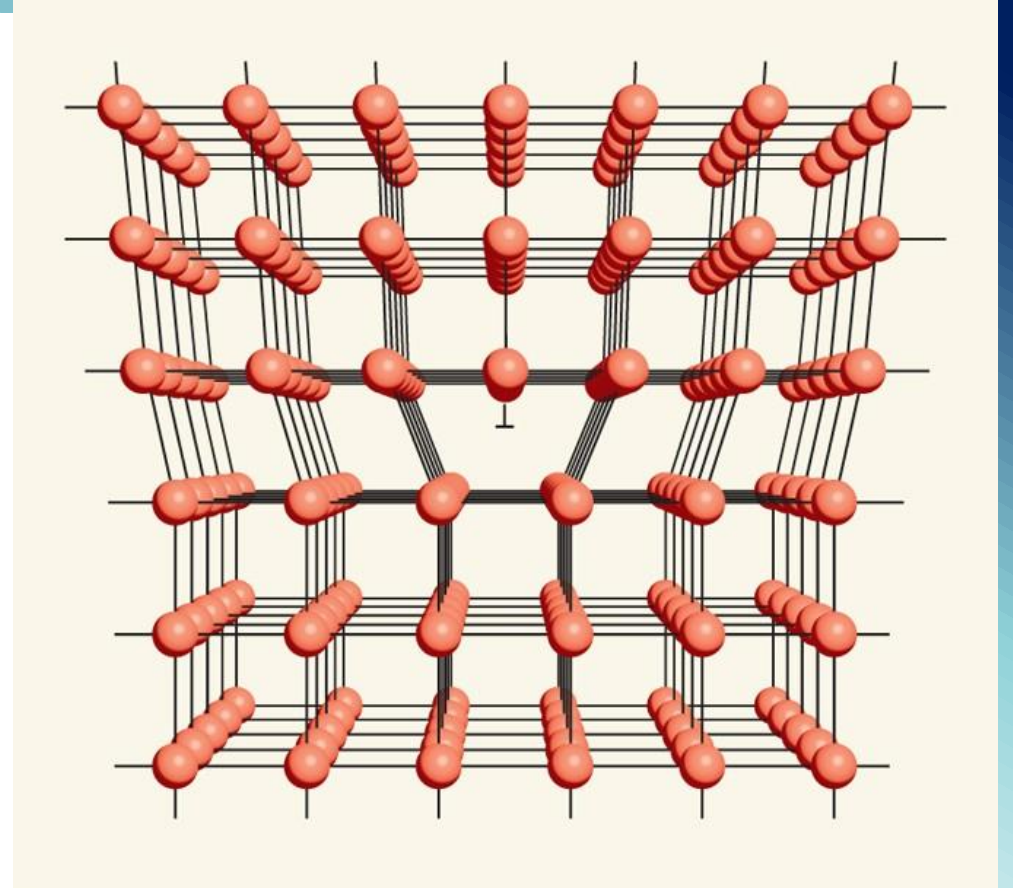


Imperfections in the Atomic Structure & Diffusion

Mohamed Hassan Khalili

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Imperfections in the Atomic Structure & Diffusion

Learning Objectives

- + Describe the various point defects in crystalline.
- + Explain how grain boundaries strengthen polycrystalline materials.
- + Explain the role of grain size in strengthening polycrystalline materials.
- + Explain the process of work hardening and its effects on the strength of crystalline materials.
- + Describe the driving forces for diffusion in solids.
- + Calculate the number of vacancies in a solid and the diffusion coefficient using an Arrhenius relationship.
- + Explain the mechanisms of diffusion in solids.
- + First and second Fick's Law

Imperfections in the Atomic Structure & Diffusion

Outline

+ Crystal Defects

Point Defects

Line Defects

Surface Defects

+ Importance of Defects

+ Applications of Diffusion

What is diffusion?

Engineering applications of diffusion

+ Mechanisms for Diffusion

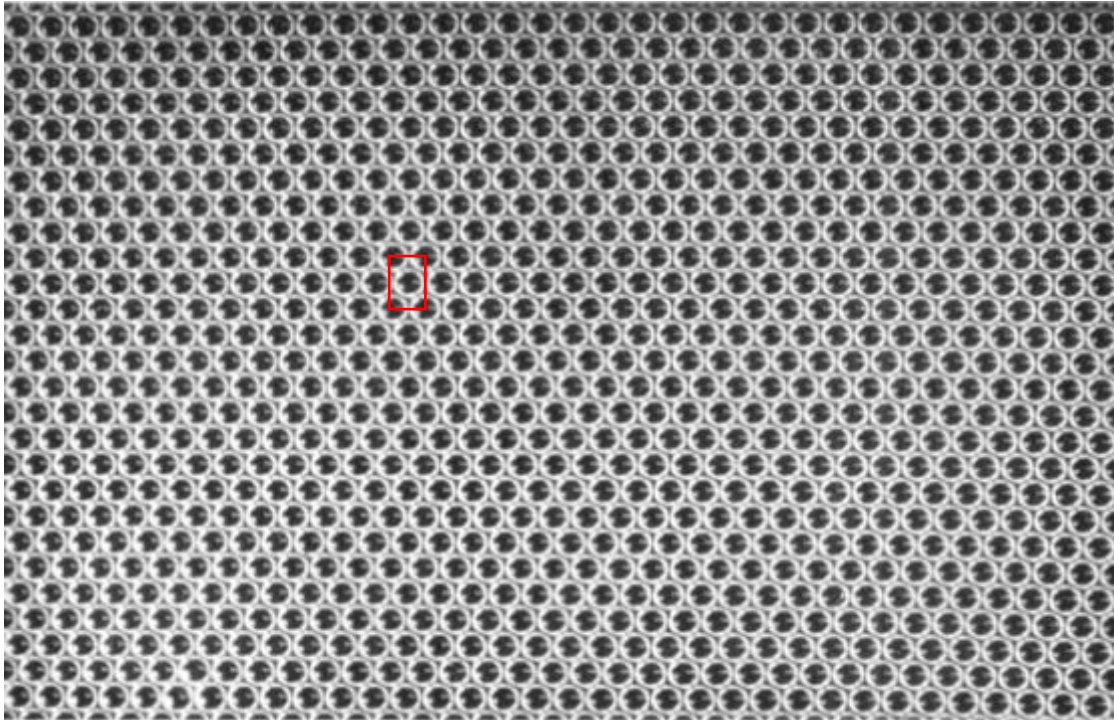
+ Fick's Laws of Diffusion

+ Permeability of Polymers

Crystal Defects

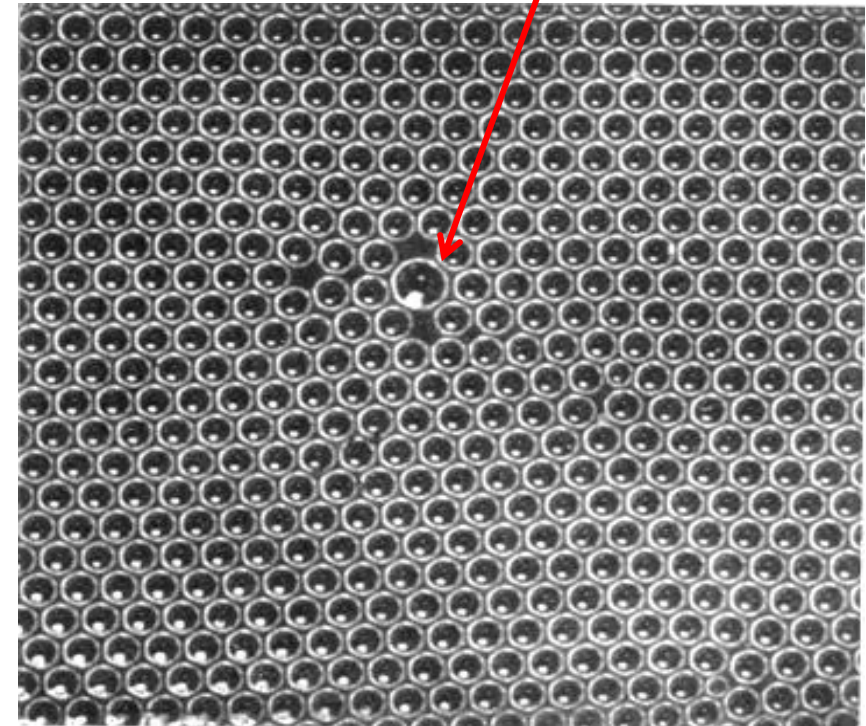
Crystal Defects

Perfect crystal of 1.41mm diameter bubbles



Sir Lawrence Bragg and J. F. Nye, Proceedings of the Royal Society of London, Series A, Mathematical Sciences and Physical Sciences, Vol. 190, No. 1023, Sept 9, 1947, pp. 474-481

Introduction of an impurity atom



Crystal Defects

Point Defects

- + Point defects are localized disruptions in otherwise perfect atomic/ionic arrangements in a crystal structure.
- + Effects of these disruptions are often felt over the surrounding region.
- + Often, these defects are caused by the introduction of other atoms/ions into the crystal structure.

Impurities are introduced due to processing conditions (O₂ in Si crystals).

Dopants are deliberately introduced to affect properties (Carbon in iron to make steel).

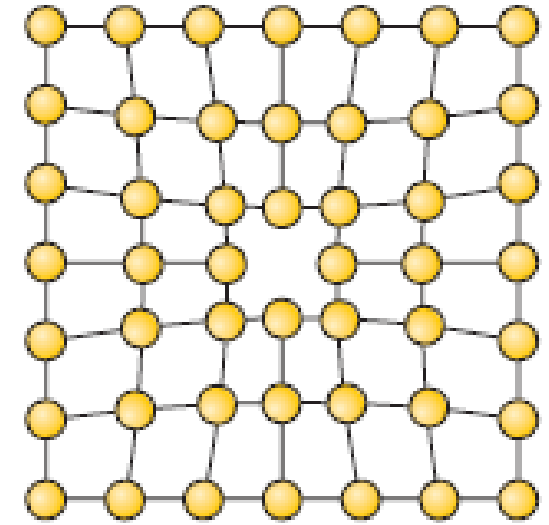
Crystal Defects

Point Defects

Vacancy

- + Is found in all crystalline materials, is when an atom/ion is missing from its normal site in the crystal structure.
- + Vacancies increase entropy, and thus thermodynamic stability of crystalline materials.

$$dG = dH - TdS$$



The vacancy concentration in a material follows an Arrhenius type behavior:

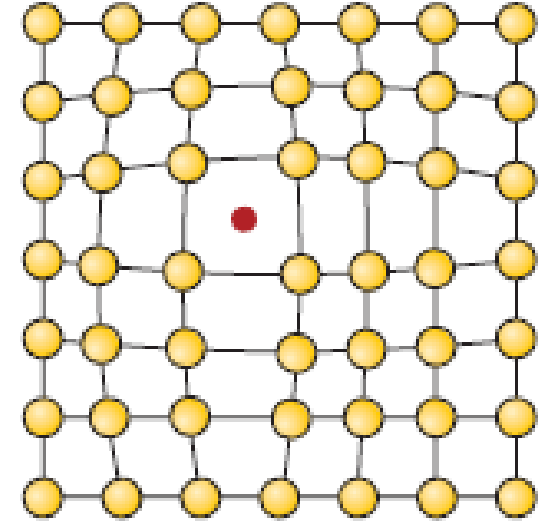
$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

Crystal Defects

Point Defects

Interstitial defect

- + An interstitial defect is formed when an extra atom/ion is inserted into the crystal structure at a normally unoccupied position.
- + Although smaller than atoms at lattice points, interstitial atoms introduce a localized stress in their vicinity.
- + This stress often strengthens the material. For instance, interstitial carbon atoms in an iron lattice strengthen the iron.

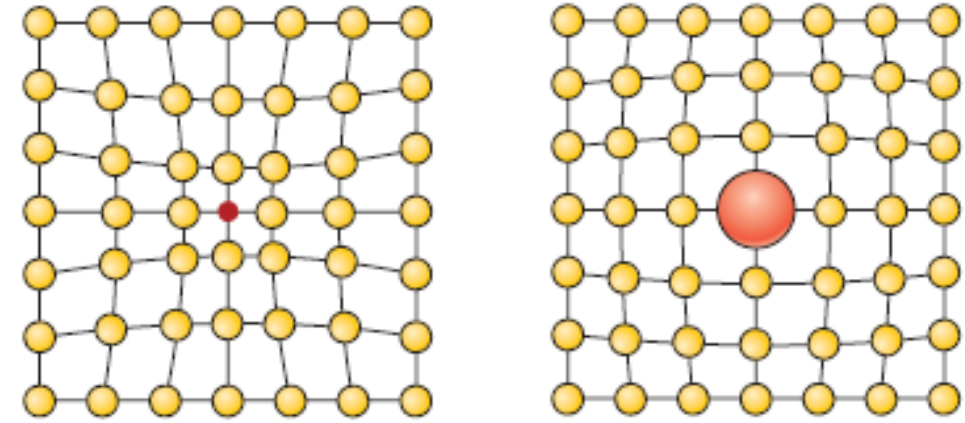


Crystal Defects

Point Defects

Substitutional defect

- + A substitutional defect is introduced when one lattice atom/ion is replaced by a different atom/ion.
- + Substitutional atoms often have different sizes than the regular lattice atoms, disturbing their surroundings.
- + Substitutional atoms often increase the strength of metallic materials.



Hume-Rothery rules are:

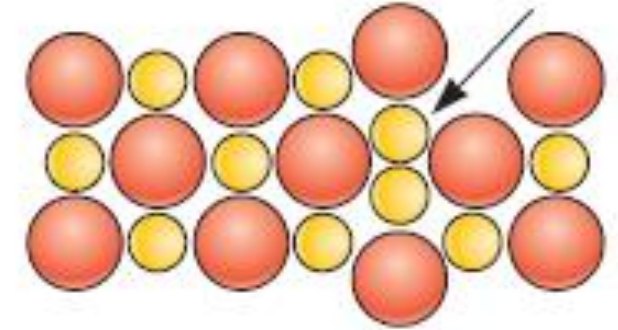
- The atomic radii of the solute and solvent atoms must differ by no more than 15%.
- The crystal structures of solute and solvent must match.
- Maximum solubility occurs when the solvent and solute have the same valency.
- The solute and solvent should have similar electronegativity.

Crystal Defects

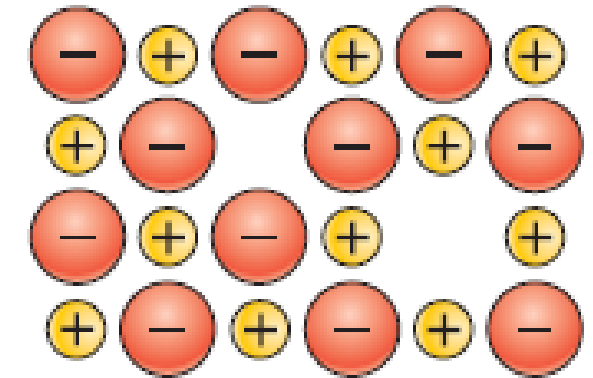
Point Defects

Other point defects

- + An **interstitialcy** is created when an atom identical to lattice atoms occupies an interstitial site.
- + A **Frenkel defect** is a vacancy-interstitial pair formed when a lattice atom jumps to an interstitial site, leaving behind a vacancy.
- + A **Schottky defect** is unique to ionic materials. To preserve electrical neutrality in ionic materials, for any vacancies, a stoichiometric number of cations & anions must be removed from the lattice.



Frenkel defect



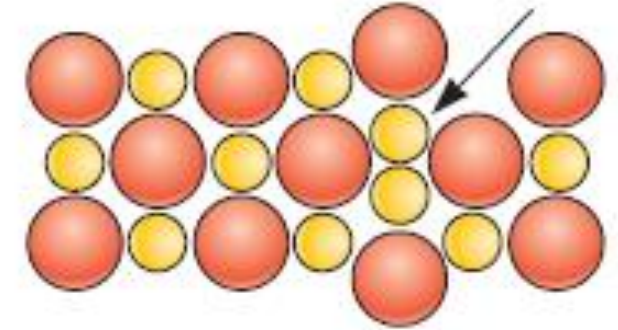
Schottky defect

Crystal Defects

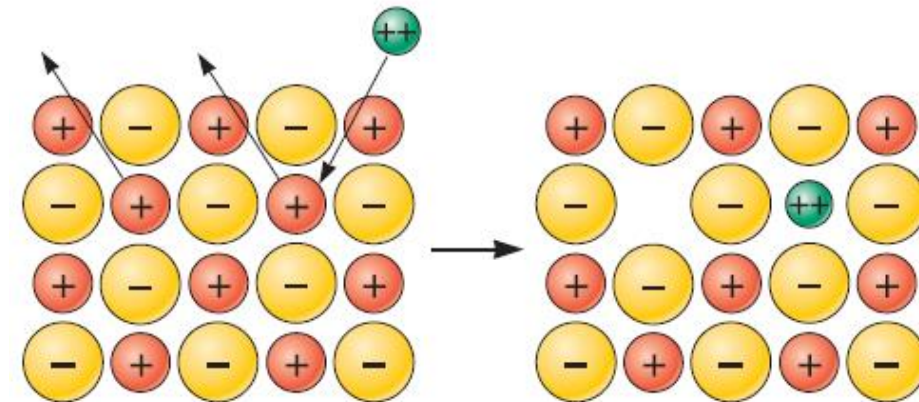
Point Defects

Other point defects

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- + A **Schottky defect** is unique to ionic materials. To preserve electrical neutrality in ionic materials, for any vacancies, a stoichiometric number of cations & anions must be removed from the lattice.



Frenkel defect



Schottky defect

Crystal Defects

Point Defects

Example: iron density again...

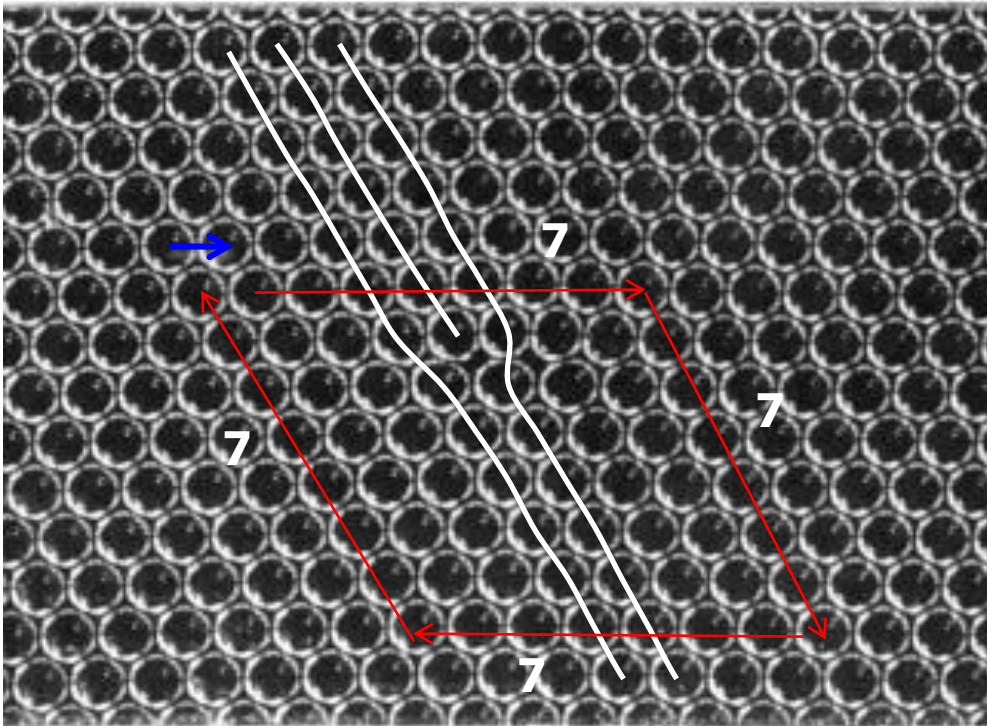
The theoretical density of BCC iron was 7.879 g/cm^3 . If the experimental density is 7.874 g/cm^3 , determine the number of vacancies in 1 cm^3 of iron.

Atomic mass of iron: 55.847 g/mol

Lattice parameter: 0.2866 nm

Crystal Defects

Line Defects: Dislocations



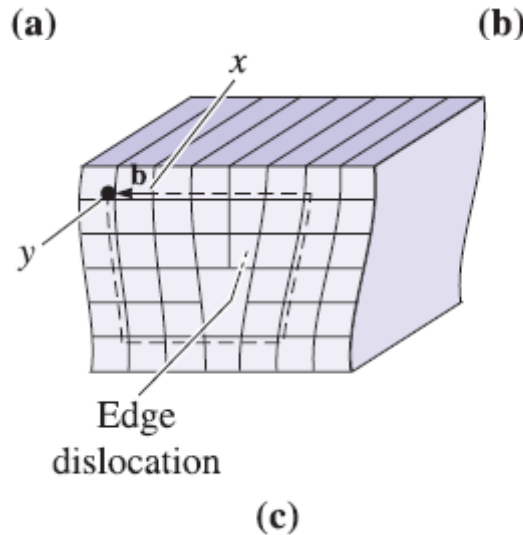
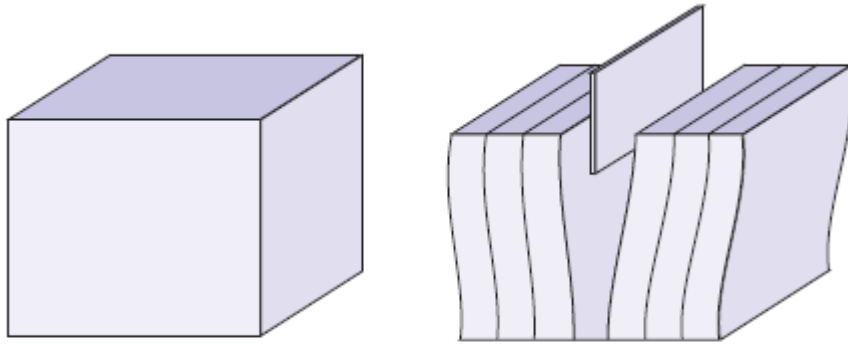
- + Dislocations are line imperfections in an otherwise perfect crystal.
- + They are present in all materials, including ceramics and polymers.
- + They are especially useful in explaining deformation & strengthening in metallic materials.
- + The 3 kinds of dislocations are the edge, screw and mixed dislocations.

Sir Lawrence Bragg and J. F. Nye, Proceedings of the Royal Society of London, Series A, Mathematical Sciences and Physical Sciences, Vol. 190, No. 1023, Sept 9, 1947, pp. 474-481

Crystal Defects

Line Defects: Dislocations

Edge dislocation

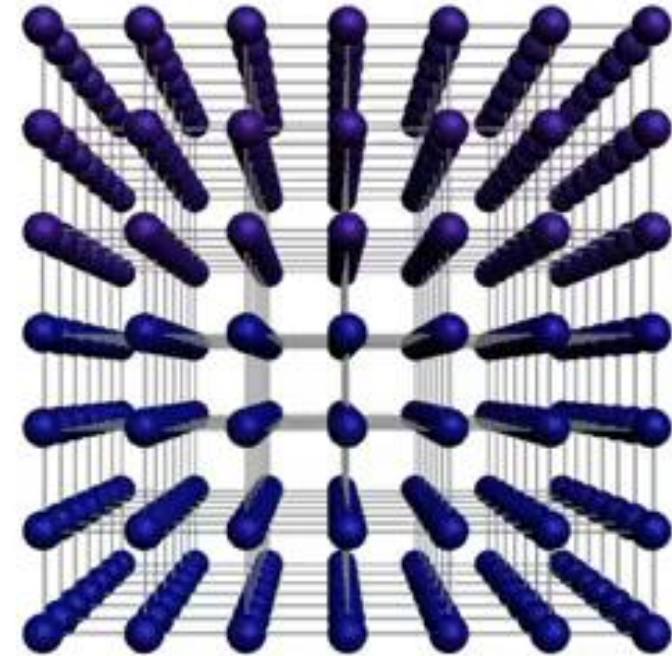
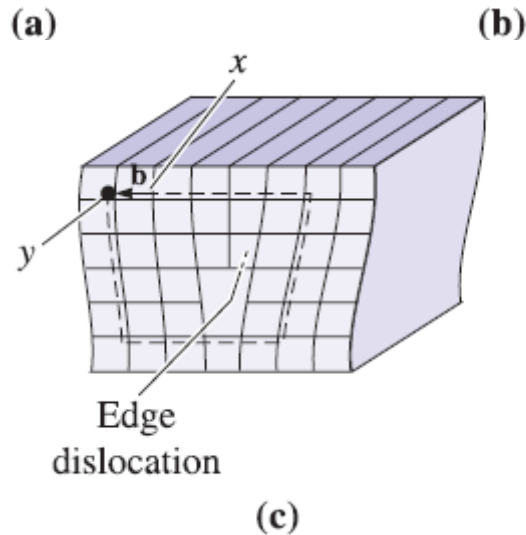
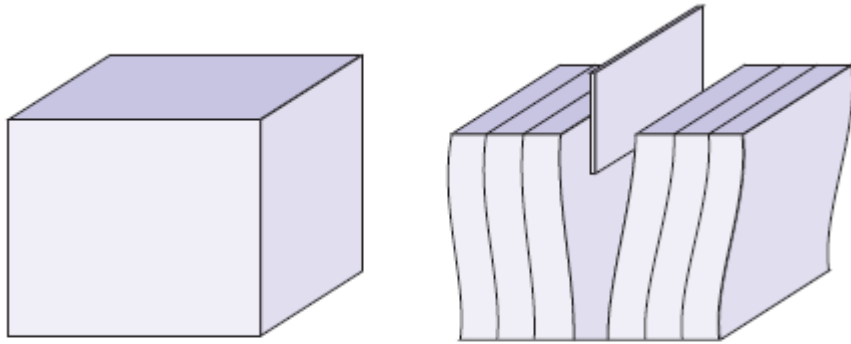


- + The perfect crystal in (a) is cut and an extra half plane of atoms is inserted (b).
- + The bottom edge of the extra half plane is an edge dislocation (c).
- + A Burgers vector **b** is required to close a loop of equal atom spacings around the edge dislocation.

Crystal Defects

Line Defects: Dislocations

Edge dislocation

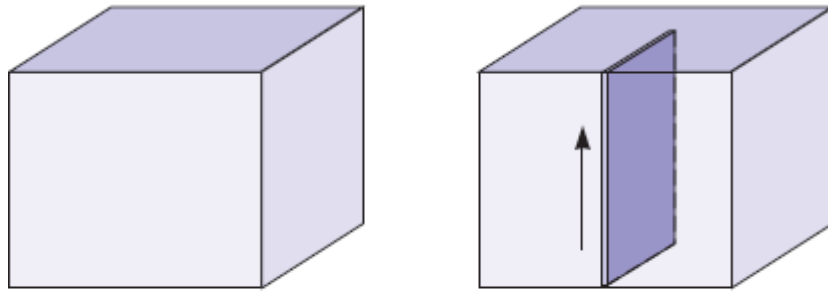


EDGE DISLOCATION

Crystal Defects

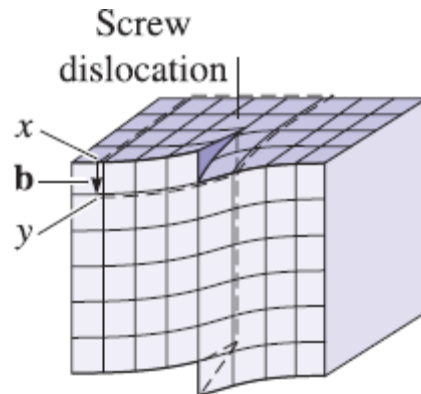
Line Defects: Dislocations

Screw dislocations



(a)

(b)



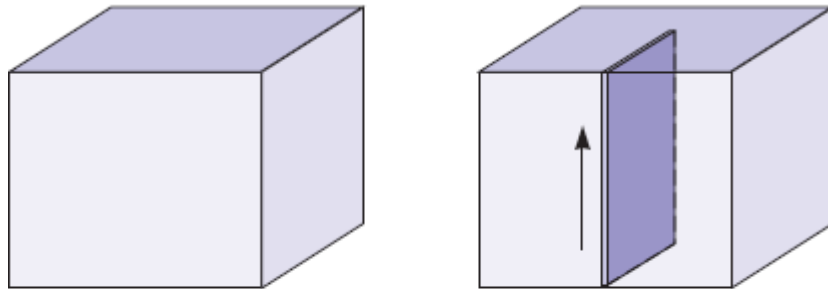
(c)

- + The perfect crystal (a) is cut and sheared one atom spacing, (b) and (c).
- + The line along which shearing occurs is a screw dislocation.
- + A Burgers vector **b** is required to close a loop of equal atom spacings around the screw dislocation..

Crystal Defects

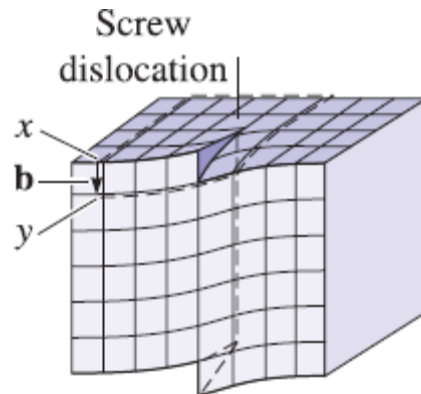
Line Defects: Dislocations

Screw dislocations

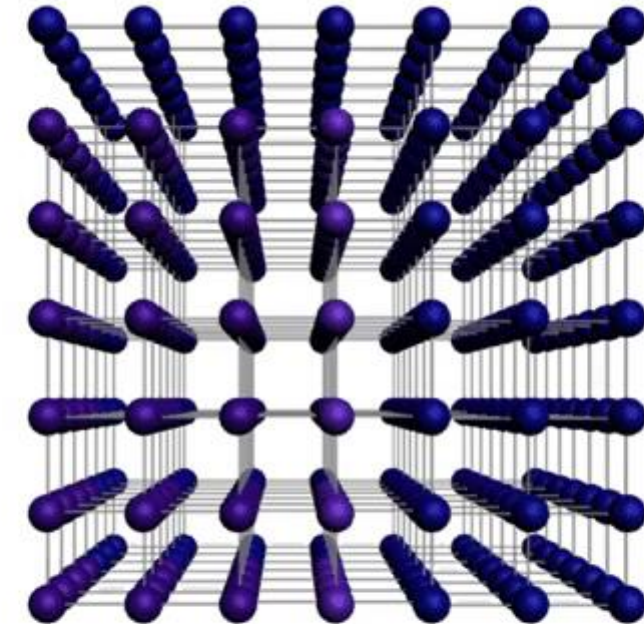


(a)

(b)



(c)

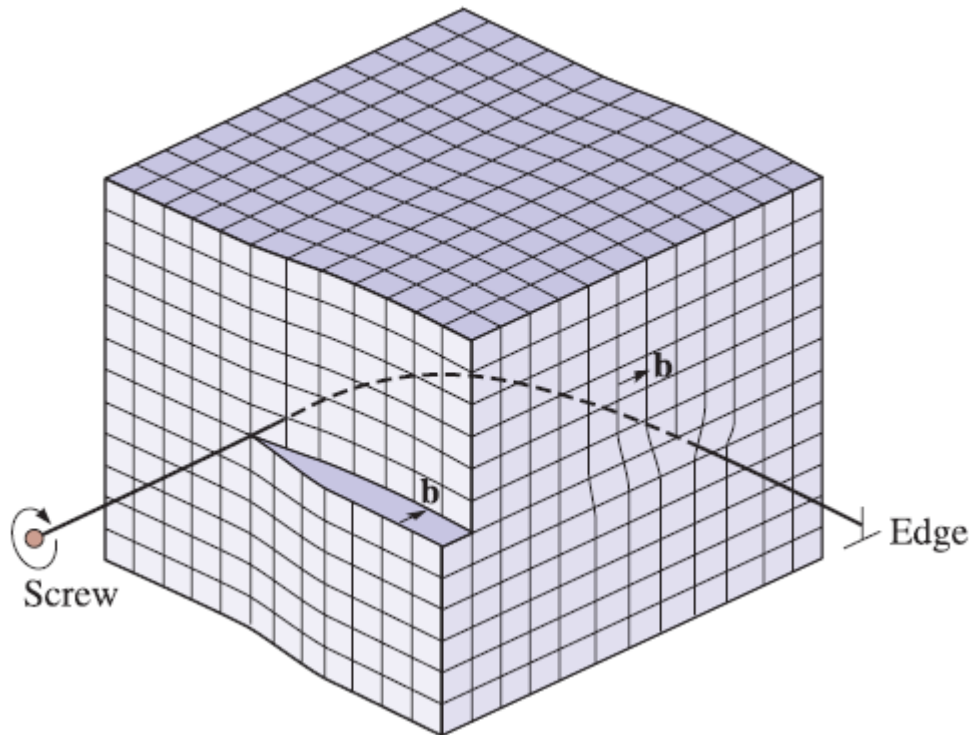


SCREW DISLOCATION

Crystal Defects

Line Defects: Dislocations

Mixed dislocations



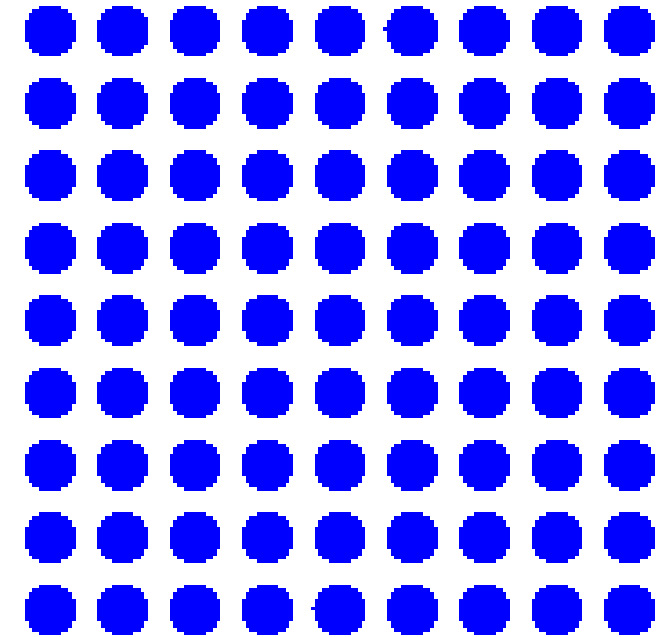
- + Mixed dislocations have both edge and screw components, with a transition region between them.
- + The Burgers vector remains the same for all portions of the mixed dislocation.
- + The screw dislocation at the front face of the crystal gradually changes to an edge dislocation at the side of the crystal.

Crystal Defects

Line Defects: Dislocations

Slip and dislocation movement

- + A plane that contains both the dislocation line and the Burgers vector is known as a **slip plane**.
- + If a sufficiently large force is applied parallel to the Burgers vector (the slip direction), dislocations can move in a crystal via the slip process.

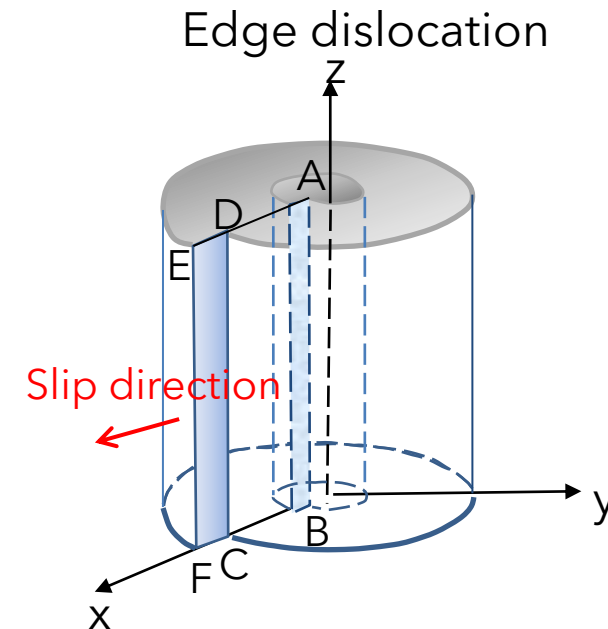
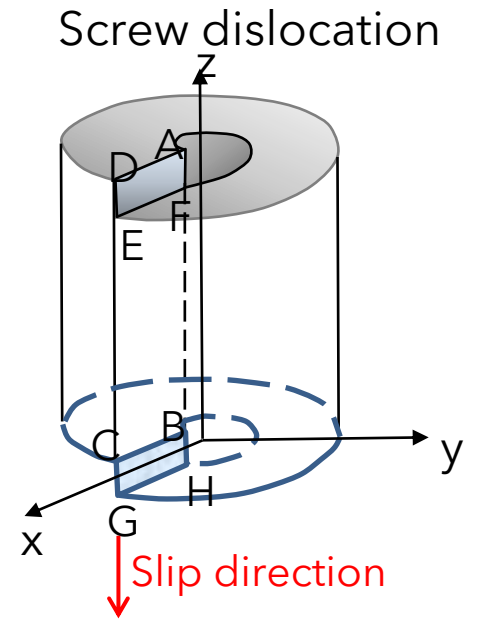


Crystal Defects

Line Defects: Dislocations

Slip and dislocation movement

- + A plane that contains both the dislocation line and the Burgers vector is known as a **slip plane**.
- + If a sufficiently large force is applied parallel to the Burgers vector (the slip direction), dislocations can move in a crystal via the slip process.
- + The slip direction (Burgers vector) and the dislocation line (z axes in figure) are parallel in a screw dislocation and perpendicular in the edge one.



Crystal Defects

Line Defects: Dislocations

- + Dislocations move in a slip system (plane + direction) which requires the least energy.

Factors determining most likely active slip systems are:

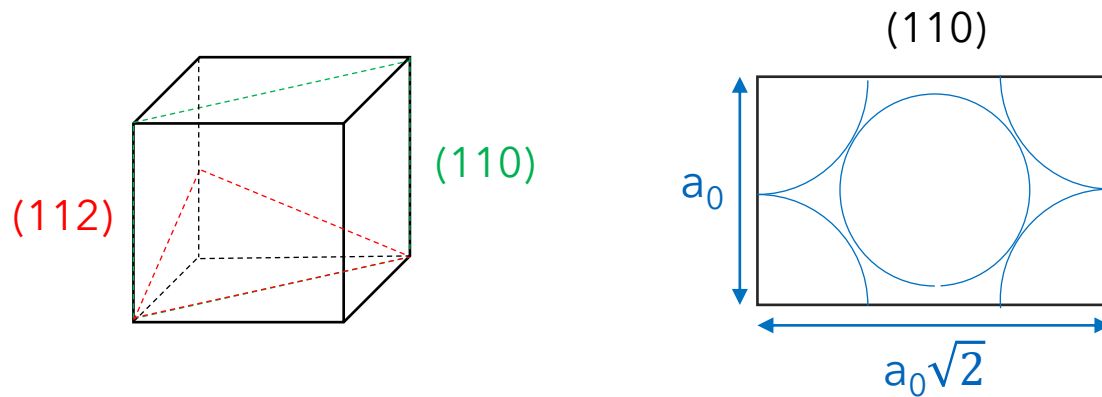
- + Slip direction should have high linear density.
- + Slip planes should have a high planar density and a high interplanar spacing.
- + Dislocations do not easily move in materials with covalent/directional bonds.
- + Materials with ionic bonding are also resistant to slip because dislocation movement disrupts charge balance between cations & anions.

Crystal Defects

Line Defects: Dislocations

Example:

Planar density of (112) plane in BCC iron is 9.94×10^{14} atoms/cm². Calculate (a) planar density of (110) plane and (b) interplanar spacings for both (112) & (110) planes if $a_0 = 0.2866$ nm. On which plane would slip occur?



Planar density of (110) is 1.72×10^{15} atoms/cm²

The interplanar spacings are:

$$d_{110} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 0}} = 2.027 \times 10^{-8} \text{ cm}$$

$$d_{112} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 2^2}} = 1.170 \times 10^{-8} \text{ cm}$$

Planar density is higher and interplanar spacing larger for (110) plane, so (110) plane is the preferred slip plane.

Crystal Defects

Surface Defects

- + Surface defects are boundaries/planes which separate a material into regions, which may have same crystal structure but different orientations.

Material surface

- + The material's exterior surface represents surfaces where the crystal abruptly ends. The surface atoms have incomplete bonding, and the surface may be rough and very reactive.

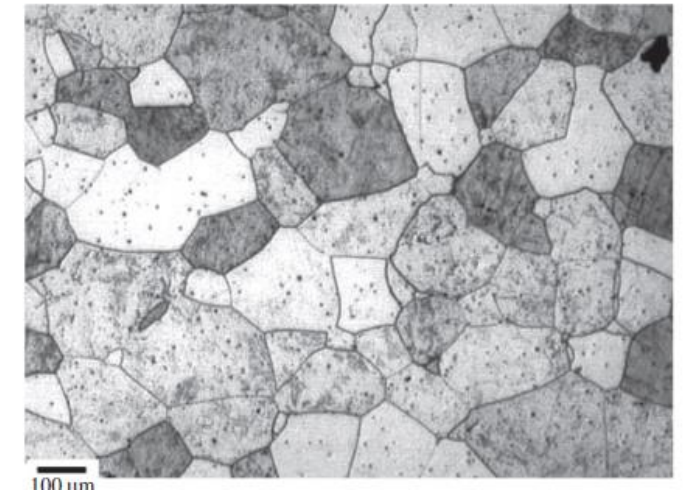
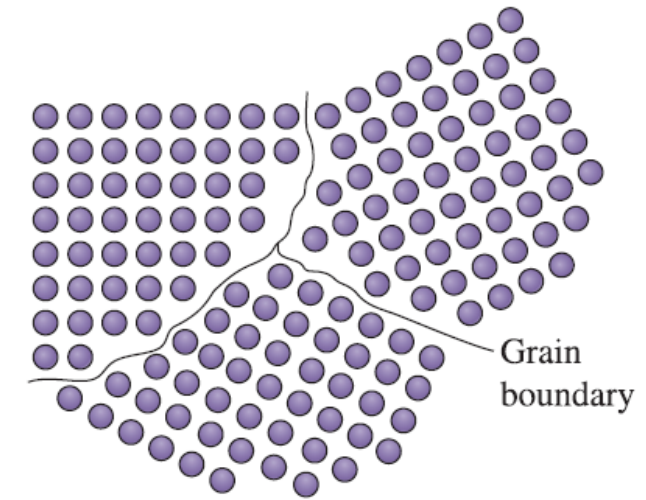


Crystal Defects

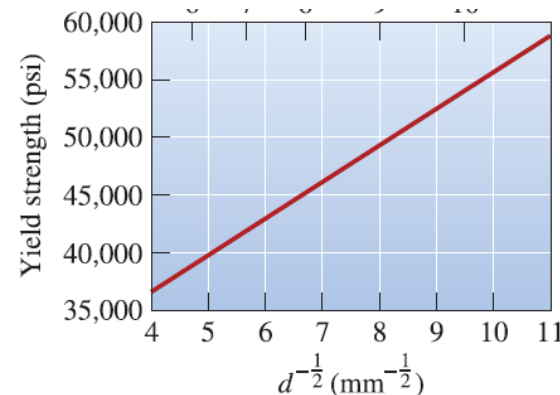
Surface Defects

Grain boundaries

- + Narrow zones where the atoms are not properly spaced.
- + We can increase a material's strength by reducing grain size/increasing grain boundaries. This way, dislocations can only travel a short distance before stopping.
- + *The Hall-Petch equation relates the grain size to yield strength*



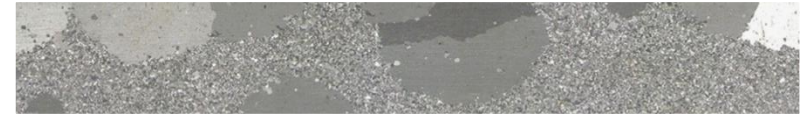
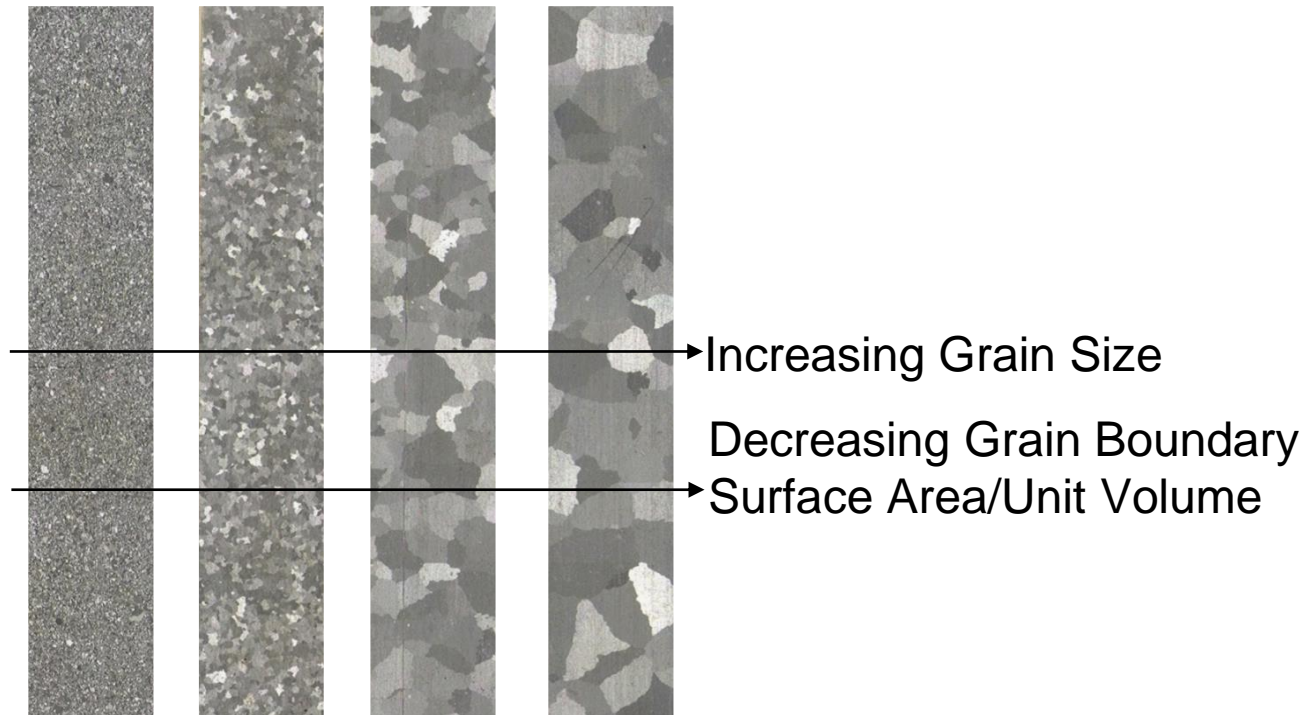
$$\sigma_y = \sigma_0 + Kd^{-1/2}$$



Crystal Defects

Surface Defects

Grain boundaries



Duplex Grain
Structure

Crystal Defects

Surface Defects

Small angle grain boundary

- + An array of dislocations that produces a small misorientation between adjacent crystals.

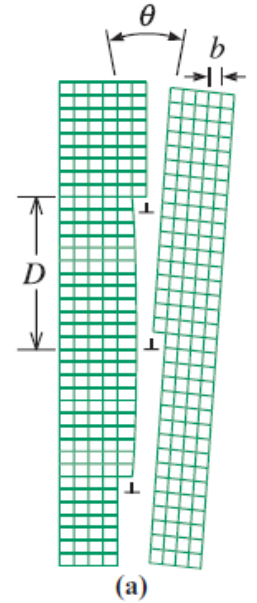
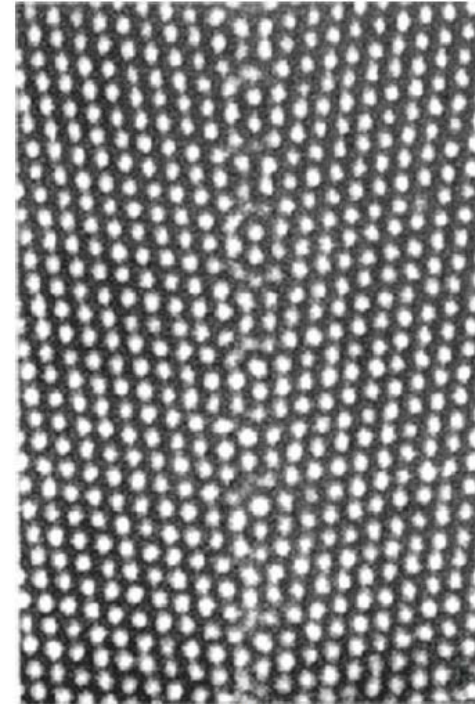
Stacking faults

- + Occur in FCC metals, and represent an error in the stacking of close-packed planes.

Other surface defects:

- Twin Boundaries
- Domain Boundaries

ABC ABAB CAB



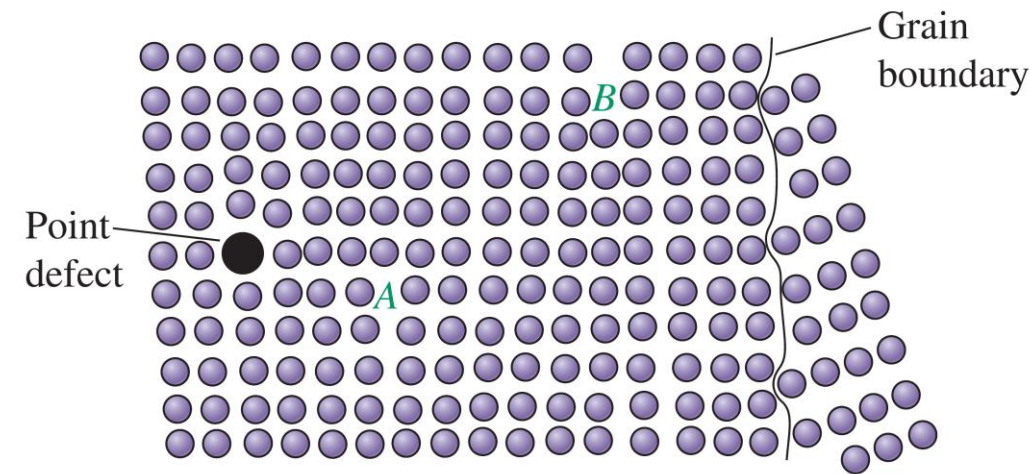
They are not as effective as regular grain boundaries in blocking slip.

Importance Of Defects

Importance Of Defects

Importance of defects (1/3):

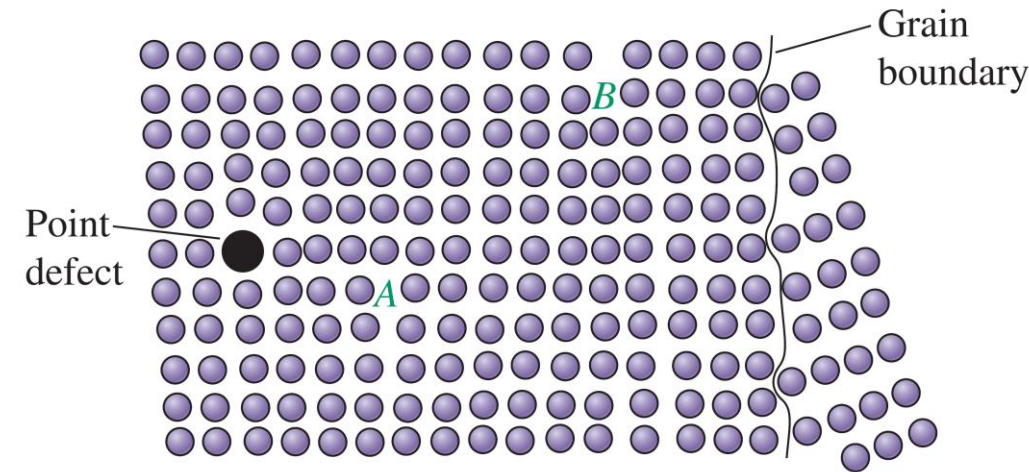
- + Defects play an important role in controlling the mechanical properties of materials (generally metals) by interfering with **slip** and **strengthening** the material.
- + Defects have less of an effect on the properties of ceramics, which are dictated more by porosity, and on polymers, which are amorphous.
- + **Strain hardening** is the process of strengthening a material by deforming it, which increases dislocation density.



Importance Of Defects

Importance of defects (2/3):

- + The effects of strain hardening can be reversed by **heat treatment/annealing**, which decreases dislocation density and increases material ductility.
- + **Solid-solution strengthening** takes place when atoms/ions of a guest material are incorporated into the crystal structure. The interstitial/ substitutional atoms are considered as defects.
- + **Grain-size strengthening** occurs by increasing the number of grains, or reducing the grain size.



Importance Of Defects

Importance of defects (3/3):

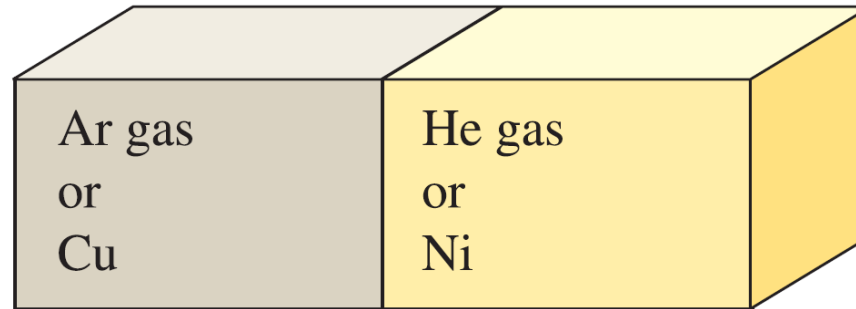
- + Point defects can also have a dramatic effect on the optical, magnetic & electrical properties of materials.
- + In semiconductors, **dopants** are critical to achieving desired performance; however, defects like dislocations negatively affect properties.
- + Addition of small amounts of foreign atoms/ions in materials can also be used to produce dramatic color changes in the original material e.g., colored glasses.

Applications of Diffusion

Applications of Diffusion

What is Diffusion?

Consider a box containing an impermeable partition that divides the box into equal volumes. On one side, we have pure argon (Ar) gas; on the other side, we have pure helium (He) gas. Explain what will happen when the partition is opened? What will happen if we replace the Ar side with a Cu single crystal and the He side with a Ni single crystal?



Diffusion:

- + Is the net flux of any species (ions/atoms/electrons, etc.), the magnitude of which depends on the concentration gradient and temperature.

Applications of Diffusion

Engineering applications of diffusion

Carburization for Steel Surface Hardening:

- + The carburization process can be used to increase surface hardness.
- + In carburization, a source of carbon, such as a graphite powder or gaseous phase containing carbon, is diffused into steel components such as gears.
- + Diffusion also plays a central role in the control of the phase transformations needed for the heat treatment of metals and alloys, the processing of ceramics, and the solidification and joining of materials



Heat treatment of steel using carburization.

Applications of Diffusion

Engineering applications of diffusion

Dopant Diffusion for Semiconductor and Conductive Ceramics:

- + The creation of some semiconductors involves diffusing dopant atoms, such as phosphorous (P), arsenic (As), antimony (Sb), boron (B), aluminum (Al), etc., into precisely defined regions of silicon.
- + In general, polycrystalline ceramics tend to be good insulators of electricity. However, diffusion of ions allows electrical conductivity of many conductive ceramics such as Lithium cobalt oxide (LiCoO_2) used in Lithium batteries.

Plastic Beverage Bottles:

- + The diffusion of carbon dioxide (CO_2) must be minimized in the creation of plastic bottles that contain carbonated beverages the retain their fizz. This is one of the major reasons why we use polyethylene terephthalate (PET) to make them.

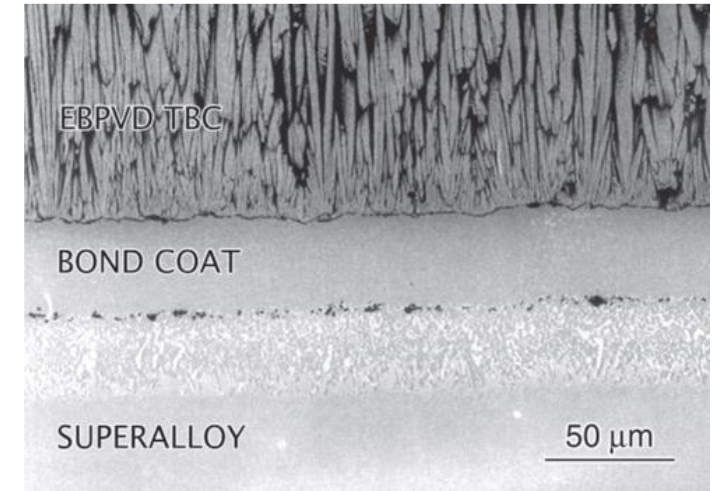


Applications of Diffusion

Engineering applications of diffusion

Thermal Barrier Coatings for Turbine Blades:

- + In an aircraft engine, some of the nickel superalloy-based turbine blades are coated with ceramic oxides. These ceramic coatings protect the underlying alloy from high temperatures.
- + The diffusion of oxygen through these ceramic coatings and the subsequent oxidation of the underlying alloy play a major role in determining the lifetime and durability of the turbine blades.



A thermal barrier coating on a nickel-based superalloy

Oxidation of Aluminum:

- + The aluminum oxide (Al_2O_3) forms a very protective but thin coating on the aluminum's surface preventing any further diffusion of oxygen and hindering further oxidation of the underlying aluminum.

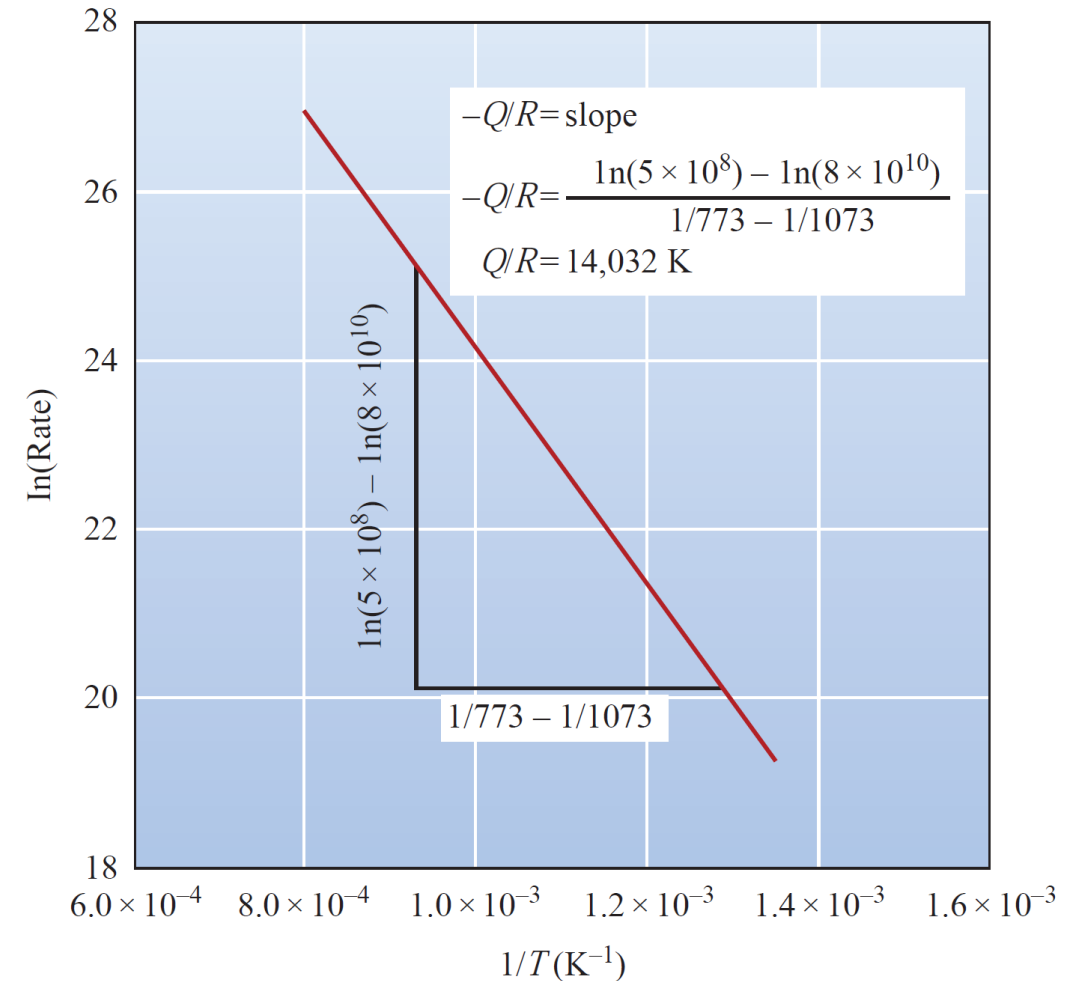
Mechanisms for Diffusion

Mechanisms for Diffusion

Stability of Atoms & Ions

- + Atoms, ions and crystal imperfection are not stable.
(An atom can move from a position to a vacancy)
- + Temperature increases the ability of atoms/ions to diffuse.
- + The relationship of the movement rate to the temperature is given by the Arrhenius equation:

$$\text{Rate} = c_0 \exp\left(\frac{-Q}{RT}\right) \quad \text{or} \quad \ln(\text{Rate}) = \ln(c_0) - \frac{Q}{RT}$$



Mechanisms for Diffusion

Stability of Atoms & Ions

Example:

Some interstitial atoms move from one site to another at the rates 5×10^8 jumps/s at 500°C and 8×10^{10} jumps/s at 800°C . Find the activation energy Q for this process.

$$R = 1.987 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$Q = 27880 \text{ cal/mol}$$

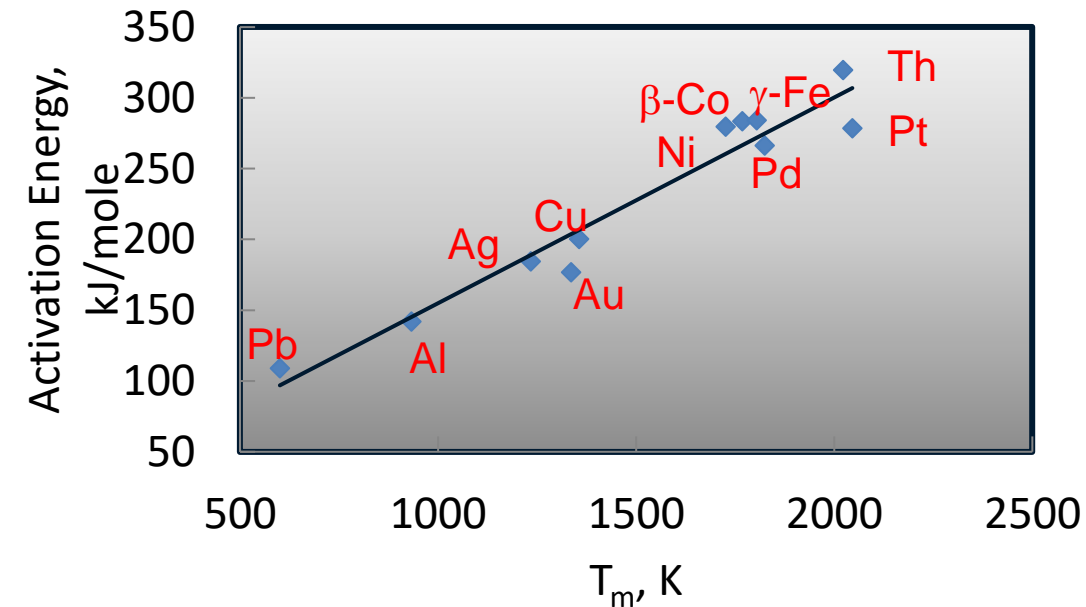
Mechanisms for Diffusion

Types of Diffusion

Self-diffusion:

- + Vacancy defects exist in crystalline materials and increase their thermodynamic stability.
- + In materials containing vacancies, atoms jump around from one lattice position to another. This is called self-diffusion.
- + Self-diffusion can be detected using radioactive tracers. However, it generally does not significantly affect material behavior.

Variation in activation energy for self-diffusion versus melting temperature for several FCC metals.



Brown, A.M. and Ashby, M.F., Acta Met, 28, 1085, 1980.

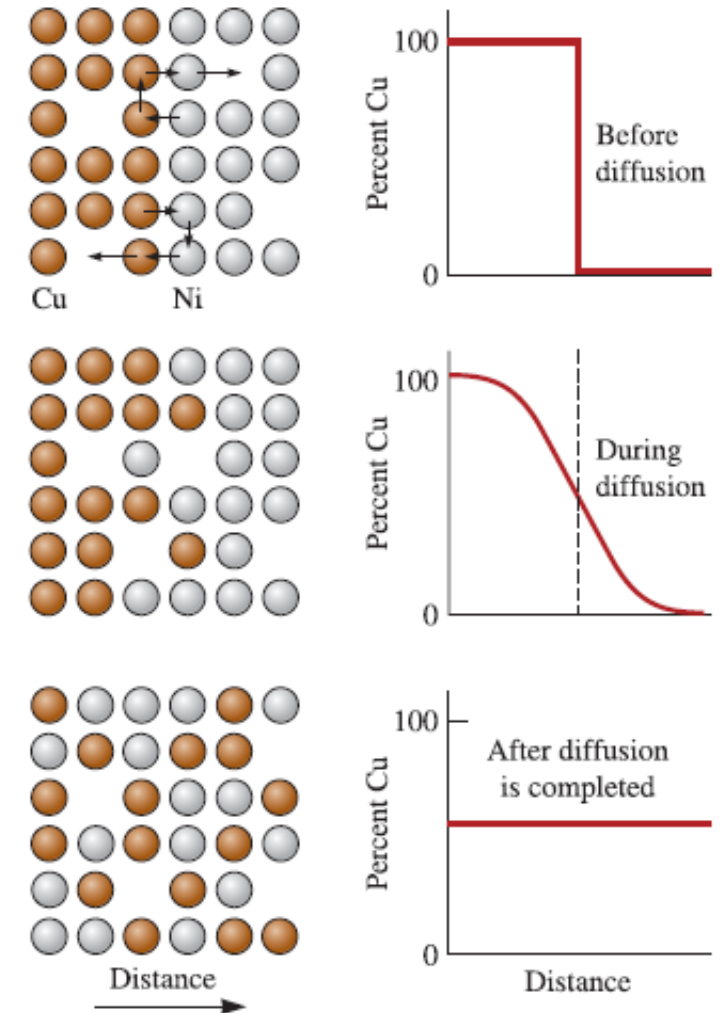
Mechanisms for Diffusion

Types of Diffusion

Interdiffusion:

- + Diffusion of unlike atoms in materials also occur.
- + At high temperatures, nickel atoms gradually diffuse into the copper, and copper atoms migrate into the nickel.

Vacancy, Substitutional and Interstitial defects are the mechanisms of interdiffusion

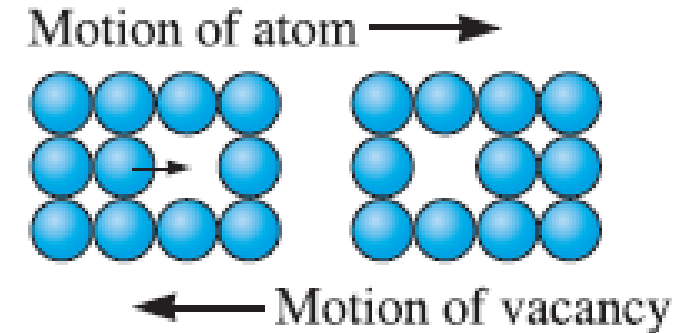


Mechanisms for Diffusion

Mechanisms for Diffusion

Vacancy diffusion:

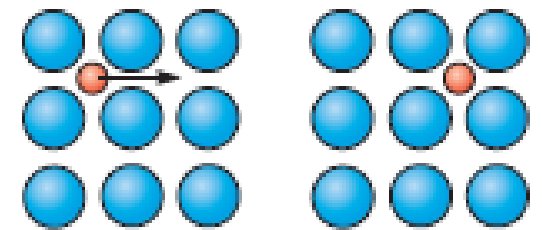
- + When an atom leaves a lattice site to fill another one, it creates a vacancy.
- + Diffusion involves counterflows of atoms and vacancies.
- + High temperature increases vacancies.



(a) Vacancy mechanism

Interstitial diffusion:

- + This occurs when a small atom/ion moves from one interstitial site to another.
- + No vacancies are required for this kind of diffusion, so it occurs more easily.
- + Generally, smaller interstitial species diffuse faster.



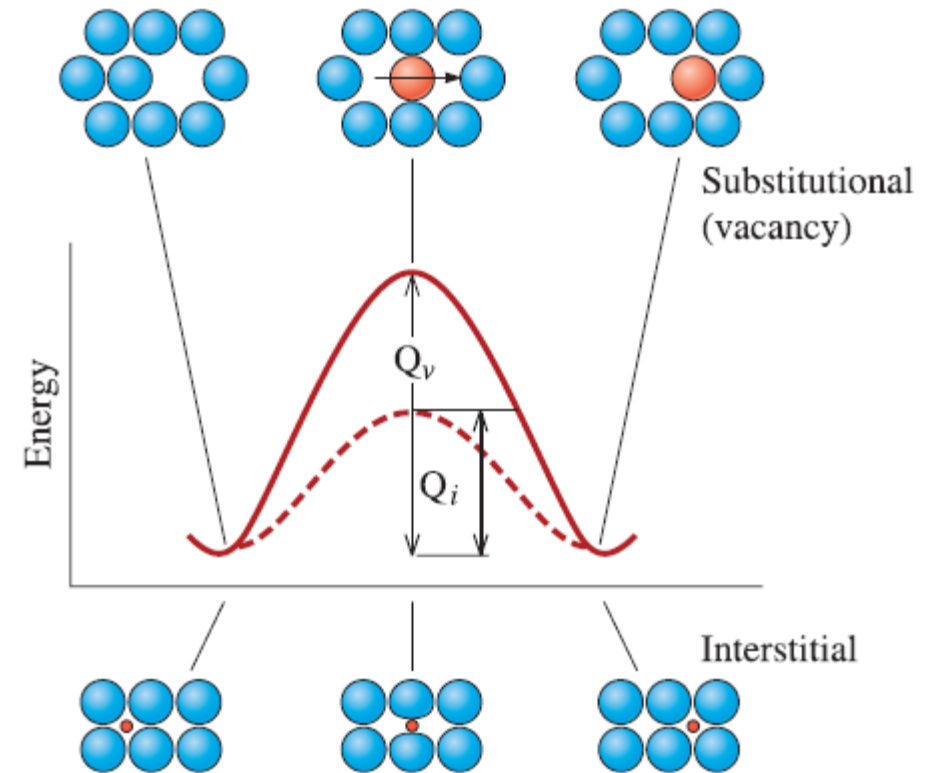
(b) Interstitial mechanism

Mechanisms for Diffusion

Mechanisms for Diffusion

Activation energy:

- + A diffusing atom must squeeze past other atoms to reach a new position, which requires activation energy.
- + A low activation energy indicates easy diffusion.
- + We use the term diffusion couple to indicate a combination of an atom of a given element diffusing in a host material (e.g., carbon in BCC iron).
- + Q depend on the phenomenon we are considering



Generally, interstitial atoms require a lower activation energy than substitutional atoms.

Mechanisms for Diffusion

Mechanisms for Diffusion

Activation energy:

- + A diffusing atom must squeeze past other atoms to reach a new position, which requires activation energy.
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- + Q depend on the phenomenon we are considering

TABLE 5-1 ■ Diffusion data for selected materials

Diffusion Couple	Q (cal/mol)
Interstitial diffusion:	
C in FCC iron	32,900
C in BCC iron	20,900
N in FCC iron	34,600
N in BCC iron	18,300
H in FCC iron	10,300
H in BCC iron	3,600
Self-diffusion (vacancy diffusion):	
Pb in FCC Pb	25,900
Al in FCC Al	32,200
Cu in FCC Cu	49,300
Fe in FCC Fe	66,700
Zn in HCP Zn	21,800
Mg in HCP Mg	32,200
Fe in BCC Fe	58,900
W in BCC W	143,300
Si in Si (covalent)	110,000
C in C (covalent)	163,000
Heterogeneous diffusion (vacancy diffusion):	
Ni in Cu	57,900
Cu in Ni	61,500
Zn in Cu	43,900
Ni in FCC iron	64,000
Au in Ag	45,500
Ag in Au	40,200
Al in Cu	39,500
Al in Al_2O_3	114,000
O in Al_2O_3	152,000
Mg in MgO	79,000
O in MgO	82,100

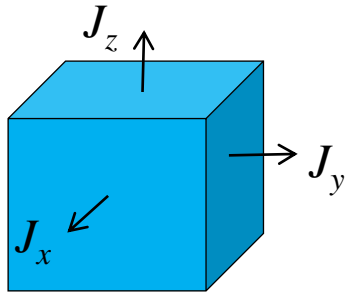
From several sources, including Adda, Y. and Philibert, J., *La Diffusion dans les Solides*, Vol. 2, 1966.

Fick's Laws of Diffusion

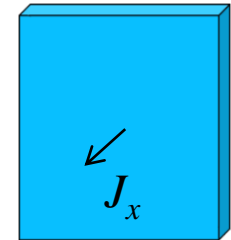
Fick's Laws of Diffusion

Rate of Diffusion (Fick's 1st Law)

Flux of atoms:



When $J_y = J_z = J$ and there is a net flux in the x direction the problem is reduced to a one dimensional problem



Where J is the flux of atoms crossing a plane/unit area (atoms/cm²)

This occurs when the composition is uniform in the y - z plane

Fick's Laws of Diffusion

Rate of Diffusion (Fick's 1st Law)

Fick's first law:

It relates the rate of diffusion (written in terms of flux J) to the diffusivity D (*diffusion coefficient*) of the diffusion couple, and the concentration gradient.

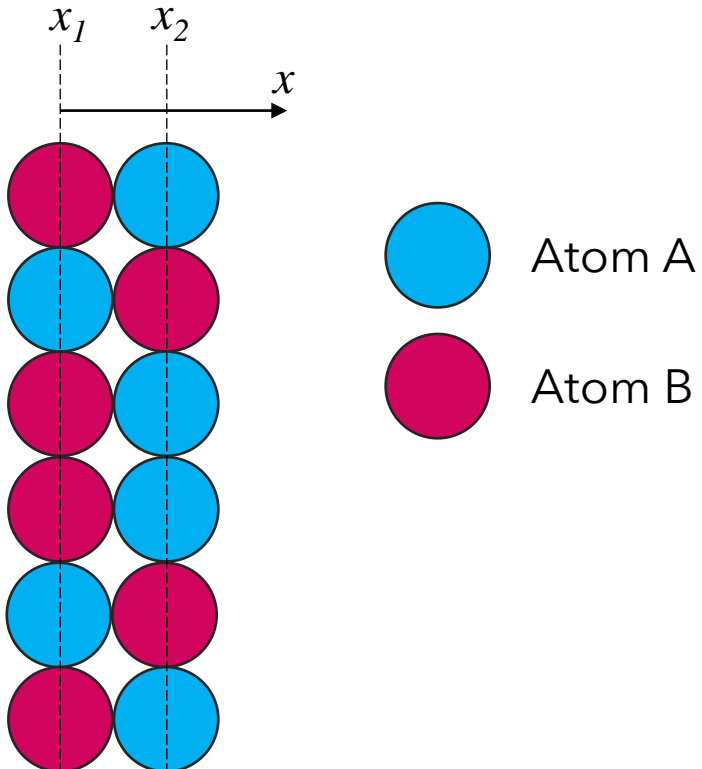
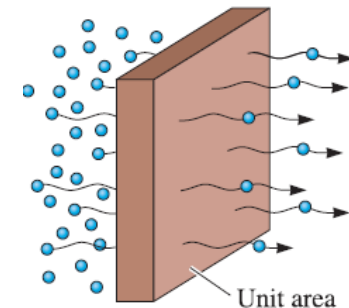
Diffusion of B in A:

Concentrations: $C(x_2) < C(x_1)$

The flux of atoms B: $J = -D \frac{C(x_2) - C(x_1)}{x_2 - x_1}$

Fick's 1st law:

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



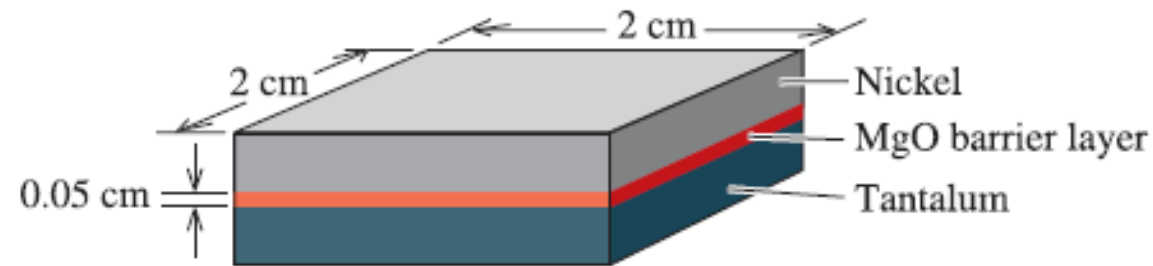
Fick's Laws of Diffusion

Rate of Diffusion (Fick's 1st Law)

Example:

A 0.05 cm layer of MgO is deposited between layers of nickel and tantalum. At 1400°C, Ni ions diffuse through the MgO to the tantalum layer. At 1400°C, the Ni (FCC) lattice parameter is 3.6×10^{-8} cm and its diffusion coefficient in MgO is 9×10^{-12} cm²/s.

- (a) Determine the number of Ni ions passing through the MgO interface per second
- (b) The thickness by which the Ni layer is reduced each second is



- (a) 6.17×10^{13} atoms/s
- (b) 1.8×10^8 cm/s

Fick's Laws of Diffusion

Factors Affecting the Diffusion Coefficient

- + Temperature & Diffusion Coefficient: *Diffusion kinetics are strongly related to temperature.*

$$D = D_0 \exp(-Q / RT)$$

- + Type of bond:

In covalently bonded materials, the D value is low because Q (activation energy) is high.

Similarly, ionic materials have high Q because ions can only diffuse into sites having same charge.

- + Type of Diffusion:

Volume diffusion: Slow, high activation energy (Q).

Grain boundary diffusion: Faster, lower Q .

Surface diffusion: Fastest, lowest Q .

- + Time: Diffusion requires time; controlling diffusion time during processing can be the key to producing uniform or unique (non-equilibrium) properties & microstructures.

- + Crystal Structure:

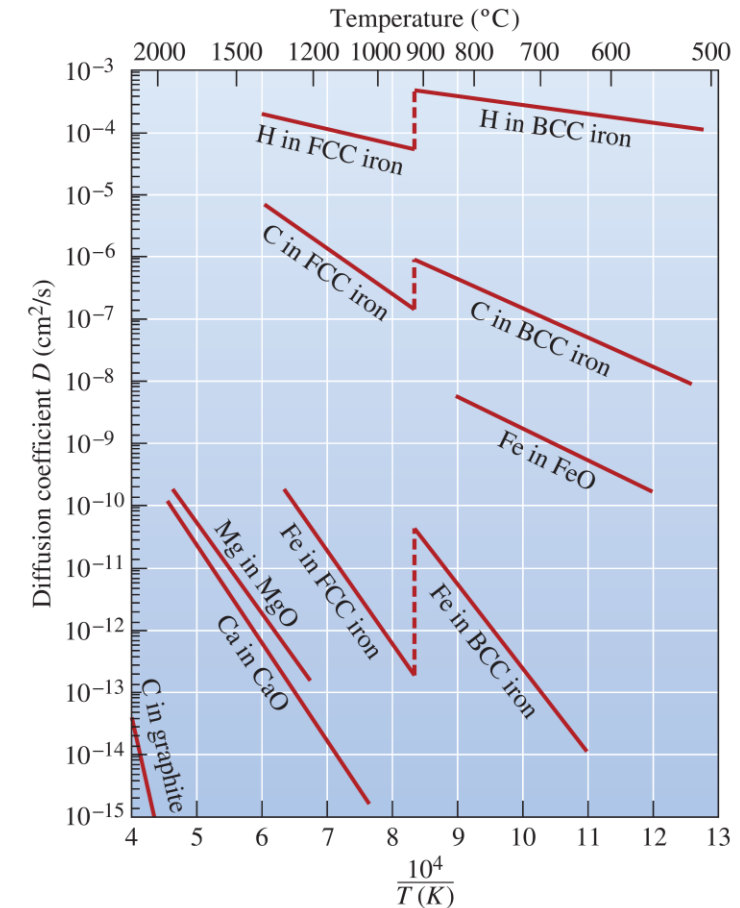
Interstitial diffusion occurs faster than vacancy or substitutional diffusion.

Close-packed crystal structures have higher Q than open crystal structures.

Cations diffuse faster than anions due to size.

Ionic diffusion also transports charge/enables conductivity.

- + The concentration of the diffusing species and composition of the matrix.

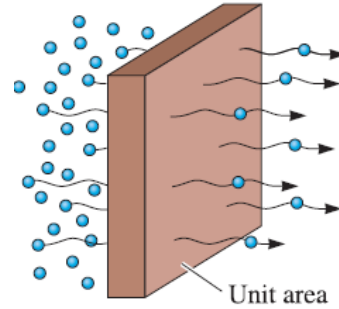


Fick's Laws of Diffusion

Composition Profile:

Fick's 1st law:

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



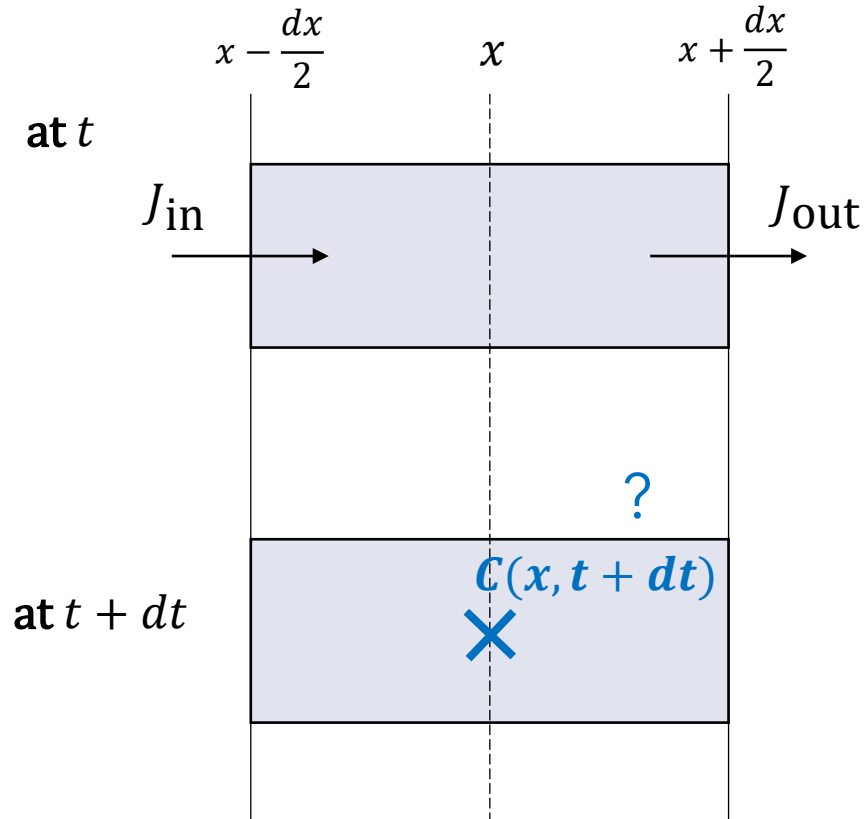
But the concentration is changing so $\frac{dc}{dx}$ also changes with time.

Fick's Laws of Diffusion

Composition Profile:

Fick's second law:

Describes the non-steady state diffusion of atoms.



Fick's 1st law:

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

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

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

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

If D is constant

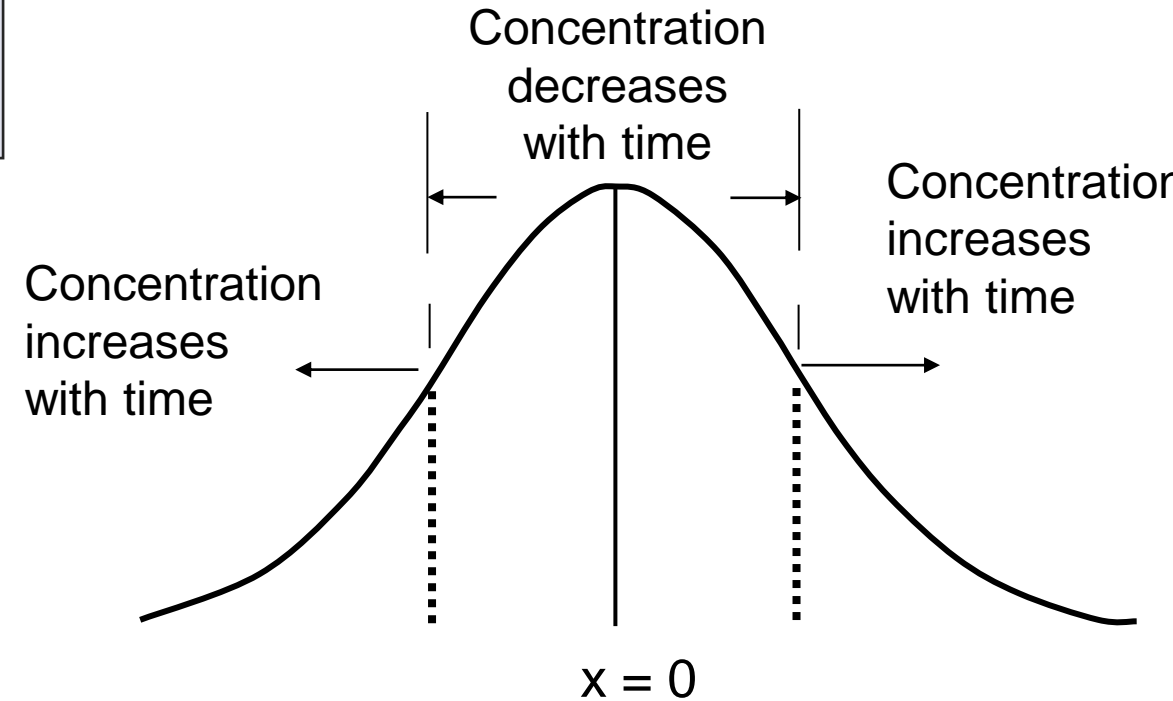
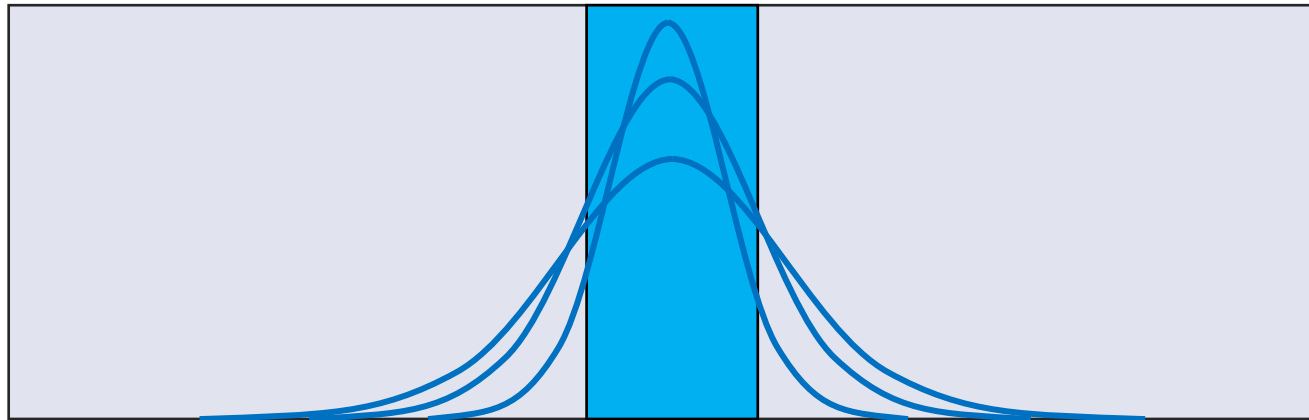
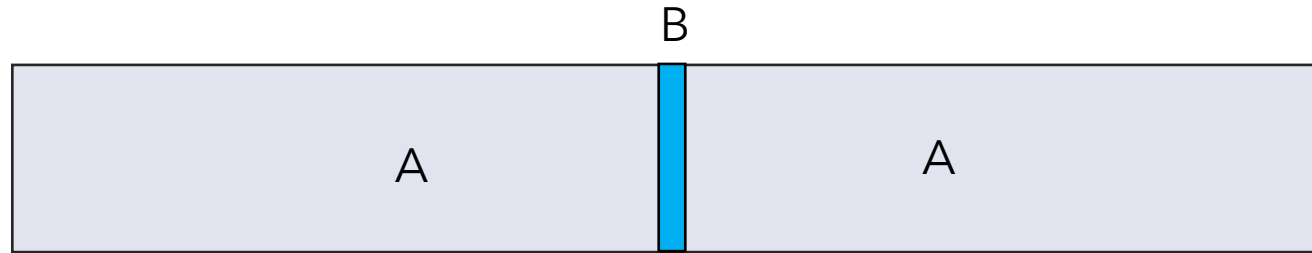
The solution of this equation depends on the conditions

Fick's Laws of Diffusion

Composition Profile:

Solution for a thin film:

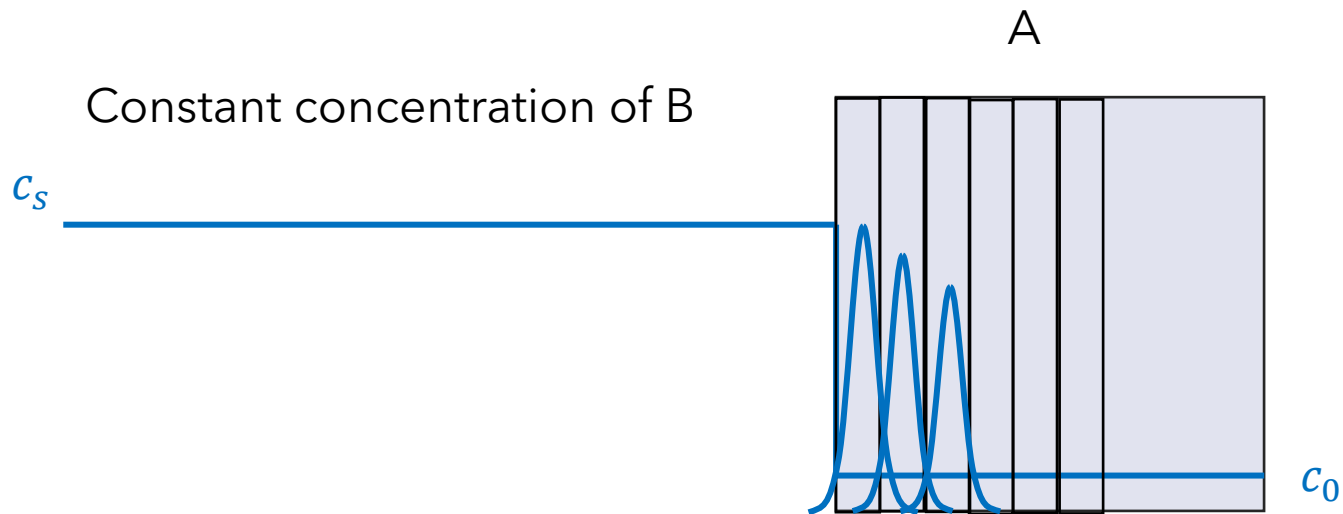
$$C(x, t) = \frac{\beta}{2\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right)$$



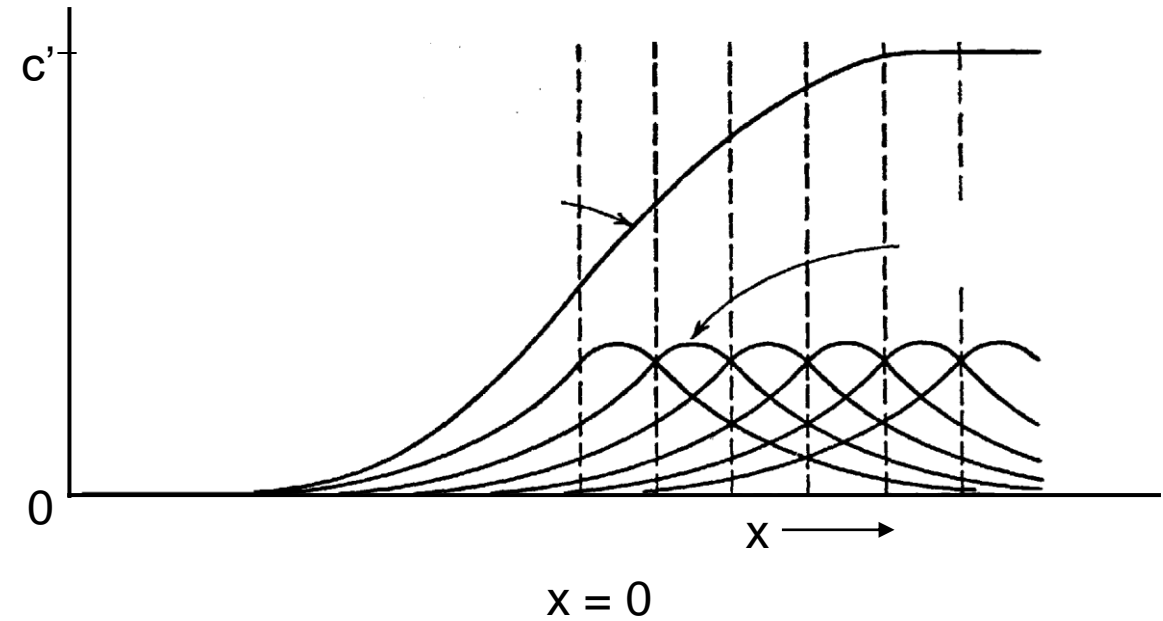
Fick's Laws of Diffusion

Composition Profile:

Particulaire case:



The solution is a sum (integral) of the solution of the thin layer problem.



$$\frac{c_s - c(x, t)}{c_s - c_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

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

Fick's Laws of Diffusion

Composition Profile: The erf function:

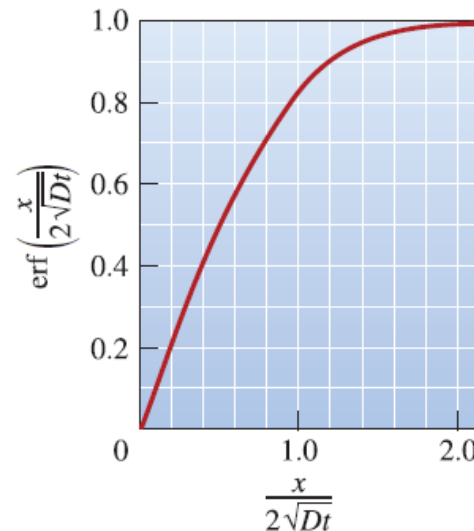
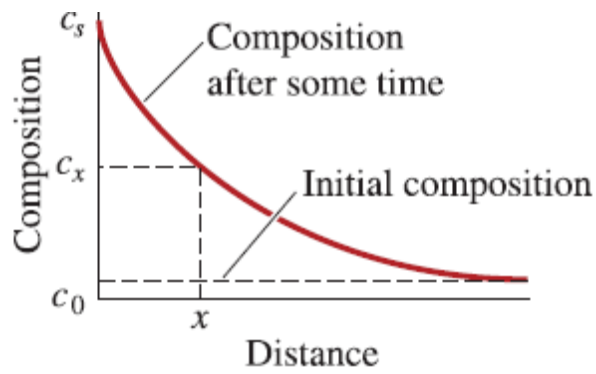
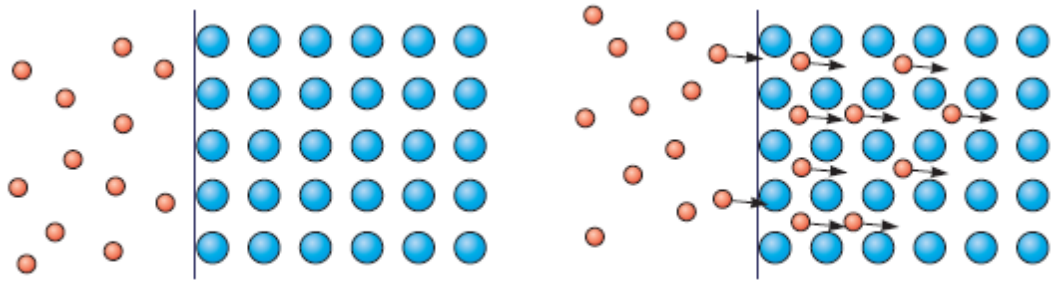


TABLE 5-3 ■ Error function values for Fick's second law

Argument of the Error Function $\frac{x}{2\sqrt{Dt}}$	Value of the Error Function $\text{erf} \frac{x}{2\sqrt{Dt}}$
0	0
0.10	0.1125
0.20	0.2227
0.30	0.3286
0.40	0.4284
0.50	0.5205
0.60	0.6039
0.70	0.6778
0.80	0.7421
0.90	0.7969
1.00	0.8427
1.50	0.9661
2.00	0.9953

Note that error function values are available on many software packages found on personal computers.

Fick's Laws of Diffusion

Composition Profile:

Example:

The surface of a 0.1% C steel gear is to be hardened by carburizing. In gas carburizing, the steel gears are placed in an atmosphere that provides 1.2% C at the surface of the steel at a high temperature. Carbon then diffuses from the surface into the steel.

For optimum properties, the steel must contain 0.45% C at a depth of 0.2 cm below the surface. Design a carburizing heat treatment that will produce these optimum properties. Assume that the temperature is high enough (at least 900°C) so that the iron has the FCC structure.

$$R = 1.987 \text{ cal/mol/K}$$



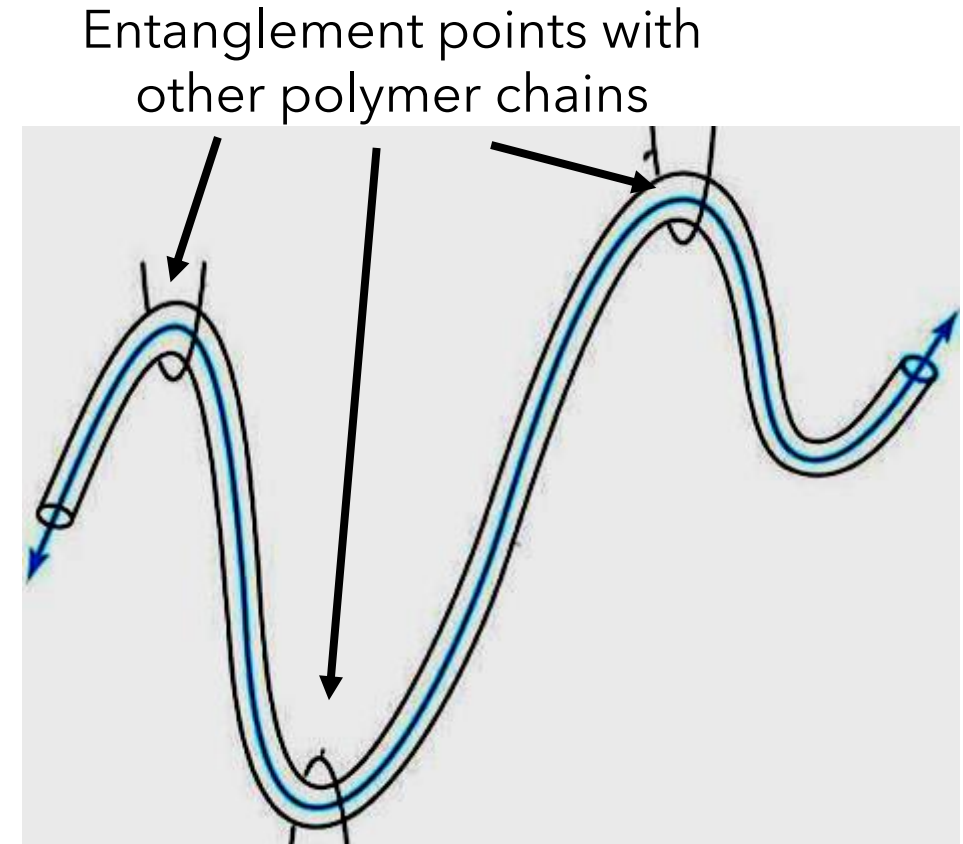
Permeability of Polymers

Permeability of Polymers

Diffusion in Polymers:

For polymers, permeability is a more important engineering parameter than diffusion coefficient.

- + It refers to the diffusion of atoms between long polymer chains.
- + Denser polymers have lower permeabilities.
- + Diffusion through a polymer is faster in amorphous polymers than in crystalline polymers.
- + Diffusion is faster for smaller diffusing species, or in polymers with many voids.
- + Permeability of polymers is an important design consideration; polymers may swell when species diffuse into them, which can be undesirable.



End of chapter

Dr. Mohamed Hassan Khalili