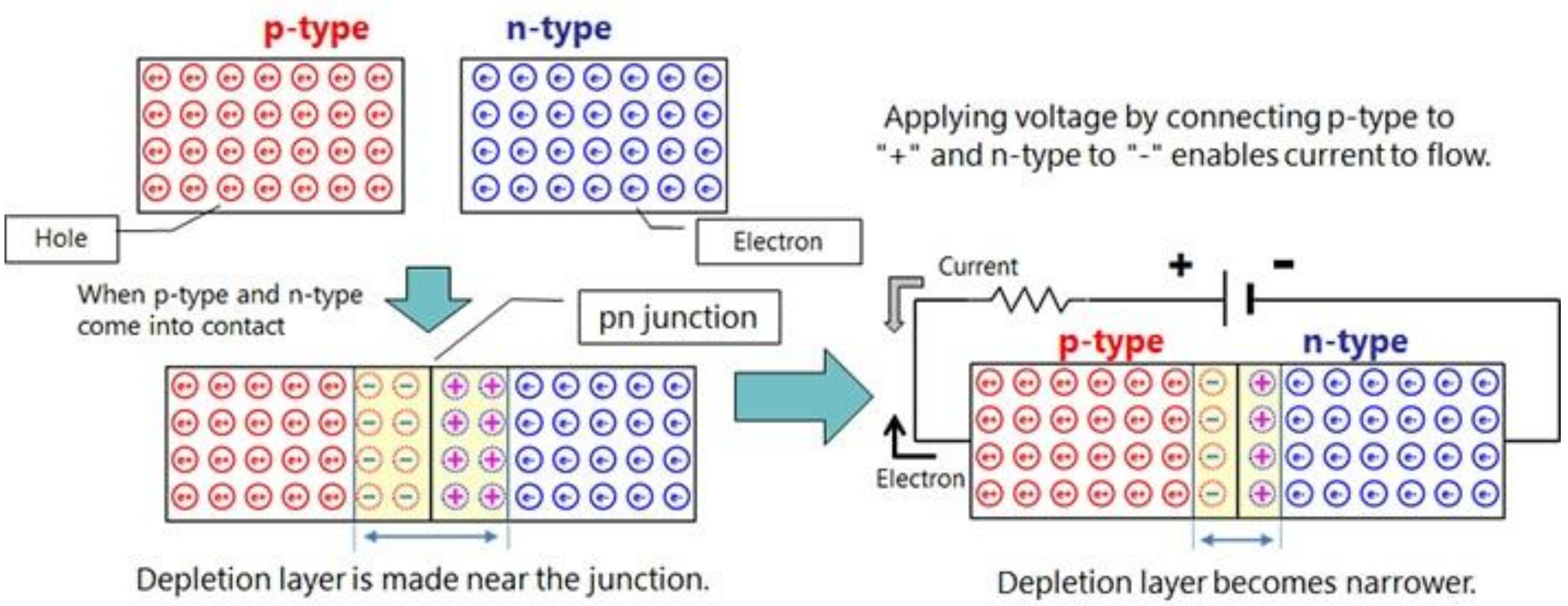
Hardening of teeth of gears



Diffusion of carbon from any carbonaceous source into steel components

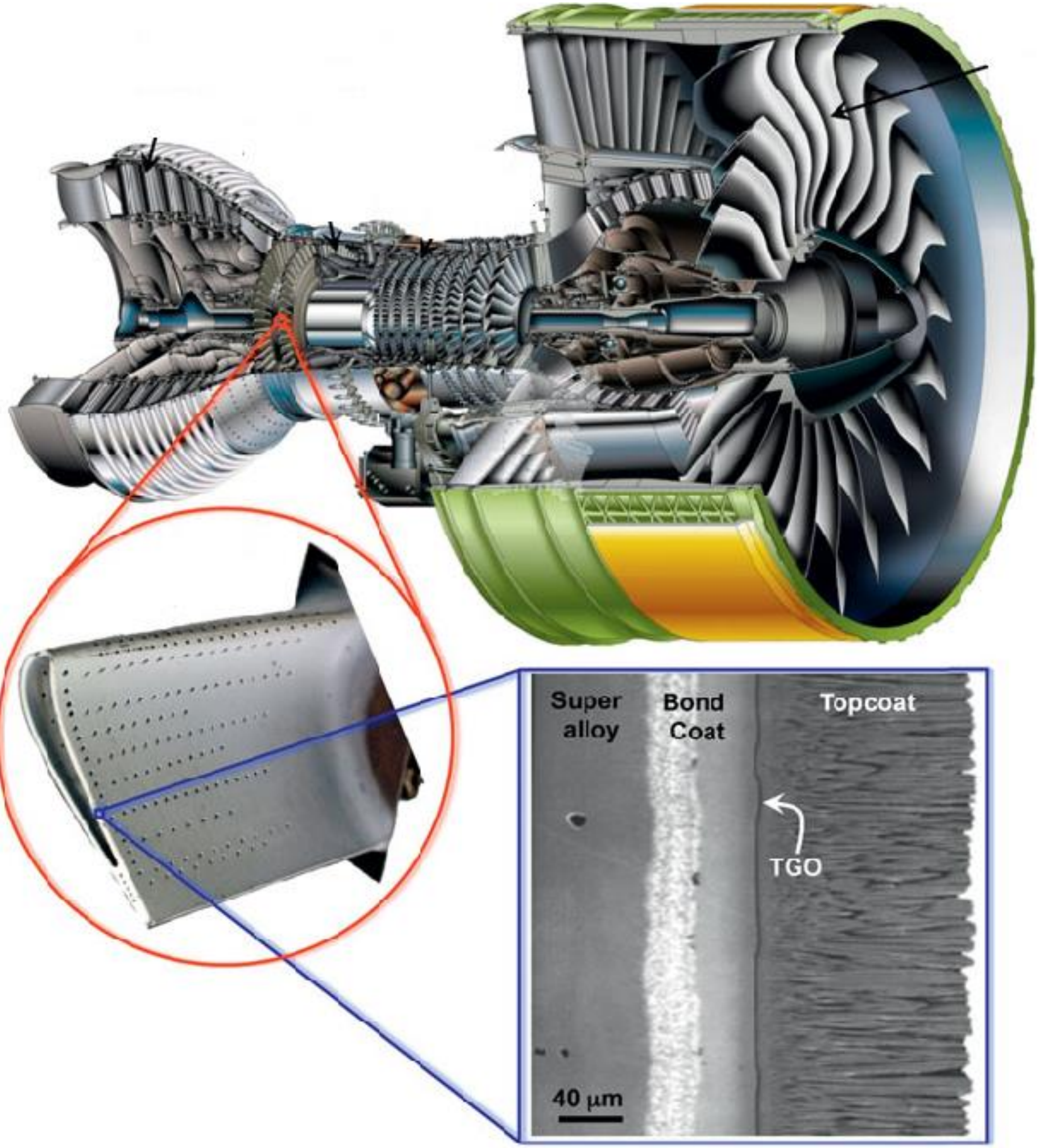


Diffusion in semiconductor applications



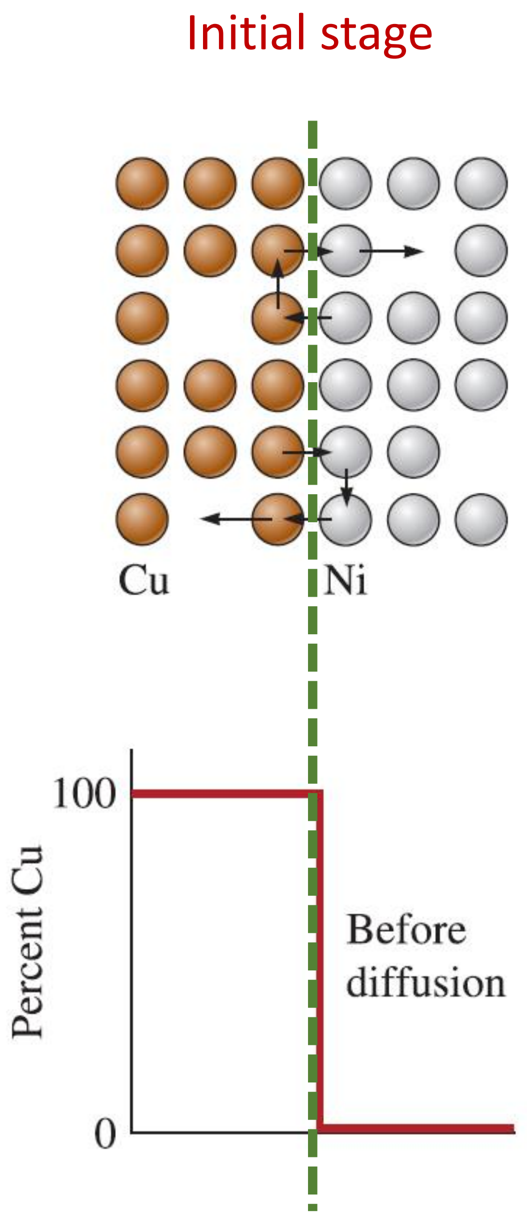
Aircraft engine

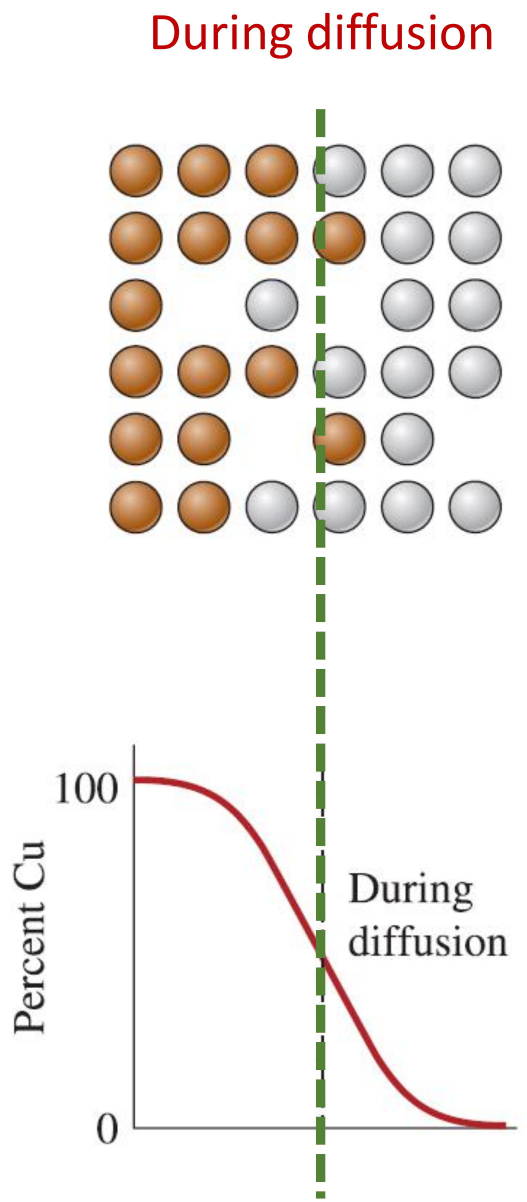
Turbine blade

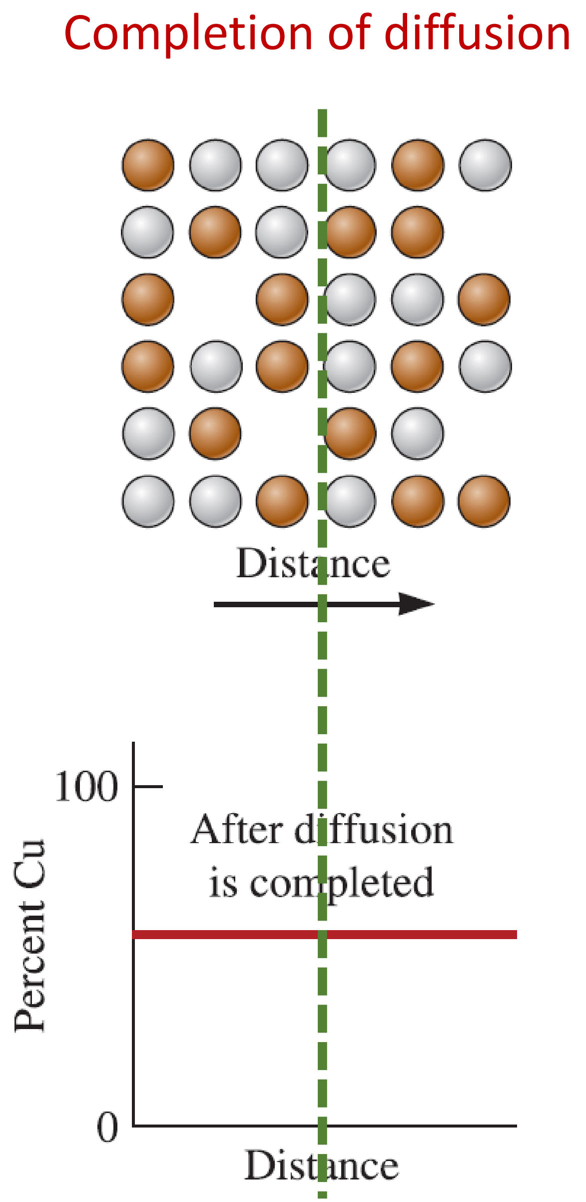


Clarke et al., *MRS Bulletin* 37 (2012)

How was the study of diffusion started off?





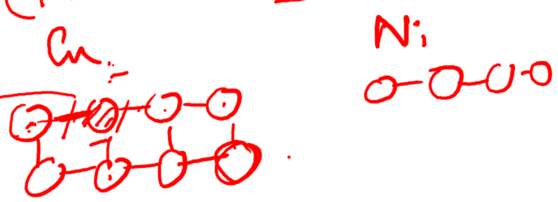


What drives diffusion?

- Temperature and a chemical potential gradient.
- Thermal energy ------> Atomic vibrations in lattice ------> Atomic jumps
- Gradient: Chemical potential *(What about the concentration gradient??)*

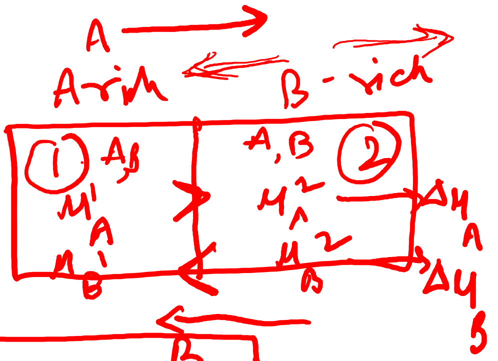
enthalpy (Heat content)

∝ Bond energy



T

entropy (Randomness)



Gibbs free energy (Minimized)

$$\boxed{\Delta G = +\Delta H - T\Delta S}$$

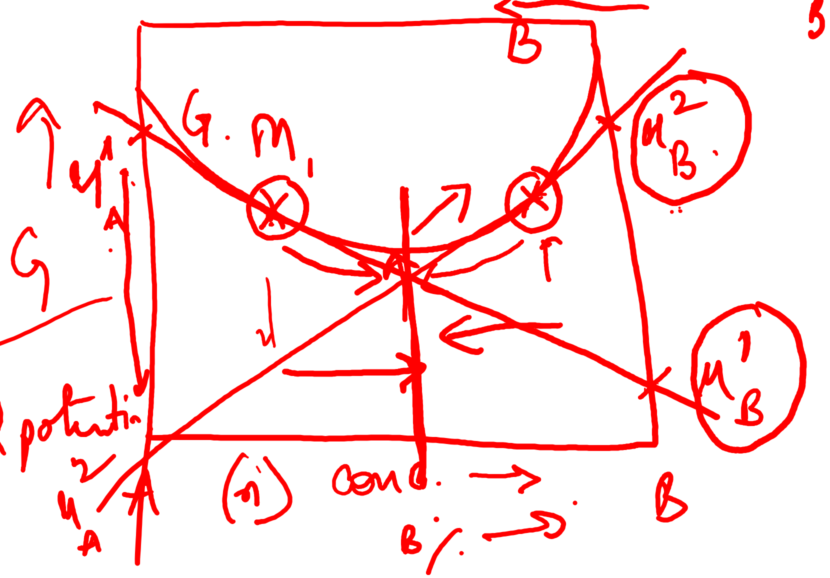
enthalpy

entropy

$$\frac{dG}{dn} = \mu$$

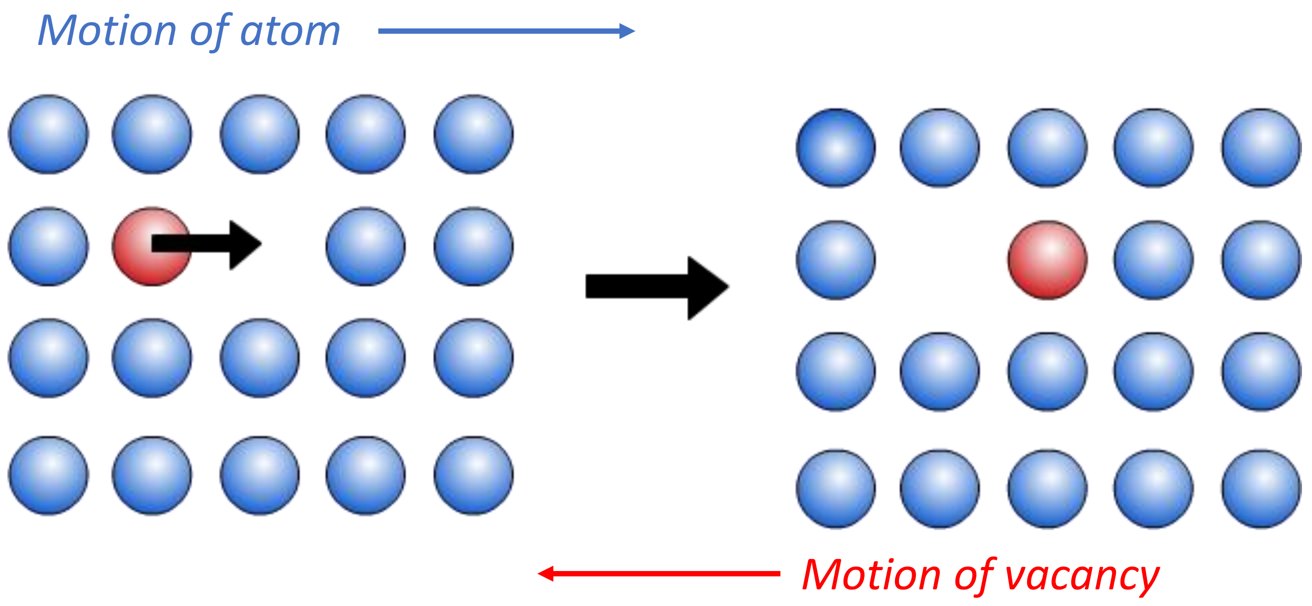
Chemical potential gradient

Chemical potential

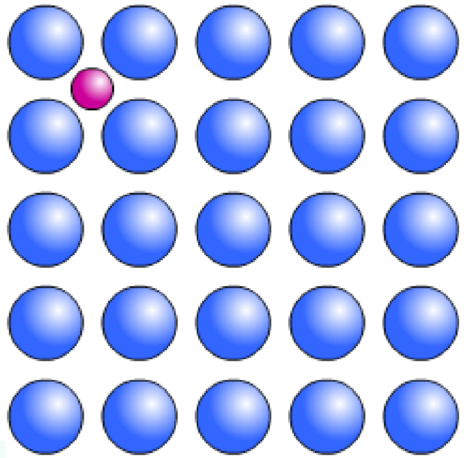


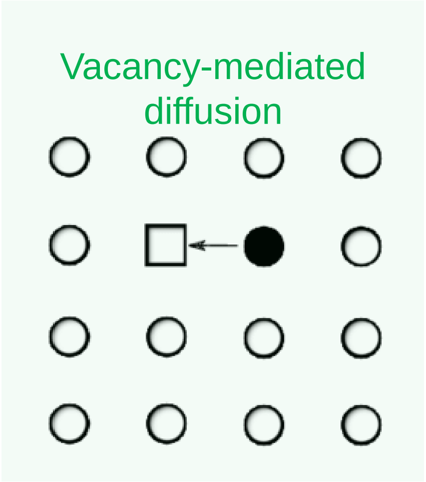
How does diffusion occur in a solid?

Substitutional diffusion



Interstitial diffusion





- ❑ Diffusion of an atom via vacancy depends on two factors:
  - How easily vacancies can form in the lattice?
  - How easy it is for an atom to move into a vacancy?

- ❑ The dependence upon the presence of vacancies makes substitutional diffusion slower than interstitial diffusion.

Defects (Imperfections) in crystalline solid

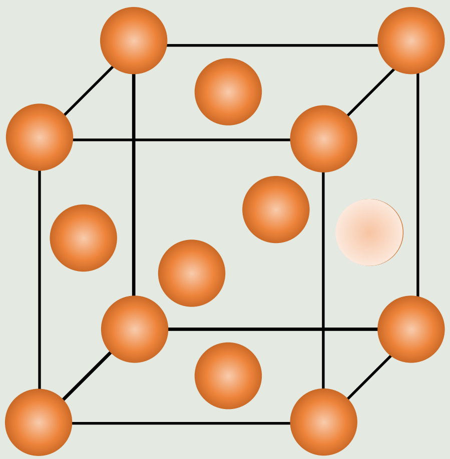
Disruption in the regular arrangement of internal constituents of a solid.

Classification based on: *(i) Dimensionality, (ii) Thermodynamics, (iii) Sources*

Equilibrium defects
(Decreases free energy of the system)

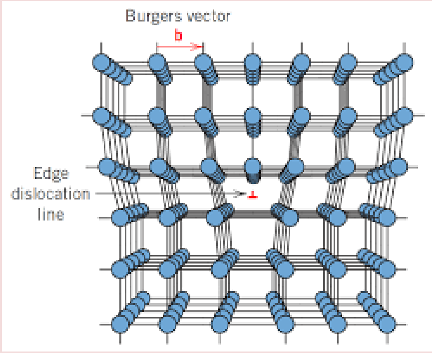
Non-equilibrium defects
(Increases free energy of the system)

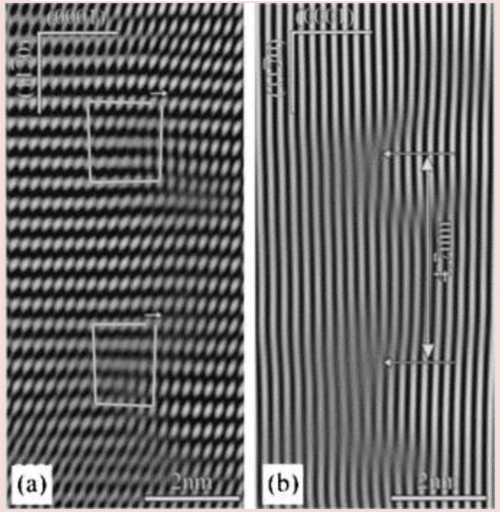
0-D: Point defect



- Vacancies
- Self-interstitials

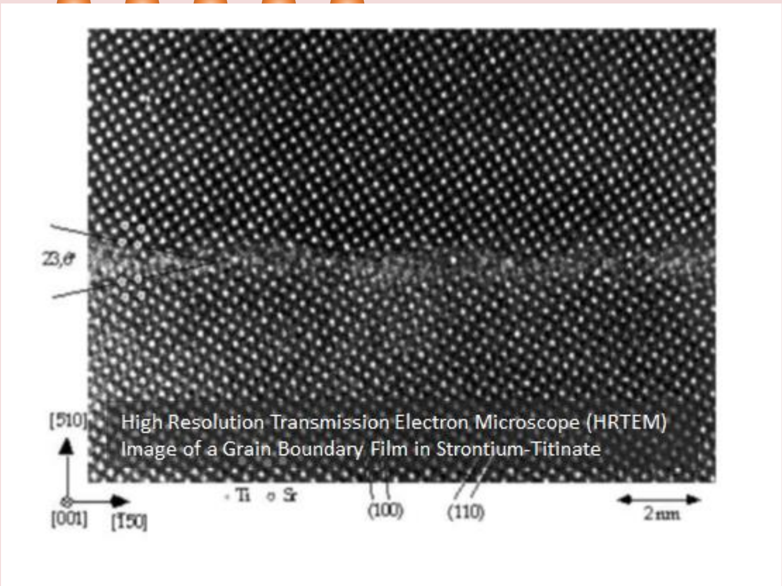
1-D: Line defect





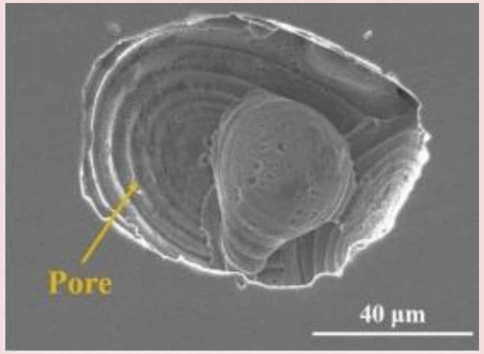
- Dislocations

2-D: Planar defect



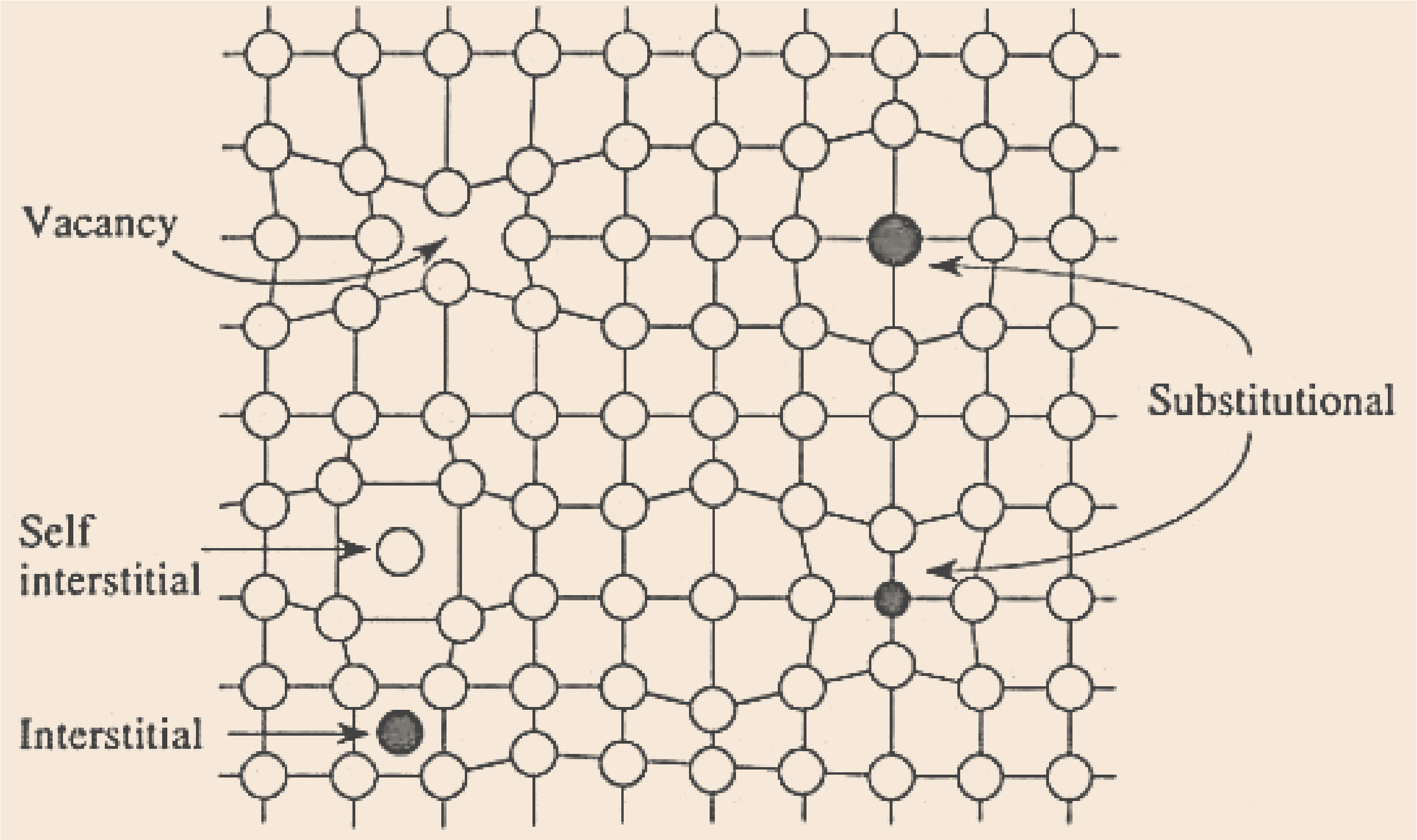
- Grain boundaries
- Interfaces

3-D: Volumetric defect



- Voids
- Precipitates

Point Defects in crystalline solid



1. Vacancy

   (Entity missing from regular lattice site)

2. Self-interstitial

   (Lattice atoms present at interstitial sites)

3. Substitutional solute

   (Foreign atoms occupying regular lattice site)

4. Interstitial solute

   (Foreign atoms typically with a size much smaller than the regular atoms occupying the interstitial sites)

Why a vacancy is thermodynamically stable defect?

Stability of a system at a constant pressure:

$$G = H - T.S$$

Let's assume that a system at state '1' has a free energy of 'G_1' and 'G_2' at state '2':

$$G_1 = H_1 - T.S_1$$

$$G_2 = H_2 - T.S_2$$

The system would like to attain state '2' only if:

$$\Delta G = \Delta H - T.\Delta S$$

Change in 'Free Energy'

(Energy which is available/free to do work or to transform from one phase to another)

Enthalpy change (Heat content)

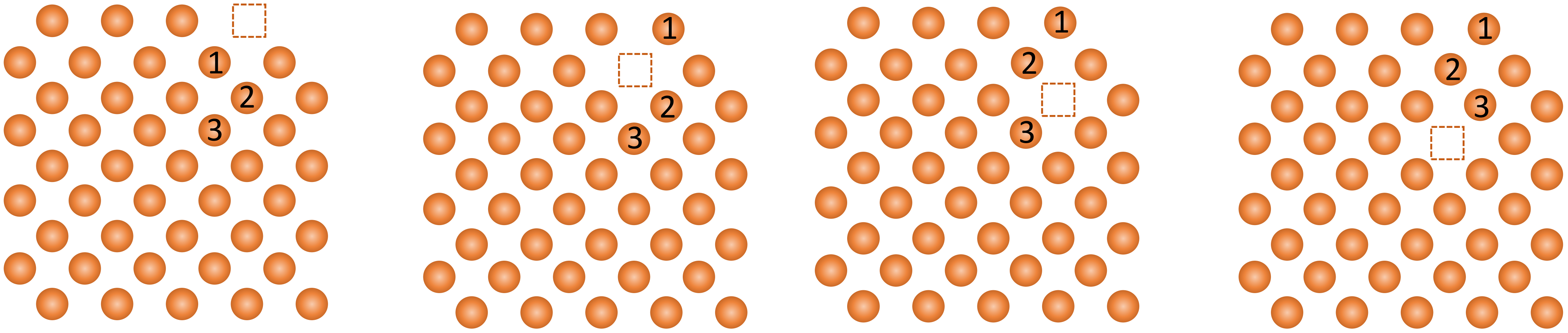
Entropy change (Randomness)

Perfect crystal

Remove balls from random positions (vacancies)

Remove balls from a line (dislocations)

Formation of a vacancy

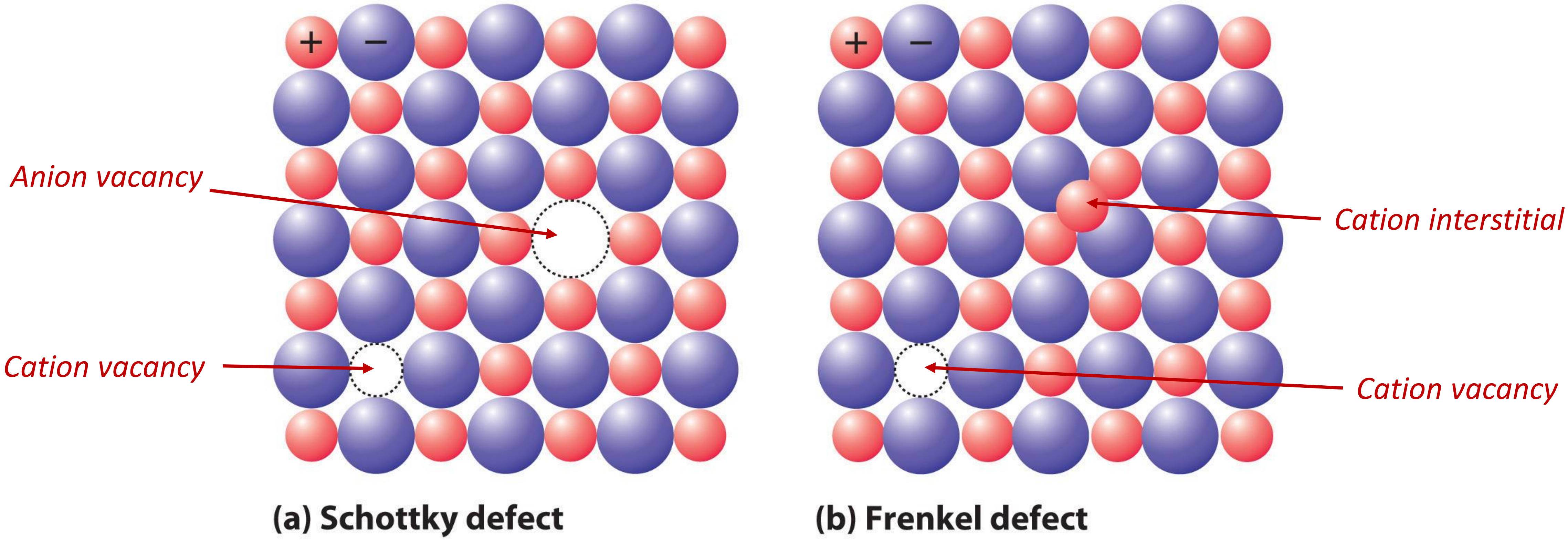


- When atoms diffuse from the interior of a crystal to the free surface, thermal vacancies get created.
- Bonds are broken because of the creation of vacancies → Increase in enthalpy, (+ve H_v) → Unfavourable for the system.
- Increase in entropy → irregular vibration of atoms surrounding the vacancies and entropy of mixing (configurational entropy), i.e., different possibilities of mixing arrangements of components and vacancies.

Point defects in ionic solids

Defects in semiconductors:

(i) Intrinsic defects (Present in a pure material at equilibrium)
(ii) Extrinsic defects (Defects resulting because of doping/alloying)



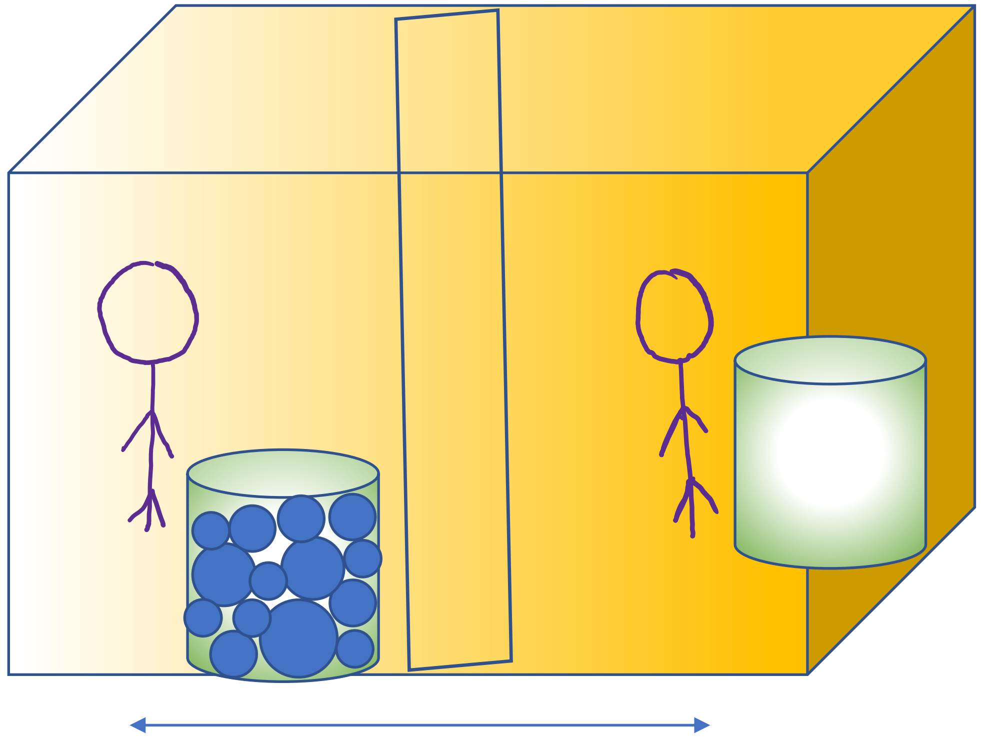
Creation of a vacancy in an ionic solid: Charge neutrality ----> anion vacancy + cation vacancy (Schottky defect)

----> Cation vacancy + interstitial (Frenkel defect)

Laws of diffusion

- ☞ Fick's first law of diffusion *(Empirical law)*

- ☞ Fick's second law of diffusion *(First Law + Mass balance)*



- Area of window (A) ↑
- Distance between two persons (x) ↓
- Time (t) ↑
- No. of balls (B) ↑

$$\text{Number of balls reaching to your friend} \propto \frac{(B_1 - B_2).A.t}{\Delta x}$$

$$\frac{(\text{Number of balls reaching to your friend})}{A.t} \propto \frac{(B_1 - B_2)}{\Delta x}$$

$$\frac{(\text{Number of balls reaching to your friend})}{A.t} = (property\ of\ a\ ball).\frac{(B_1 - B_2)}{\Delta x}$$