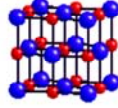
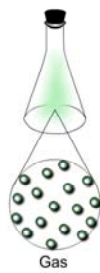


Department of Civil Engineering IIT Madras



Structure of Solids



Modern Construction Materials
– Lecture 3



Prof. Ravindra Gettu
IIT Madras

Classification of Solid Structures

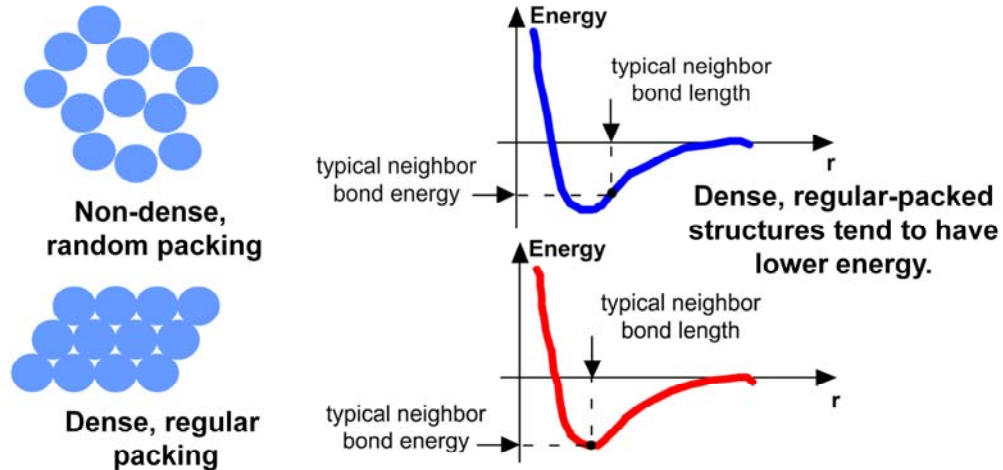
Type	Description	Examples
Ionic crystals	Close-packed array of ions (alternate M^{n+} and X^{n-})	Crystalline salts, common salt (NaCl), fluorite (CaF_2)
Metallic crystals	Close-packed array of metal cations	Iron, copper
Covalent crystals	Packing of atoms to satisfy directional covalent bonds	Diamond, silica, clay minerals
Molecular crystals	Packing of specific molecules held together by van der Waals bonds	Crystalline polyethylene, ice
Amorphous materials	Irregular packings of ions covalently bonded atoms, or distinct molecules	Metglas, soda glass, amorphous polymers
Composite materials	Particles or fibers dispersed in a continuous matrix	Fiber-reinforced plastics, portland cement concrete

Young et al.

The Crystalline State

Crystal Structure of Metals

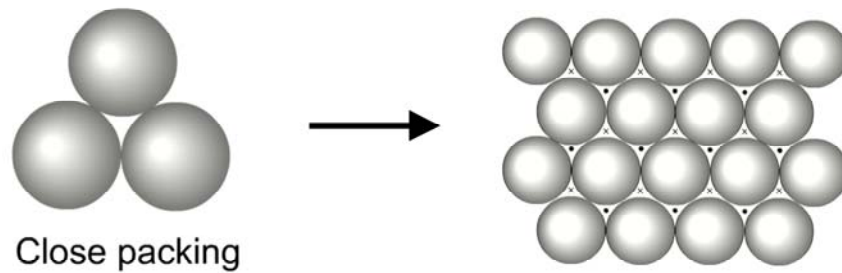
The metallic bond allows the development of crystalline structures in which ions are bound non-directionally. This leads to close-packed structures.



The Crystalline State

Crystal Structure of Metals

Let us define closely-packed structures considering the ions to be equally-sized incompressible balls:

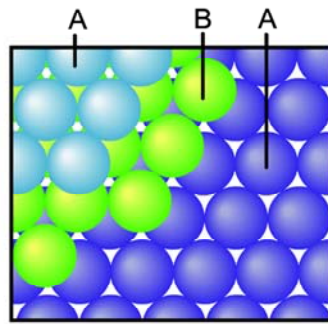


Close packing

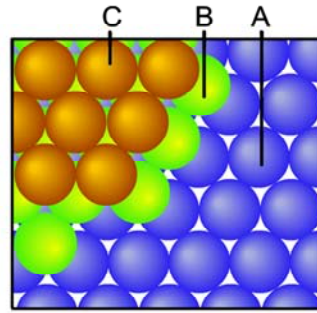
Close-packed plane of spheres

The Crystalline State

First layer of spheres A; Second layer placed with spheres over gaps BBB; Third layer can be placed (a) with spheres above AAA (gives ABABAB) or (b) in gaps CCC (gives ABCABC) – in both, 74% of space is occupied



(a)



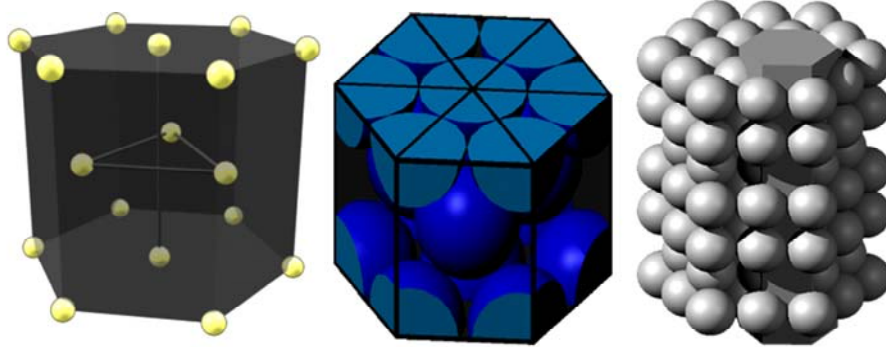
(b)

Ilston & Domone

The Crystalline State

Hexagonal Close-Packed (hcp) Structure

The ABABAB arrangement

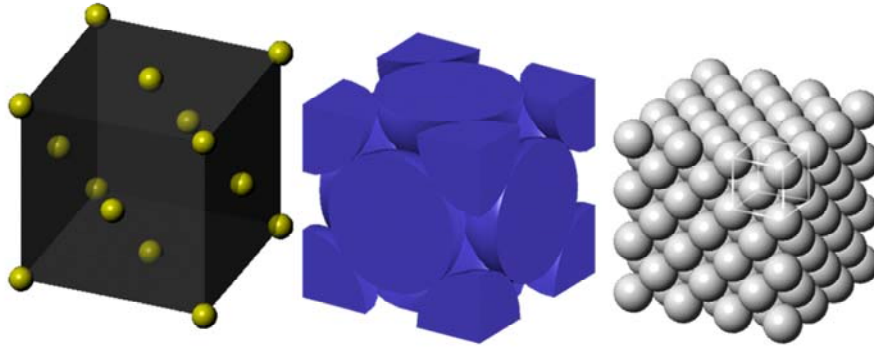


Metals crystallising in the hcp structure: magnesium, zinc, cadmium, cobalt, titanium

The Crystalline State

Face-Centred Cubic (fcc) Structure

The ABCABC arrangement

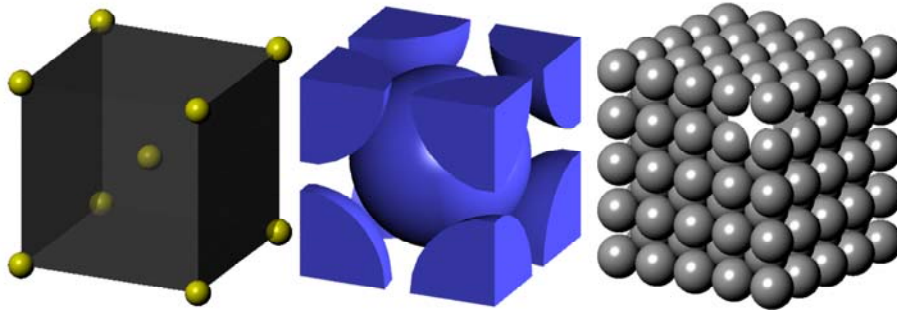


Metals crystallising in the fcc structure: aluminium, copper, nickel, iron (above 910°C), lead, silver, gold

The Crystalline State

Body-Centred Cubic (bcc) Structure

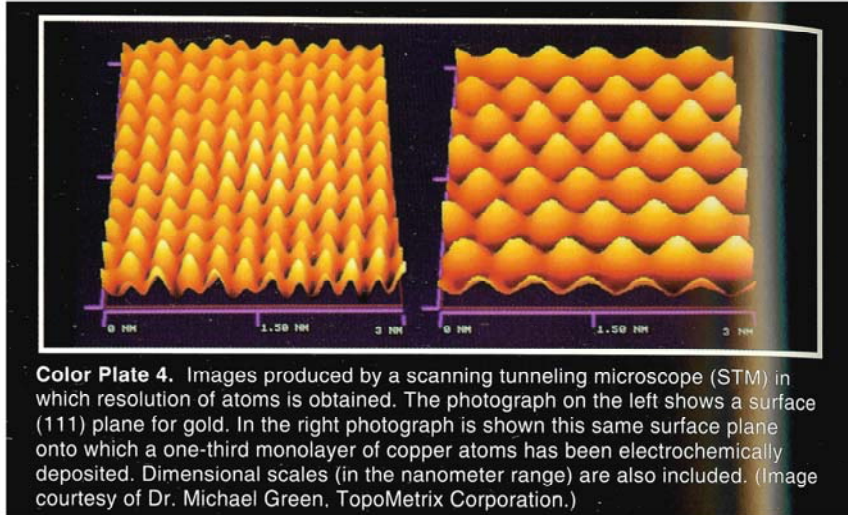
Here, the ions are not as closely-packed



Metals crystallising in the bcc structure: iron (below 910°C), chromium, molybdenum, niobium, vanadium

The Crystalline State

Atomic Structure of Metals



Callister

The Crystalline State

Why the Different Structures?

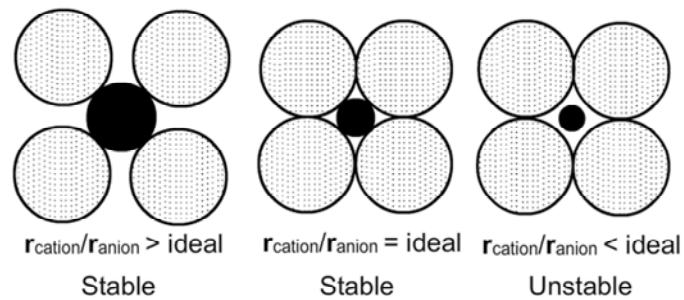
- The structure adopted is that which gives the crystal the least internal energy.
- A crystal structure that has the least energy at one temperature need not necessarily have the least energy at another temperature.
- The change in structure brought about by temperature (e.g., in iron) forms the basis of metallurgy.

Illston & Domone

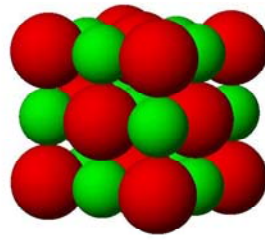
The Crystalline State

Ionic Solids: Ions of the same charge

- Ionic crystal structures are packed arrays of anions with cations located in the holes of the array.
- The geometries depend on the radius ratio,
 $R = r_{\text{cation}} / r_{\text{anion}}$



The Crystalline State



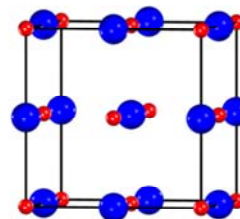
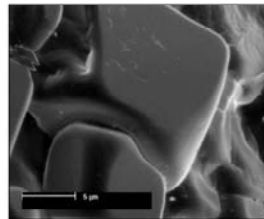
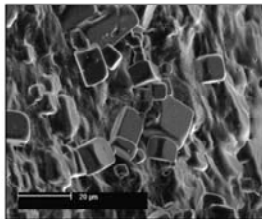
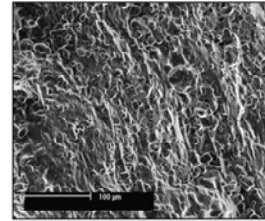
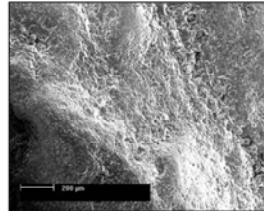
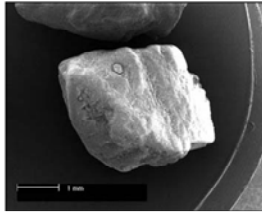
NaCl cell

- The most stable crystal structures are those where the ions are surrounded by as many neighbours of the opposite charge as possible, since this increases the total binding energy.

Young et al.

The Crystalline State

Ionic Solids: Microstructure of Sea Salt (NaCl+I+K)



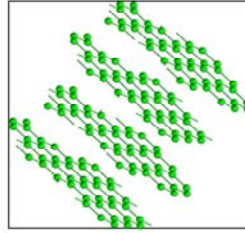
Electron Microscope: Manchester Materials Science Center

The Crystalline State

Covalent Solids

- The directional nature of bonding is typical of covalent structures.
- The solid is often formed by chains or sheets held together by weak van der Waal or hydrogen bonds.

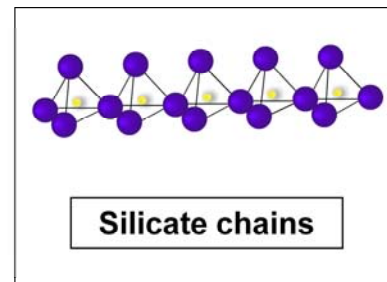
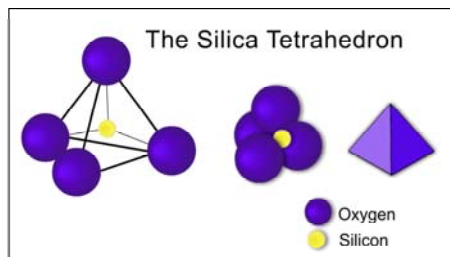
The Crystalline State



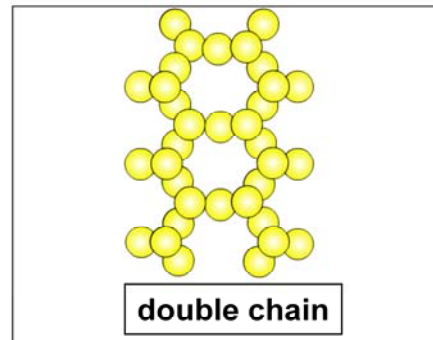
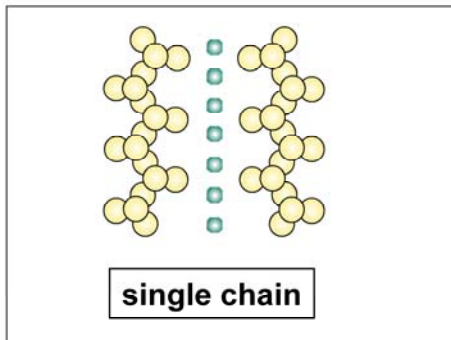
- Graphite is composed of covalently bonded sheets held together by van der Waal forces.
- The weak intersheet bonding leads to the softness of graphite (compared to diamond); graphite is an excellent dry lubricant.
- Graphite is a good conductor of electricity in two-dimensions.

Silica and Silicates

- The silicate tetrahedron is the basic repeating structure of silica and the silicates. The tetravalent silicon ion is surrounded by 4 oxygen anions, resulting in $(\text{SiO}_4)^{4-}$.
- The negative charge is neutralized when the oxygen anions are shared with other silicate tetrahedra or other cations.



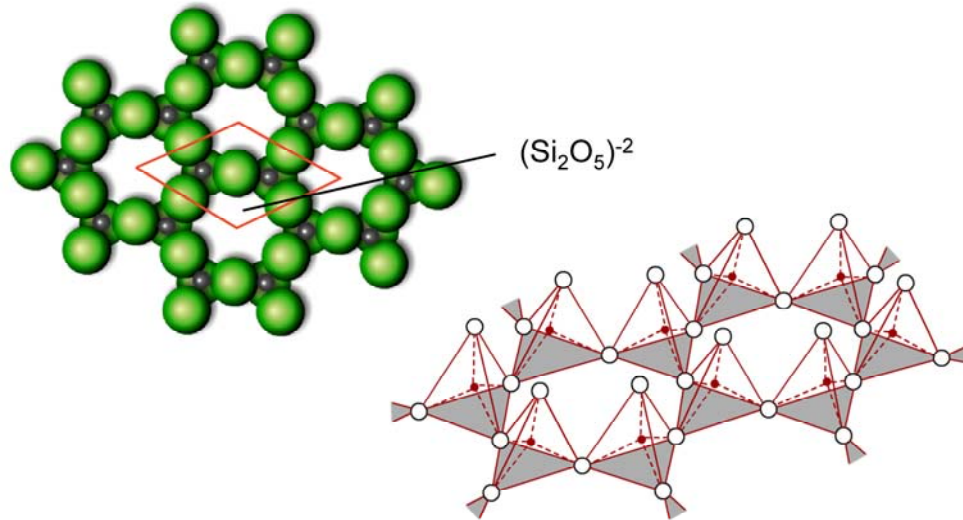
Silica and Silicates



Certain double chain silicate structures form long thin crystals that can be bent and made into fabric, such as asbestos.

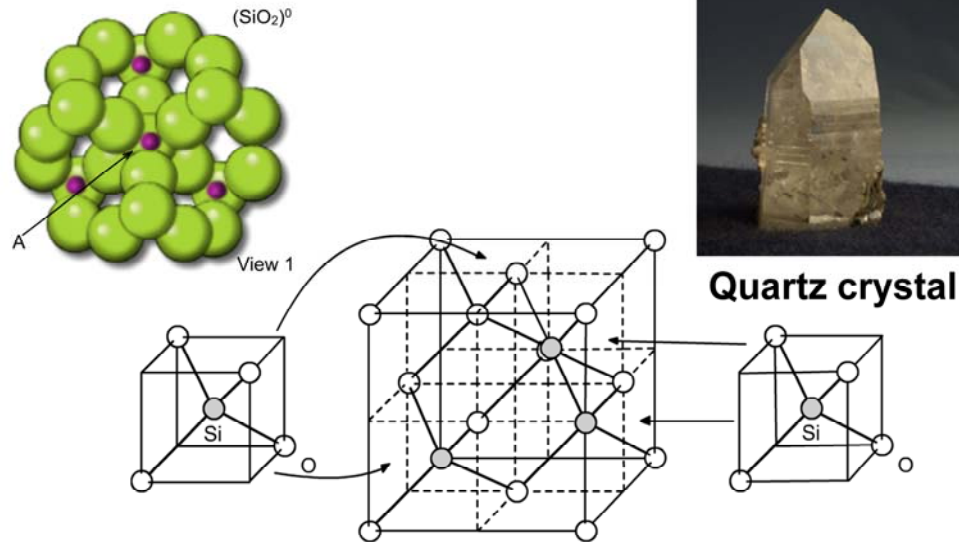
Silica and Silicates

- In silicate sheets, each tetrahedron shares three oxygen ions with its neighbours.

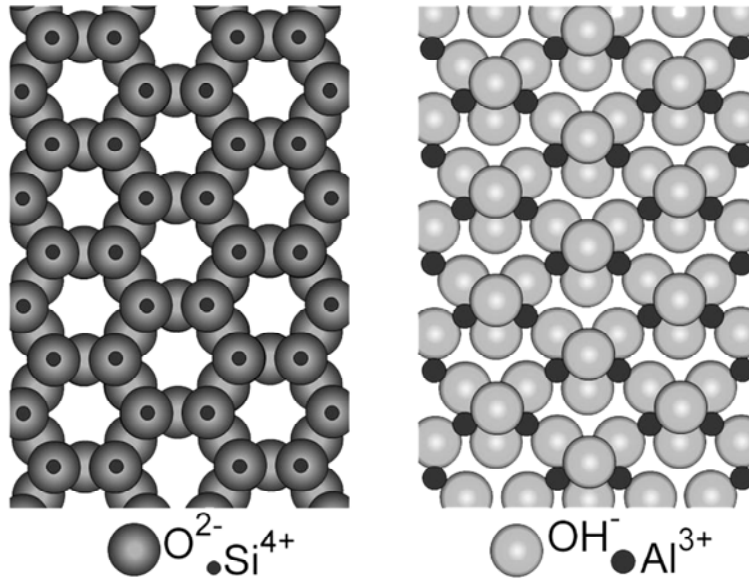


Silica and Silicates

- By sharing all the oxygen ions, three-dimensional lattices can be formed, as in quartz.



Structure of Kaolinite (A type of clay)

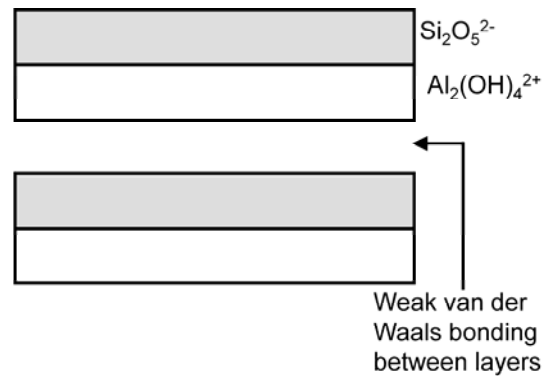


Typical “two-layer” clay

Structure of Kaolinite

- Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ can be visualised as having layers of tetrahedral $[\text{Si}_2\text{O}_5]^{2-}$ fitting together with layers of octahedral $[\text{Al}_2(\text{OH})_4]^{2+}$ through ionic bonds.
- The charge and the geometry of the two sheets match perfectly to form 0.7 nm thick sheets.
- The sheets are bound to each other by van der Waal forces.

Structure of Kaolinite



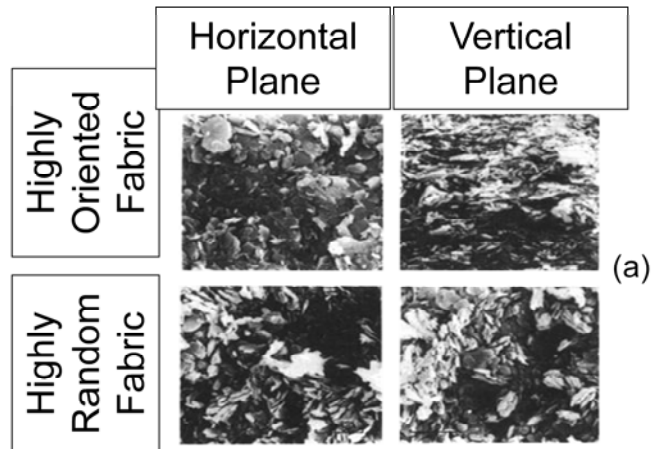
- Kaolinite crystallises as flat sheets. It does not absorb water but adsorbs it as a thin external layer.
- Halloysite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}]$ has a similar structure but with water between the sheets.

Young et al.

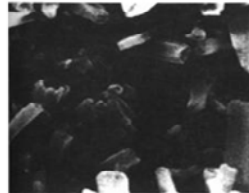
Structure of Kaolinite

Scanning Electron Micrographs

*a: Kaolinite
crystallises as
flat sheets.*



*b: Halloysite sheets are
rolled into tubes.*



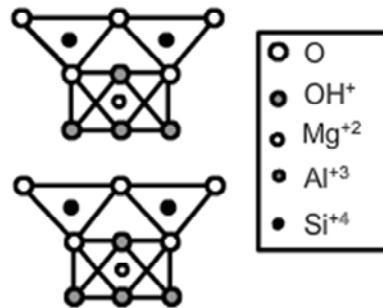
(b)

Bowles

Main Classes of Clays

Kandites such as Kaolinite and Halloysite have two-layer structures (T-O), with no charge imbalance. Interlayer bonding is through weak van der Waals forces.

Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

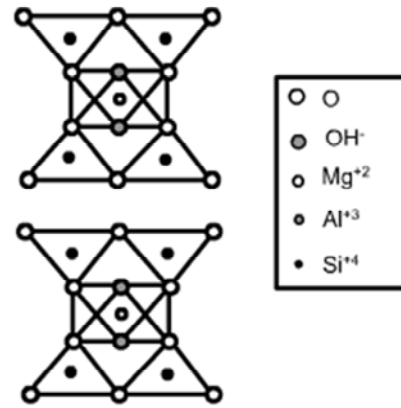


Main Classes of Clays

Smectites such as Pyrophyllite and Montmorillinite have three-layer structures (T-O-T), with some charge imbalance.

These clays readily adsorb water between the layers, which generally reduces the strength and causes swelling.

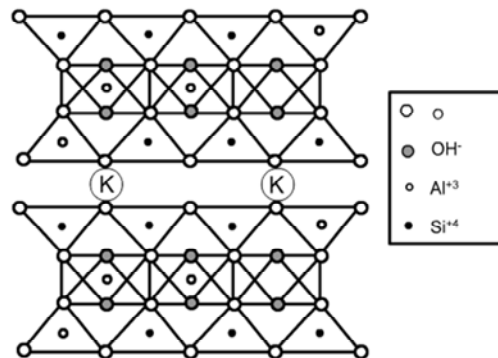
Pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$



Main Classes of Clays

Illites like Muscovite are three-layered (T-O-T) with K, Ca, or Mg interlayer cations, which prevent the entrance of water into the structure. Therefore, these clays are non-expanding.

Muscovite $\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$



Features of Flat Sheet Structures

- Clay crystallises as flat plates that cleave easily along the weakly bonded plane.
- Similarly, mica can be cleaved into very thin sheets.
- Dry clay (and talc) has a slippery feel due to the plates sliding across one another.

Young et al.

Polycrystalline Structure

Most crystalline solids are composed of a collection of small crystals; such materials are called polycrystalline.

Solidification of a polycrystalline material

Various stages of solidification:

(a) small nuclei,

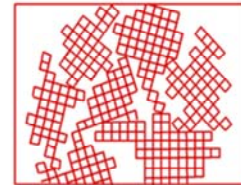
(b) growth of crystallites,

(c) growth of crystals as solidification continues, and

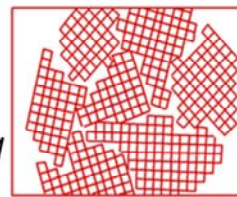
(d) solidified material showing grains and grain boundaries.



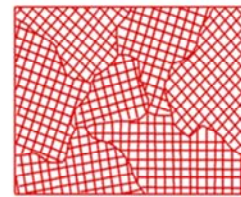
(a)



(b)



(c)



(d)

Polycrystalline Structure

**Aluminium ingot
(about 5 cm wide)**



Polycrystalline Structure



Color Plate 6. Photomicrograph of a polycrystalline alpha brass. The specimen was tint-etched after a light pre-etch in order to produce the multicolored grains and twins. 100X. Courtesy of George F. Vander Voort, Carpenter Technology Corporation.)

Callister

Defects in Crystals

Classification of Crystal Defects

Type	Specific Examples	Influence on Material Properties
Point	Interstitial	Solid solution strengthening
	Substitutional	Swelling of clays
Line	Dislocations	Ductility in metals Work hardening
Surface	Grain boundaries	Grain size strengthening
Volume	Pores	Sites of stress concentrations and crack initiation
	Inclusions	Precipitation hardening

Defects in Crystals

- Point defects are points in a crystal lattice where an atom is missing, an extra atom is present or an atom of different size replaces the expected atom.
- Line defects are imperfections in a crystal lattice in which a line of atoms become mismatched with their surroundings.
- Surface defects are areas of defect concentrations in the interfacial zone between crystals.
- Volume defects are three-dimensional regions of defects (i.e., voids and inclusions).

Young et al.

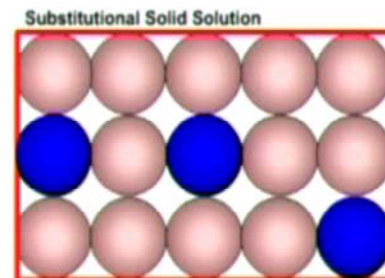
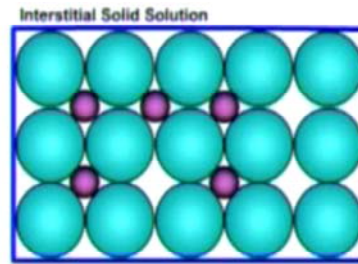
Point Defects in Crystals

Solid Solutions or Alloys

Some elements dissolve in the basic metal to form solid solutions.

There are two principal classes of solid solutions:

- Interstitial (small atoms fit into the spaces between the larger atoms)
- Substitutional (some atoms of the host metal are replaced by other atoms of similar size and chemistry).



Illyson & Domone

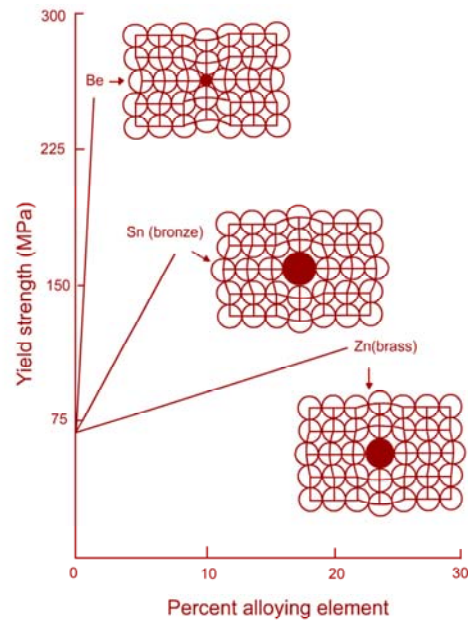
Point Defects in Crystals

- These defects distort the surrounding lattice. The additional strain increases the energy of the crystal (i.e., lowers the lattice binding energy). Therefore, the number of point defects that can occur is limited before the crystal becomes unstable.
- However, point defects lead to the strengthening of alloys.

Point Defects in Crystals

Strengthening of pure copper through alloying with substitutional atoms.

The greater the mismatch in atomic size, greater the strengthening effect (because slip planes become rougher).

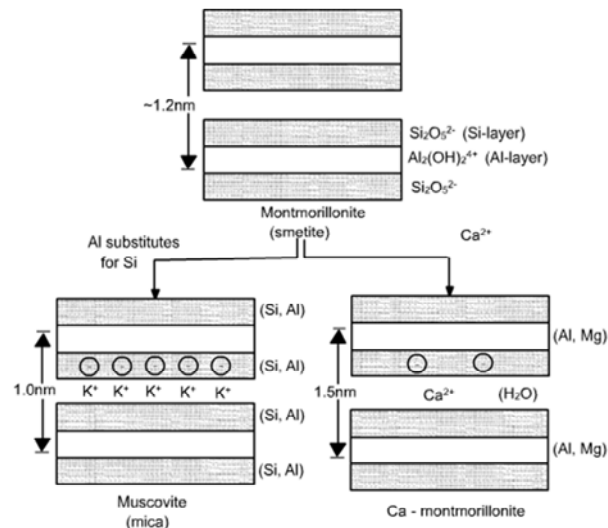


Young et al.

Point Defects in Crystals

- Point defects can also lead to charge imbalance, where an ion of one charge substitutes for an ion with a different charge.

- Consider a smectite that is made up of SiO_2 and $\text{Al}(\text{OH})_3$ sheets that combine to give polar but electroneutral layers.



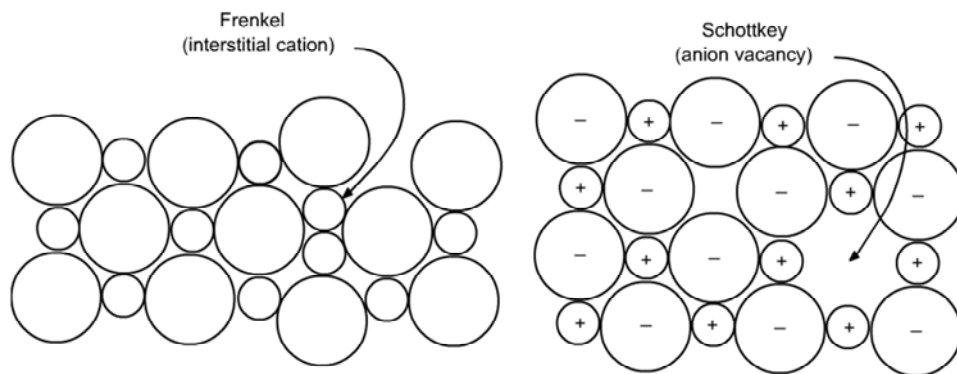
Point Defects in Crystals

- *Partial substitution of aluminium in the silicate sheets leaves the layer with a negative charge since Al^{3+} replaces Si^{4+} . Therefore, external cations must be located between the layers to balance the charges.*
- *The size and charge of the interlayer cations determines the distance between the layers and the extent to which water can enter.*

Young et al.

Point Defects in Crystals

Frequently, point defects occur in pairs to avoid charge imbalances. This also leads to the minimisation of the strain within the crystal lattice caused by the defects.



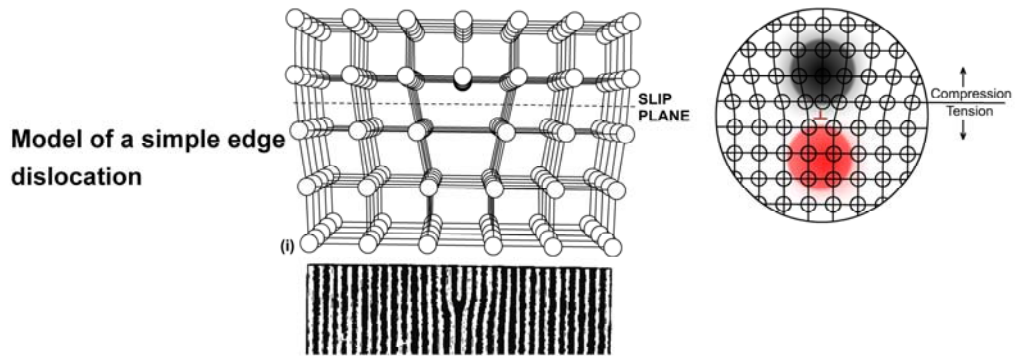
Young et al.

Line Defects in Crystals

- These are imperfections in a crystal lattice where a line of atoms becomes mismatched with their surroundings.
- Line defects are called dislocations.

Line Defects in Crystals

Edge dislocation: Formed by the addition of an extra partial plane of atoms in the lattice

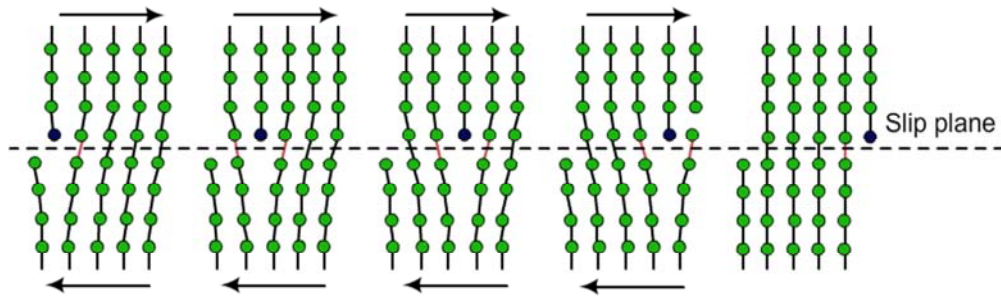


Crystallographic planes showing dislocation in aluminium
at a magnification of several millions

Ilston & Domone, Callister

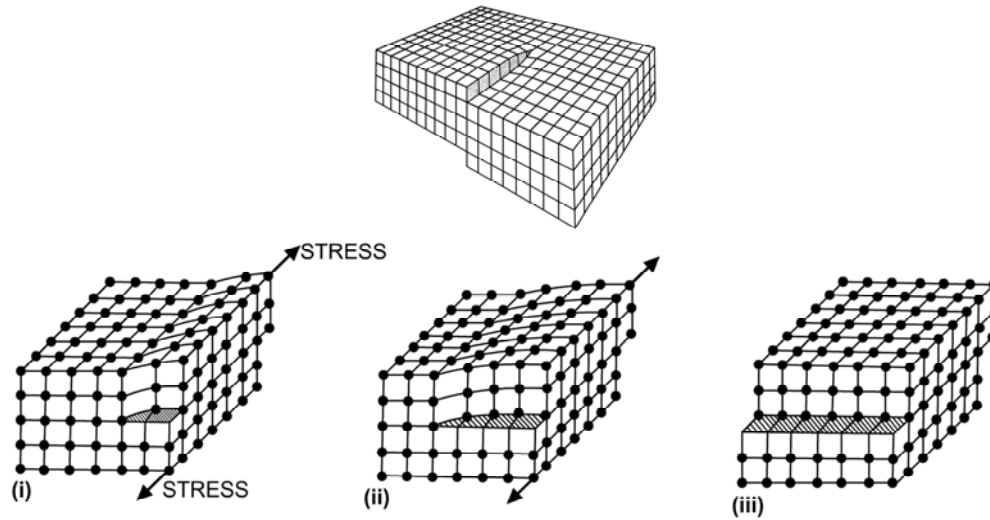
Line Defects in Crystals

Movement of an edge dislocation



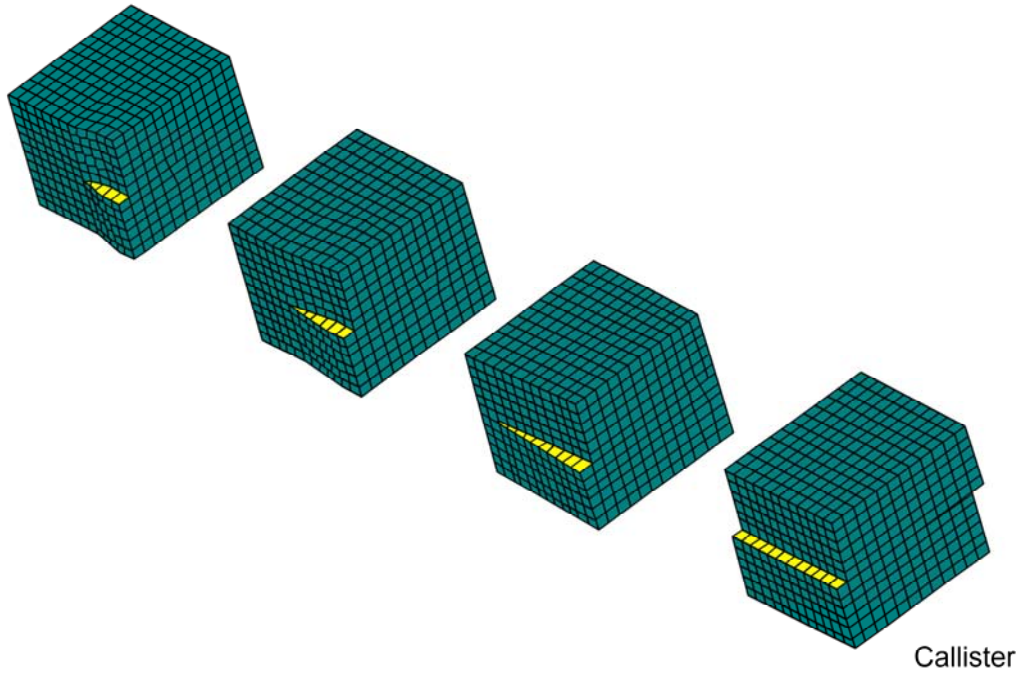
Line Defects

Screw dislocation: A region of distorted crystal lattice in the form of a spiral ramp of atoms.

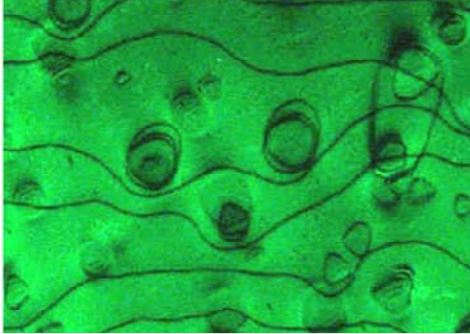


Movement of a screw dislocation

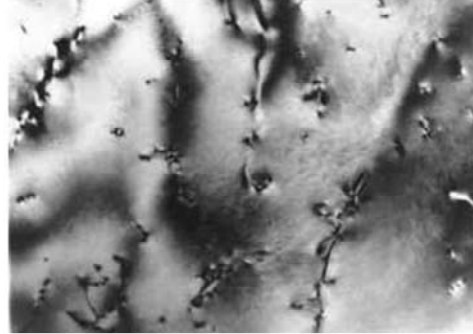
Line Defects: Mixed Dislocations



Line Defects: Dislocations



Nickel

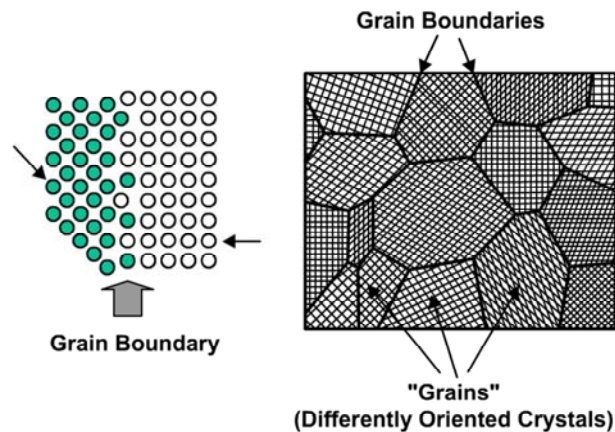


Aluminium

Electron Microscopy: Manchester Materials Science Centre

Plane Defects in Polycrystalline Solids

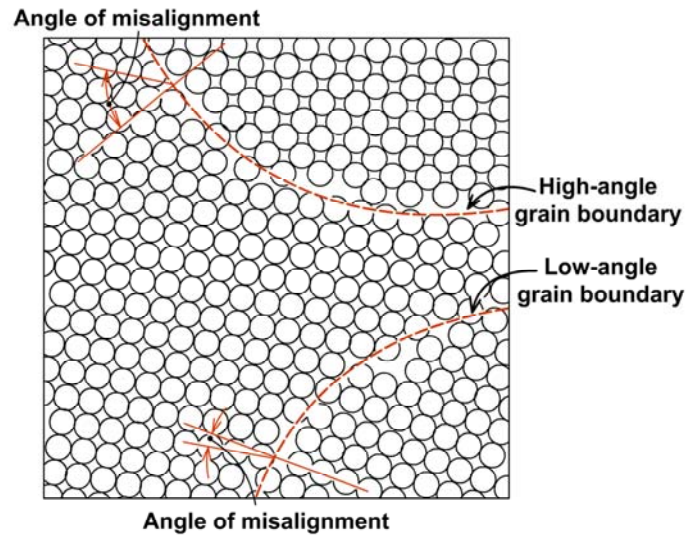
The interfacial zone between different crystals, called the grain boundary, represents an area of defect concentrations within the solid. This occurs because the orientation of atoms is different in each crystal.



Plane Defects: Grain Boundaries

Various degrees of crystallographic misalignment between adjacent grains are possible.

Not all atoms at the grain boundary are bonded to other atoms.



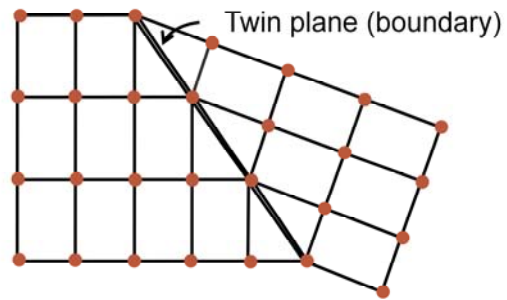
Plane Defects: Grain Boundaries

- Consequently, there is an interfacial or grain boundary energy, the magnitude of which depends on the angle of misalignment.
- Due to this interfacial energy, the atoms at the grain boundary are chemically more active than those within the grain. Also, impurity atoms tend to segregate along the interfaces.

Callister

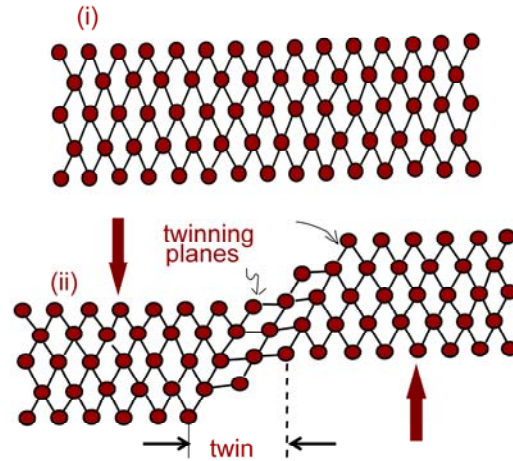
Plane Defects in Polycrystalline Solids

- A twin boundary is a special grain boundary across which there is a specific mirror lattice symmetry. The region of material between the these boundaries is called a twin.



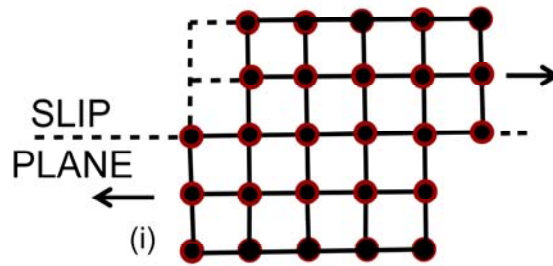
Plane Defects in Polycrystalline Solids

- Twins can occur due to the application of shear forces or heat.

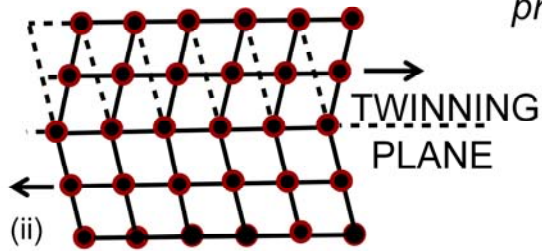


Deformation by twinning (due to stress)

Plane Defects in Polycrystalline Solids



The stress required to produce twinning tends to be higher than that required to produce slip.



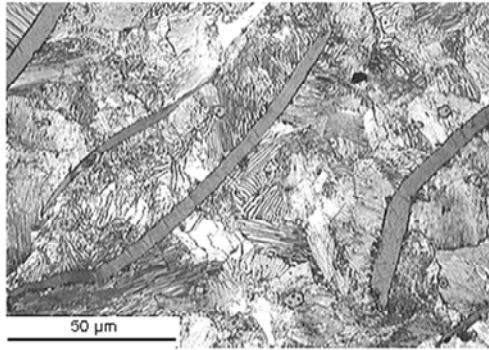
Difference between (i) slip and (ii) twinning

Higgins, Callister

Volume Defects in the Crystal Structure

- Three-dimensional regions of defects, called volume defects, are voids and inclusions; they are considered to be external to the crystal structure.
- Voids are small pores left by incomplete filling of the available space.
- Inclusions are regions of a second phase contained wholly within a single grain.

Volume Defects in the Crystal Structure



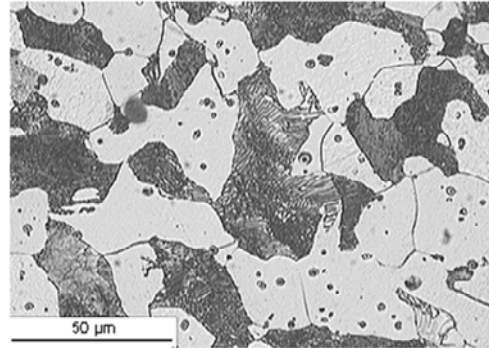
**Microstructure of Grey
Cast Iron**

This is an alloy of iron (Fe) with 4% carbon (C), by weight. The microstructure has two main constituents. The long pale regions are flakes of graphite. The background or matrix of the alloy is pearlite. This is a fine mixture of ferrite and iron carbide, which is seen as a "wormy" texture.

Electron microscopy: Manchester Materials Science Centre

Volume Defects in the Crystal Structure

This is a low carbon steel, with about 0.1% C, by weight, alloyed with iron. It has two major constituents, which are ferrite (light-coloured) and pearlite. The small spots within the ferrite grains are inclusions or impurities such as oxides and sulphides.

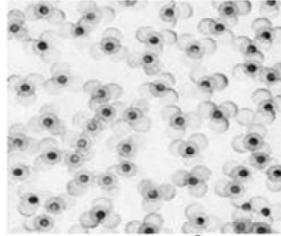


Microstructure of Mild Steel

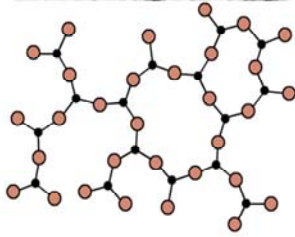
Electron microscopy: Manchester Materials Science Centre

The Amorphous State

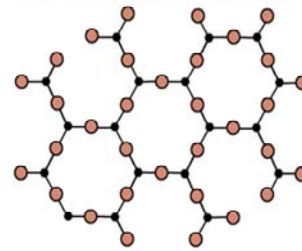
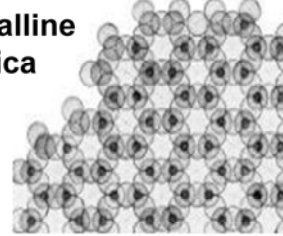
When the regularity of atomic packing is completely absent, a solid is said to be non-crystalline or amorphous.



Amorphous
Silica



Crystalline
Silica



- Silicon atom
- Oxygen atom

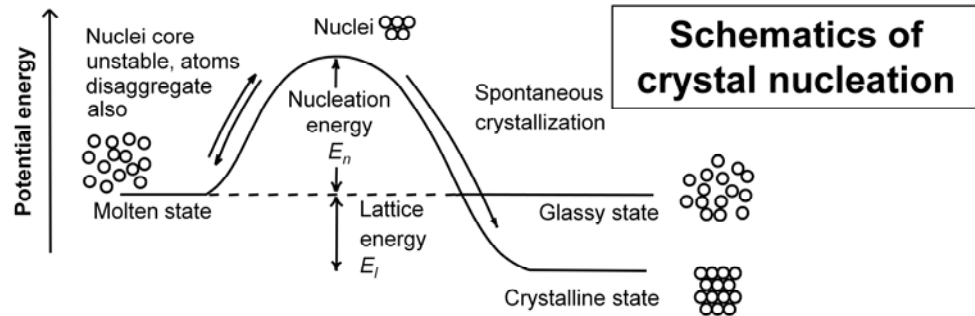
The most familiar kind of amorphous solids are glasses.

Young et al.

The Amorphous State: *Glasses*

- Glasses form from melts when the rate of cooling is too fast to allow nucleation and growth of ordered crystals.
- For a crystal to grow, enough atoms must come together in the right packing to create an energy minimum. Until this happens, energy will have to be used to overcome the mutual repulsion.
- This results in a nucleation energy barrier that must be overcome before crystal growth can occur. Thermal energy can help atoms to overcome the nucleation barrier.

The Amorphous State: Glasses



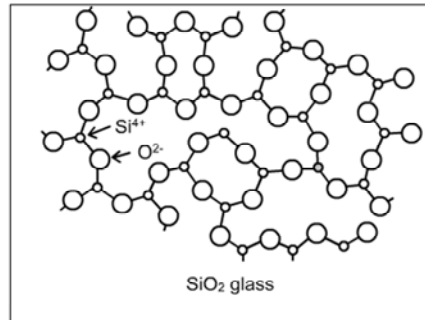
Thermal energy (E_t)

- $E_t \gg E_n$ Rapid spontaneous nucleation occurs.
- $E_t \approx E_n$ Nucleation occurs if cooling is slow;
glass formation if cooling is rapid.
- $E_t \ll E_n$ Glass formation will occur

Young et al.

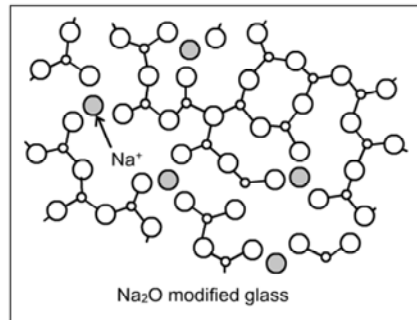
The Amorphous State: *Glasses*

- Although they have random packings, glasses can be considered in terms of ideal, defect-free structures.



- Fused silica has a random arrangement of silica tetrahedra.

The Amorphous State: Glasses



- In soda glass, this arrangement is disrupted by the presence of sodium ions: some Si-O-Si bonds are replaced by Si-O-Na⁺ bonds.
- Soda glass has a lower binding energy and melts at a lower temperature than fused silica (~600°C versus 1200°C).

Young et al.

The Amorphous State: *Metallic Glasses*

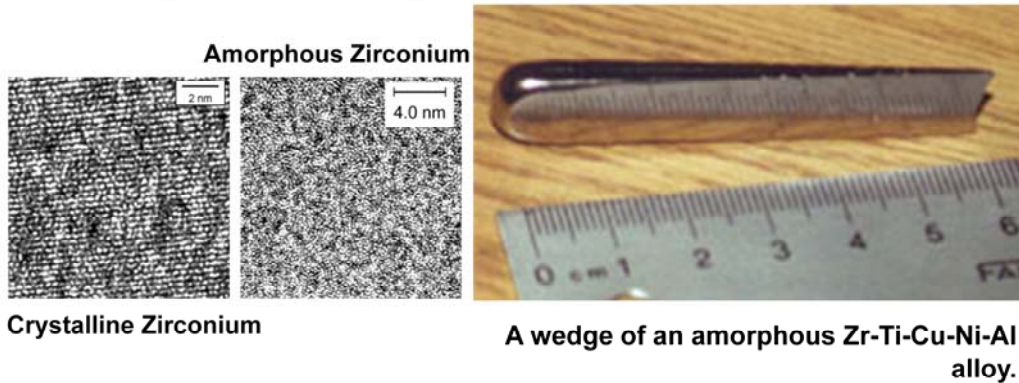
- Most metallic materials have a crystalline structure consisting of single crystal grains of varying size arranged in a microstructure. Such structures are produced by the nucleation and growth of crystalline phases from the molten alloy during solidification.
- Some researchers have recently developed multicomponent metal alloys which vitrify with the same ease as observed in silicate melts. These bulk metallic glasses (BMGs) have unusual properties. They are typically much stronger than their crystalline metal counterparts (by factors of 2 or 3), are quite tough (much more so than ceramics), and have very high strain limits for elasticity.

The Amorphous State: *Metallic Glasses*

- It is quite unusual for a metallic material to be amorphous. The trick to making a metallic glass is to cool the metallic liquid (which has a disordered structure as well) down so rapidly that there is not enough time for the ordered, crystalline structure to develop.
- Liquid metals and alloys crystallize so rapidly on cooling that it was not until 1960 that the first true metallic glass, an alloy of gold and silicon ($\text{Au}_{80}\text{Si}_{20}$) was obtained by a method capable of achieving rates of cooling of the order of 2×10^6 °C per second.

The Amorphous State: *Metallic Glasses*

- More recently, new alloys have been developed that form glasses at much lower cooling rates, around 1-100 degrees per second. While still fairly rapid, it is slow enough to cast bulk ingots of these metallic alloys, and solidify them to form glasses.

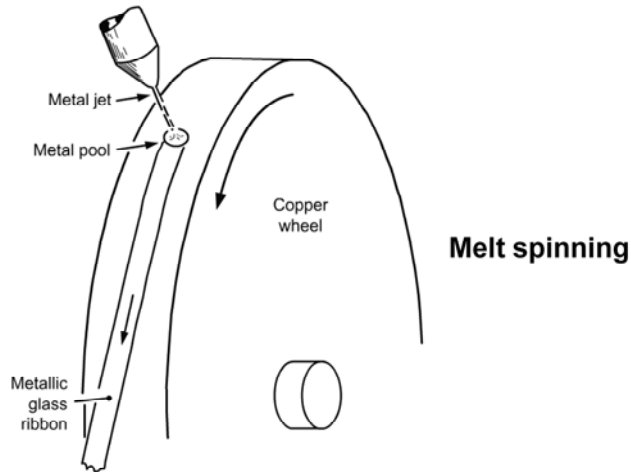


The Amorphous State: *Metallic Glasses*

- Metallic glasses having magnetic properties are typically iron-rich amorphous solids with compositions such as $\text{Fe}_{0.8}\text{B}_{0.2}$ (iron-boron) and $\text{Fe}_{0.8}\text{B}_{0.1}\text{Si}_{0.1}$ (iron-boron-silicon).
- They are readily formed as long metallic glass ribbons by techniques such as melt spinning, where a jet of molten metal is propelled against the moving surface of a cold, rotating copper cylinder.

The Amorphous State: *Metallic Glasses*

- A solid film of metallic glass is spun off as a continuous ribbon at a speed that can exceed a kilometre per minute.

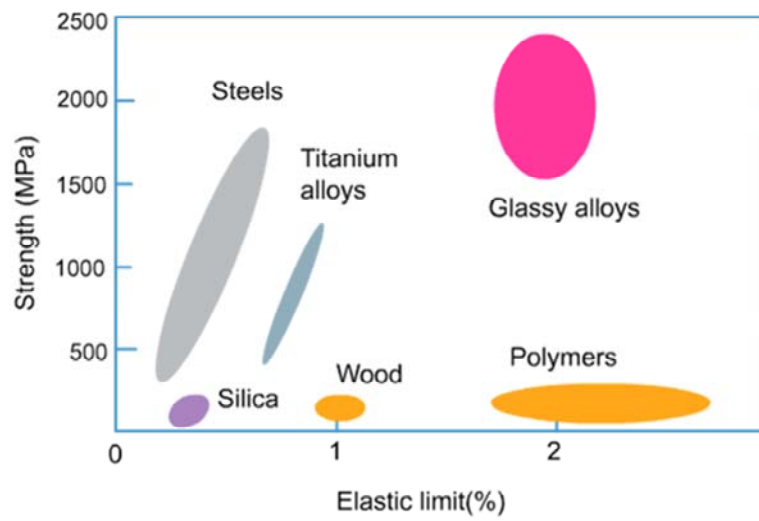


Higgins

The Amorphous State: *Metallic Glasses*

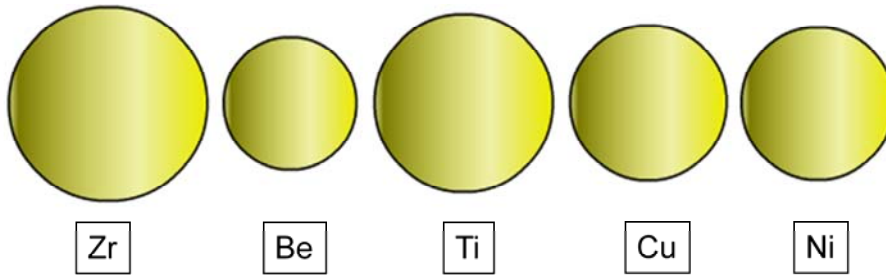
- Metallic glasses can be quite strong yet highly elastic, and they can also be quite tough (resistant to fracture).
- Even more interesting are the thermal properties; for instance, just like an oxide glass, there is a temperature (called the “glass transition temperature”, T_g) above which a metallic glass becomes quite soft and flows easily.
- This means that there are lots of opportunities for easily forming metallic glasses into complex shapes.

The Amorphous State: *Metallic Glasses*



The Amorphous State: *Metallic Glasses*

- Liquidmetal® is a metallic glass containing five elements, with the elemental composition is 41.2% zirconium, 22.5% beryllium, 13.8% titanium, 12.5% copper, and 10.0% nickel.



The Amorphous State: *Metallic Glasses*

- Because of the varying sizes of these atoms, and their random arrangement in the solid, there are no groups of atoms that can easily move past one another. One consequence of this atomic gridlock, is that some amorphous metals are very hard.



The Amorphous State: *Precipitates*

- Another kind of amorphous material is that formed by the rapid precipitation of solids from solution.
- Amorphous precipitates are a collection of individual particles (which may, however, strongly agglomerate).
- The precipitate forms a solid matrix with packed particles. The microstructures are severely defected, with high concentrations of planar and volumetric defects.

The Amorphous State: *Precipitates*

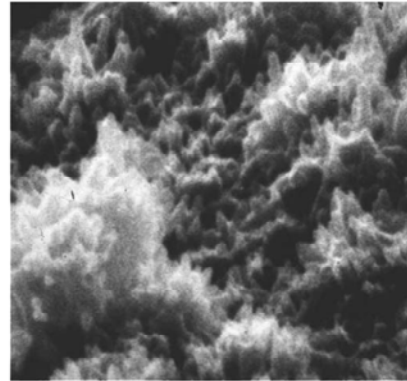
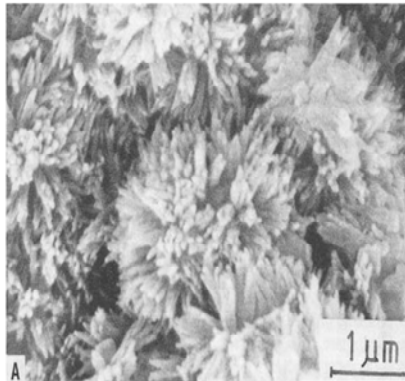
The high surface areas of amorphous precipitates lead to significant van der Waals interactions between adjacent particles, which can cause gelling.

Young et al.

Amorphous Precipitates: *C-S-H* gel

Hydrated calcium silicate (formed by the reaction of portland cement with water) is an amorphous precipitate.

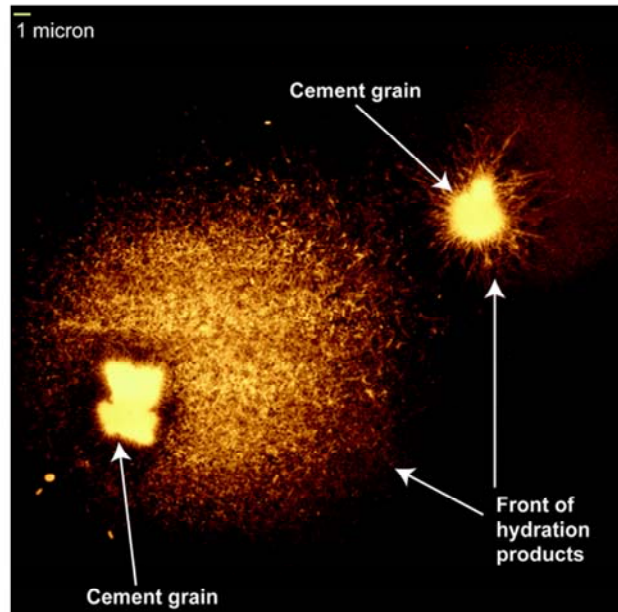
Calcium Silicate Hydrate



Taylor; Mehta and Monteiro

Amorphous Precipitates: *C-S-H* gel

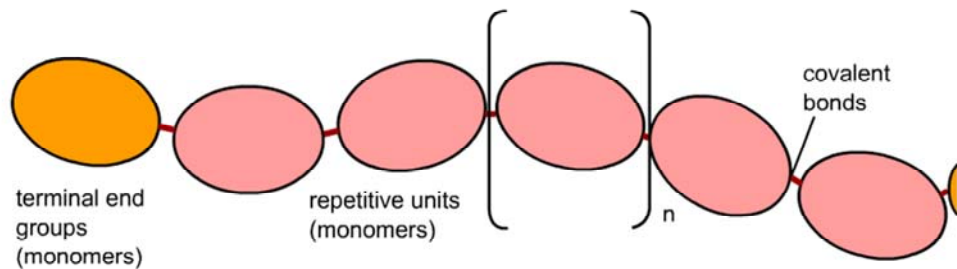
Initial formation of
hydrates during the
reaction of cement
and water, as
observed through
Soft X-ray
Microscopy



www.ce.berkeley.edu/~paulmont/ASCE.tif

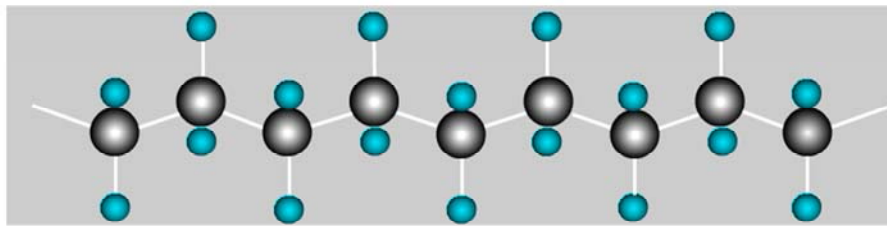
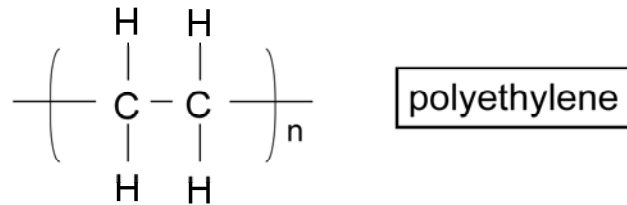
The Polymeric State

- Polymers are large molecules that are composed of a large number of repeating units (monomers). The monomers react chemically with each other to form extended molecular chains containing several hundred to several thousand monomer units.



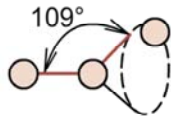
The Polymeric State

- Most monomers are organic compounds, and the typical polymer is, therefore, characterized by a carbon chain backbone.

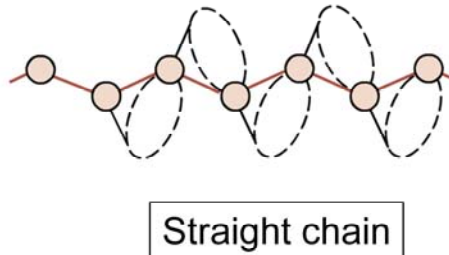
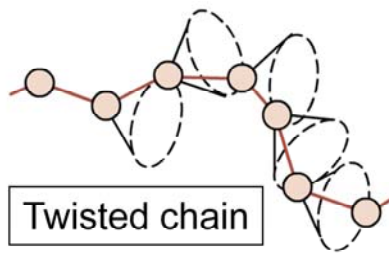


The Polymeric State

- An important characteristic of the carbon backbone is the tetrahedral bonding configuration, which allows largely free rotation of one segment of the carbon backbone relative to another.

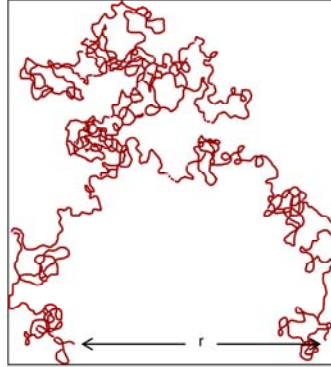


Right-most atom can be anywhere
on the dashed circle



The Polymeric State

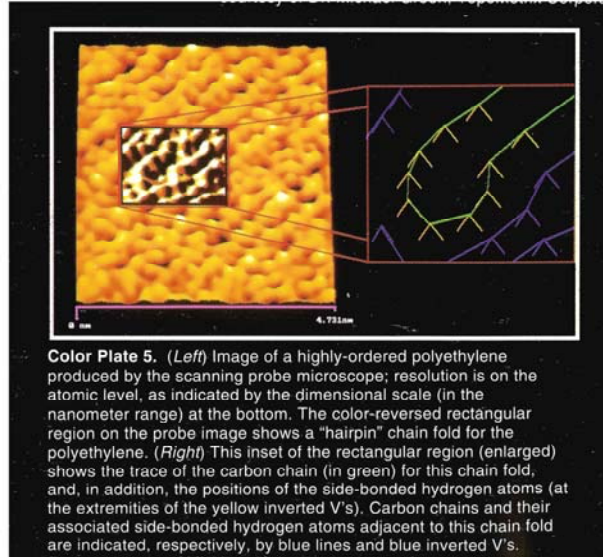
- Single chains are capable of rotation and bending in three dimensions.
- Entanglement of chains prevents crystallisation and causes high viscosity in the liquid state.



Callister

The Polymeric State

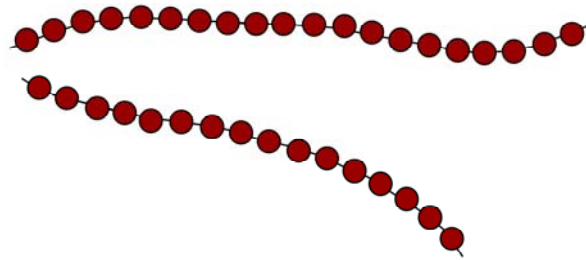
Structure of Polyethylene



Callister

The Polymeric State: *Molecular Structure*

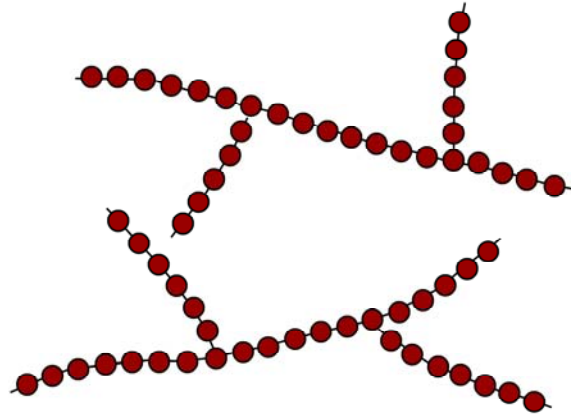
- **Linear polymers:** Long, flexible chains; Extensive van der Waals bonding between chains.
E.g., polyethylene, polyvinyl chloride, polystyrene, polymethyl methacrylate and nylon.



Callister

The Polymeric State: *Molecular Structure*

- **Branched polymers:** Polymers with side branches connected to main ones. The branches result from side reactions during the polymerisation. The chain packing is reduced and the density of the polymer is lower.

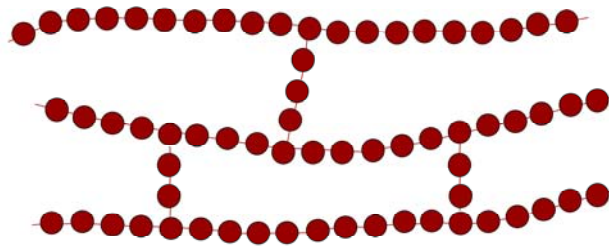


Callister

The Polymeric State: *Molecular Structure*

- **Cross-linked polymers:** Adjacent linear chains are joined to one another by covalent bonds. This cross-linking is achieved by additive atoms or molecules that are covalently bonded to the chains.

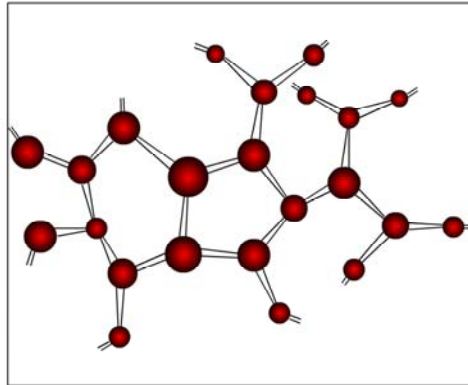
E.g., rubbery elastic materials.



Callister

The Polymeric State: *Molecular Structure*

- **Network polymers:** Trifunctional *mer* units, having three active covalent bonds, form three-dimensional networks. E.g., epoxies.



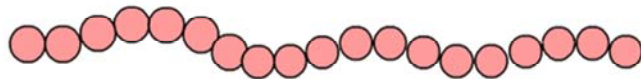
Callister

The Polymeric State

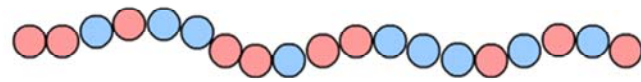
Major Classes of Polymers

(a) **Thermoplasts** (will melt under high temperatures)

- Polymers derived from single monomers are homopolymers.
- When different monomers are used in the synthesis of a polymer, it is called a copolymer.



homopolymer



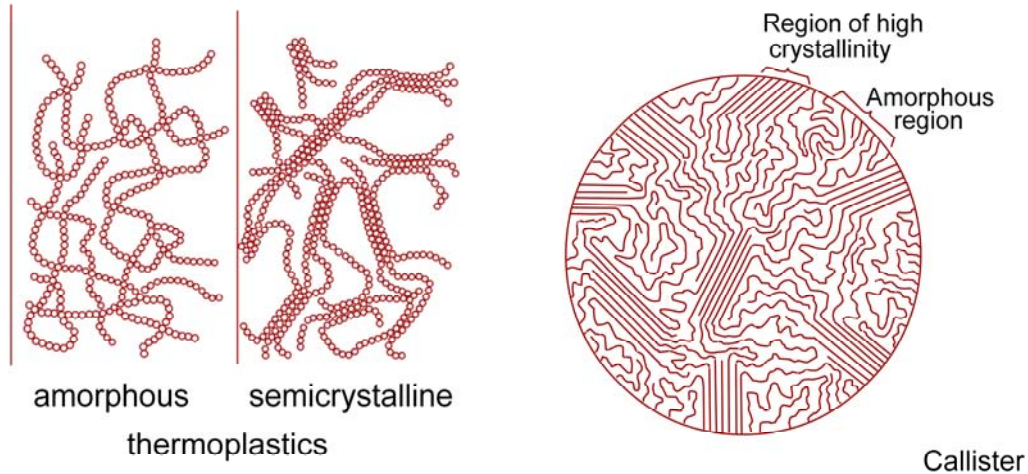
Statistical
copolymer



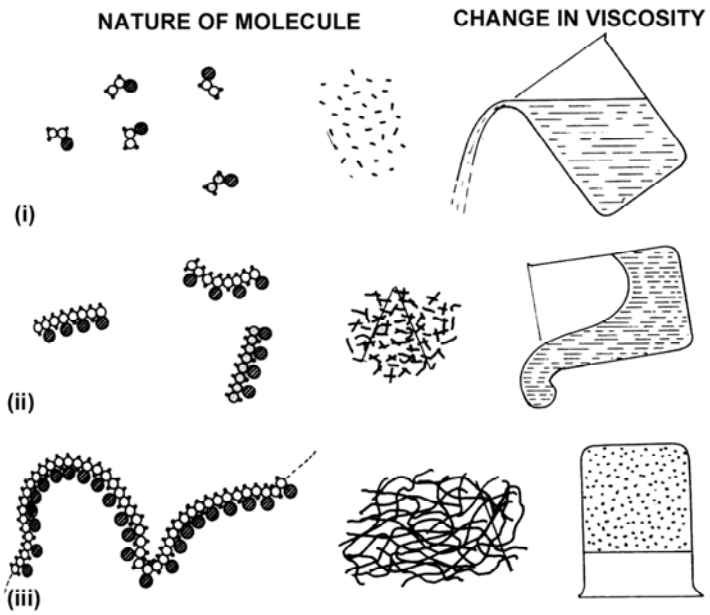
Block- copolymer

The Polymeric State

- The crystalline state may exist in polymeric materials.
- Polymer crystallinity is the packing of molecular chains to give an ordered atomic array.



Thermoplastics: *Polymerisation*

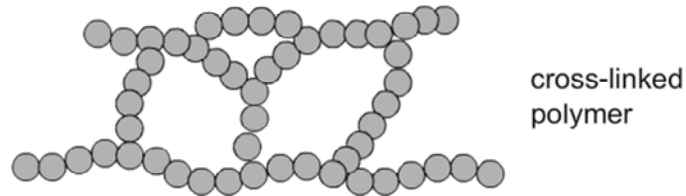


Higgins

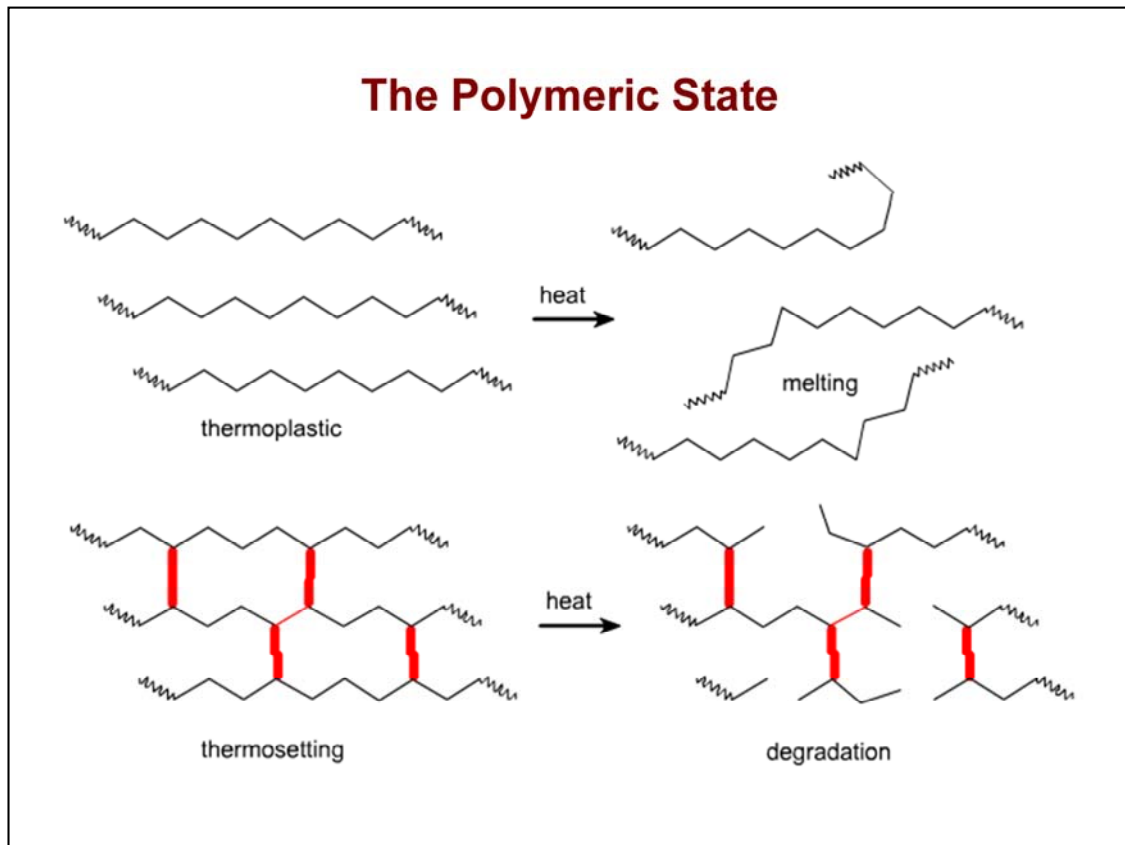
The Polymeric State

Major Classes of Polymers

b) **Thermosets** (will not melt but decompose at high temperatures)



- Thermosetting polymers are plastic in the primary stages of manufacture but once moulded (“set”) they cannot be softened by “re-heating”.
- Thermosetting is due to covalent bonds between the chains.



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