



## **TOPIC 2: STRUCTURE OF MATERIALS**

### **Topic 2.1:**

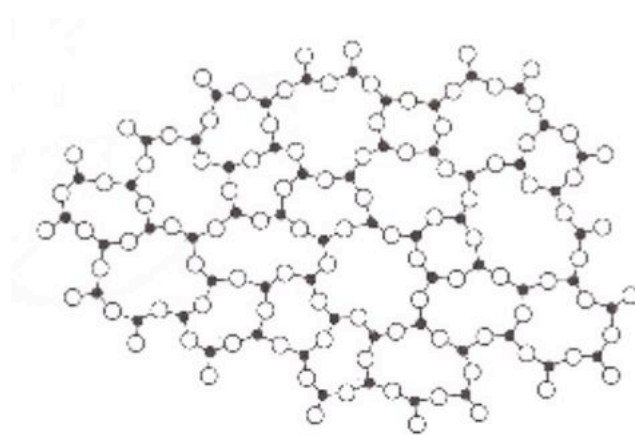
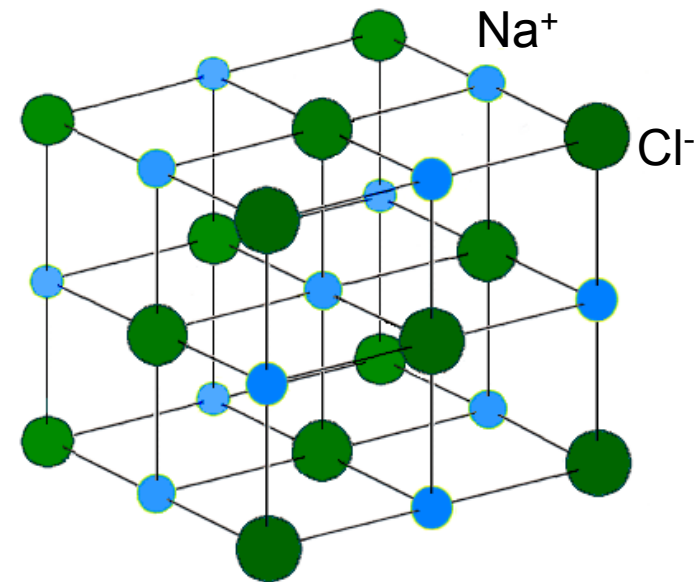
- **Crystalline systems.**
- **Important metallic and ceramic structures.**
- **Amorphous materials.**

## CRYSTALLINE STATES

The atoms tend to  $\Rightarrow$  minimum energy  $\Rightarrow$  position = f (bond, forces attraction...)  $\Rightarrow$  REPETITIVE spatial ordering  $\Rightarrow$  **CRYSTALLINE LATTICE**

The majority of solids  $\Rightarrow$  Crystalline State

- Metals and alloys.
- Ceramics.
- Some polymers.



*Amorphous  $\equiv$  Non crystalline*

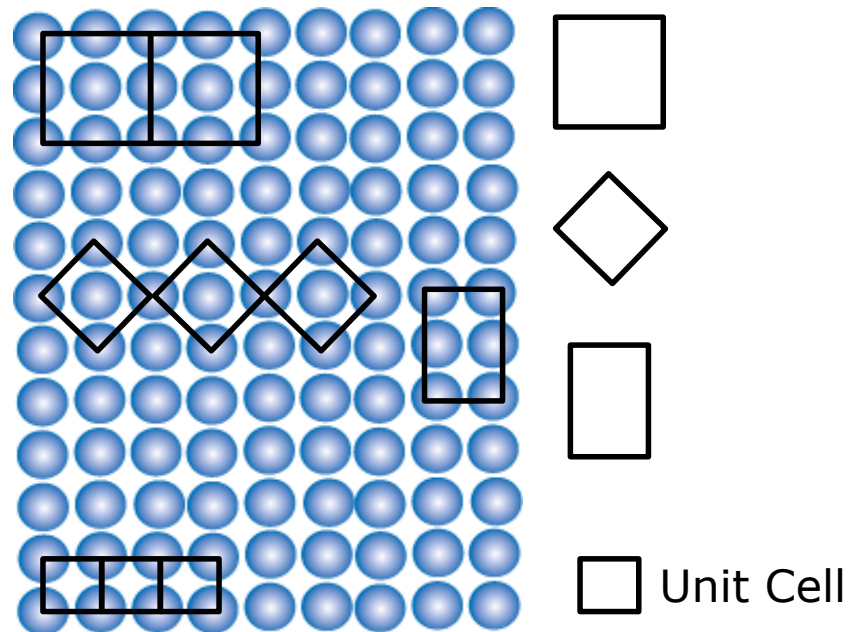
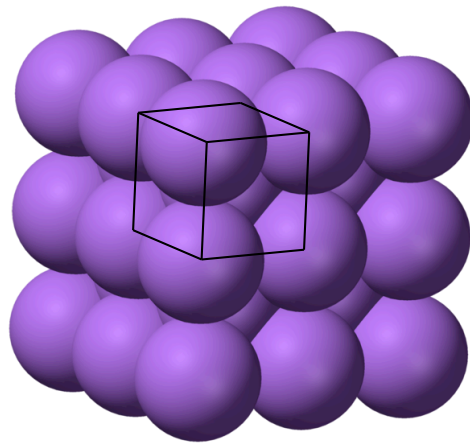
**Non** crystalline solids: They do not maintain a periodic ordering

## UNIT CELL

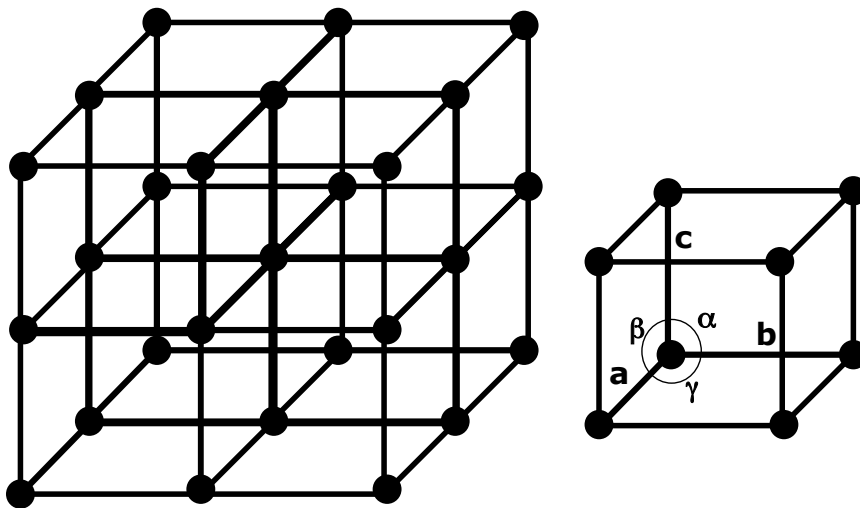
**Spatial lattice:** Infinite 3D arrangement of points

**Unit Cell:** The smallest lattice unit that contains all the elements of symmetry of the crystal.

*Parallelepiped capable of reproducing the crystal-“master model”*



## UNIT CELL: LATTICE PARAMETERS

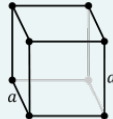

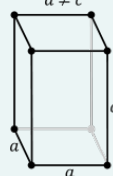
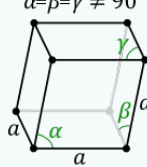
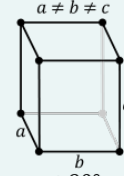
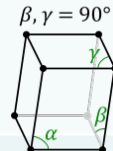
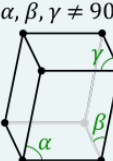


- (a) Lattice of a solid in 3D space
- (b) Unit cell showing the lattice parameters

**Lattice parameters or constants**  $\equiv$  Vectors and angles of the lattice

- 3 lattice vectors:  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  with common origin  $\Rightarrow$  Directions of the 3 independent axes
- 3 lattice angles:  $\alpha$ ,  $\beta$ ,  $\gamma$

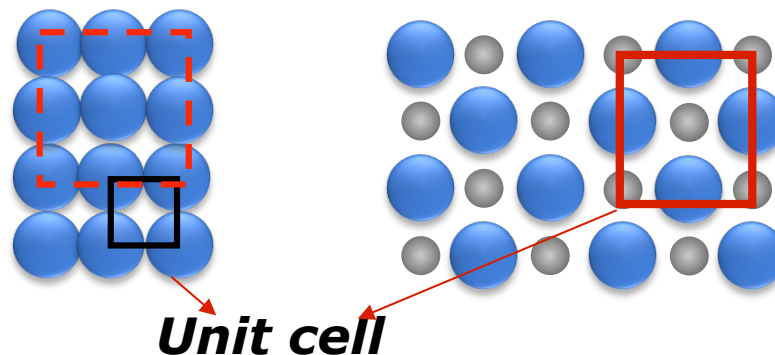
## THE 7 CRYSTALLINE SYSTEMS

Crystal System	Axis	Angles	
Cubic	$a=b=c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a=b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a=b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral	$a=b=c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

[http://commons.wikimedia.org/wiki/Crystal\\_structure](http://commons.wikimedia.org/wiki/Crystal_structure)

## BRAVAIS LATTICES

The 7 crystalline systems define the geometric form of the lattice, but there is also the need to establish the positions occupied by the atoms/ ions/molecules in the solid → BRAVAIS LATTICES



## BRAVAIS LATTICES AND CRYSTALLINE STRUCTURES

- The simplest case: **one atom per lattice point** → **P**
- Other cases: many atoms around a point in the lattice

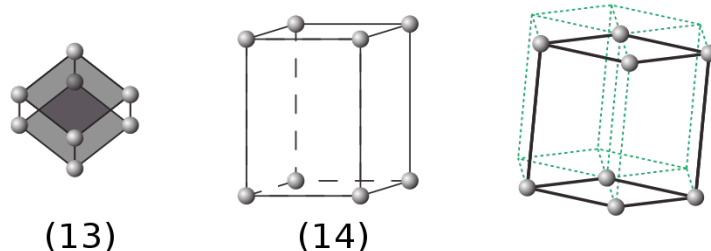
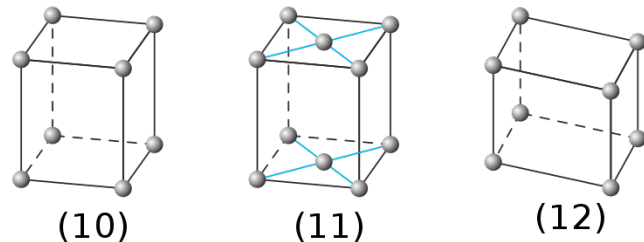
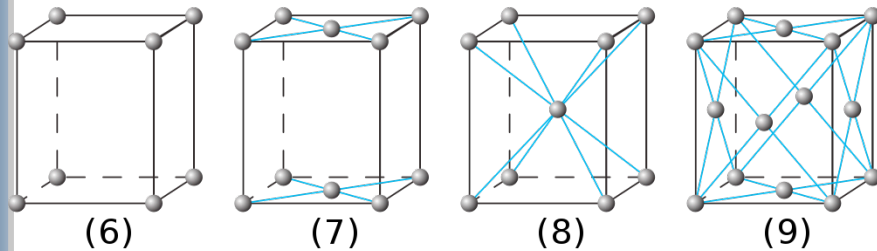
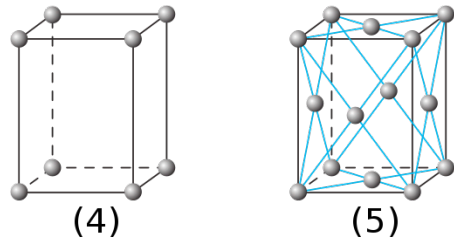
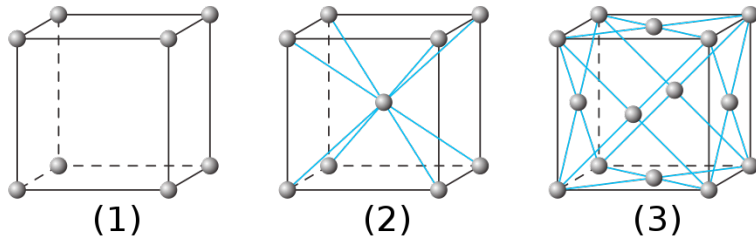
### Centered cell

- In all the faces **F**
- In 2 opposite faces **C**
- In the centre **I**

The combination of the 7 crystalline systems and the 4 unit cells (P, F, C, I) → **gives 14 fundamental lattices:**  
**They are called *Bravais Lattices***

**If we consider that each point is an atom, we have**  
**crystalline structures**

## THE 14 BRAVAIS LATTICES



1. Simple cubic (Cubic P)
2. Body-centered-cubic (bcc) – (Cubic I)
3. Face-centered-cubic (fcc) – (Cubic F)
4. Simple tetragonal – (Tetragonal P)
5. Body-centered tetragonal – (Tetragonal I)
6. Simple orthorhombic – (Orthorhombic P)
7. Body-centered orthorhombic – (Orthorhombic C)
8. Base-centered orthorhombic – (Orthorhombic I)
9. Face-centered orthorhombic – (Orthorhombic F)
10. Simple monoclinic – (Monoclinic P)
11. Base-centered monoclinic – (Monoclinic C)
12. Triclinic
13. Rhomboedral
14. Hexagonal

[http://commons.wikimedia.org/wiki/Category:Bravais\\_lattices](http://commons.wikimedia.org/wiki/Category:Bravais_lattices)



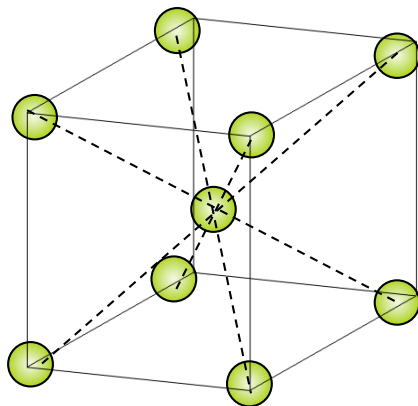
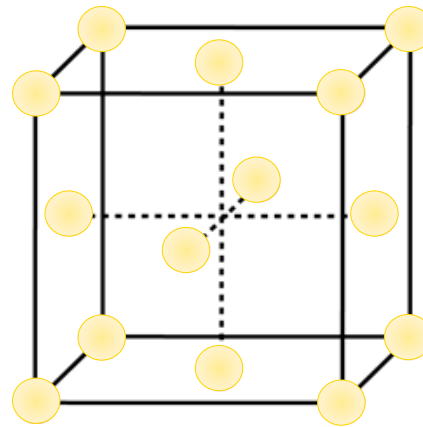
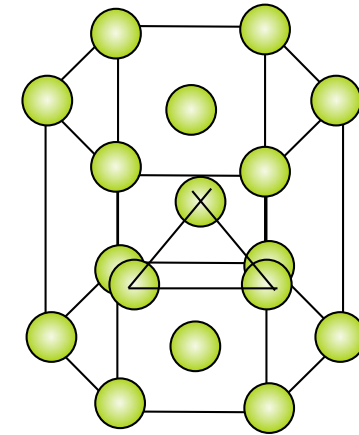
## MAIN METALLIC STRUCTURES

90% of the metals crystallize in 3 densely packed (compact) structures as they :

- Normally they consist of a unique element, and therefore the atomic radius is the same.
- The metallic bond is non directional.
- In order to reduce the lattice energy the distance between the atoms tends to be small.

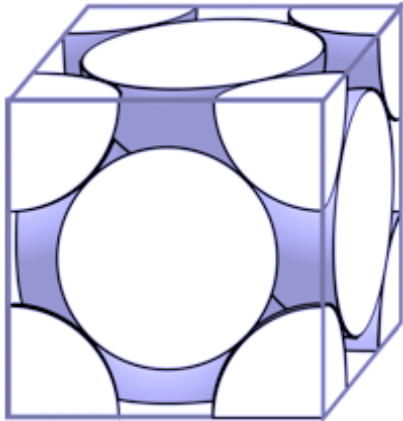
## MAIN METALLIC STRUCTURES

- Body- Centered Cubic (BCC)
- Face-Centered Cubic (FCC)
- Hexagonal Close-Packed (HCP)

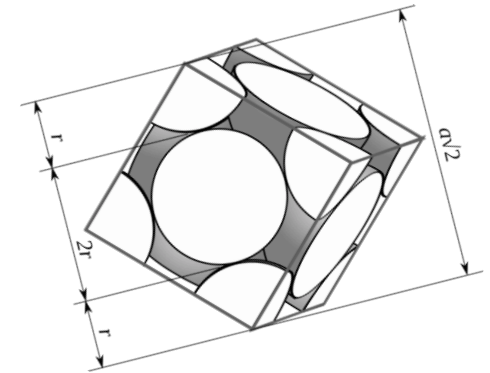
**BCC****FCC****HCP**

**Atomic Arrangement  $\Rightarrow E_{\text{minimum}}$**

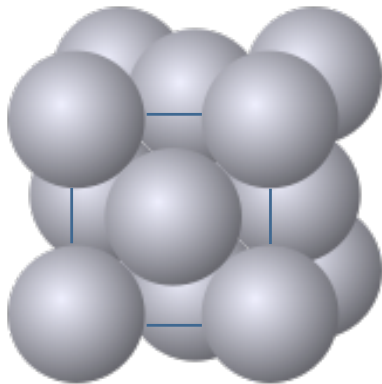
## FACE-CENTERED CUBIC STRUCTURE (FCC)



- Coordination Number: **12**
- N° atoms per cell =  $8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} = 4$
- $V_{\text{cell}} = a^3$  since  $4R = a\sqrt{2}$



[http://commons.wikimedia.org/wiki/File:Geometrie\\_cubique\\_faces\\_centrees.svg](http://commons.wikimedia.org/wiki/File:Geometrie_cubique_faces_centrees.svg)

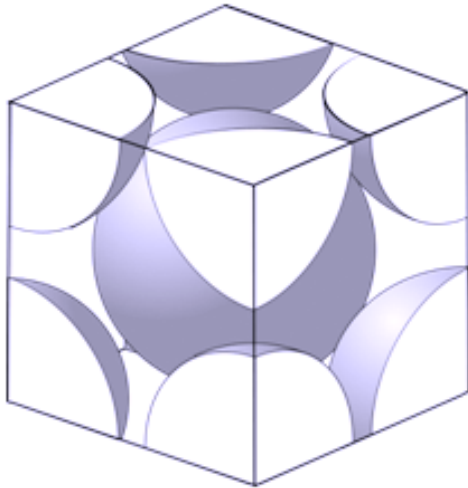


$$V_{\text{cell}} = \left[ \frac{4R}{\sqrt{2}} \right]^3 \quad V_{\text{atoms}} = \left[ \frac{4}{3} \pi \cdot R^3 \right] \cdot 4$$

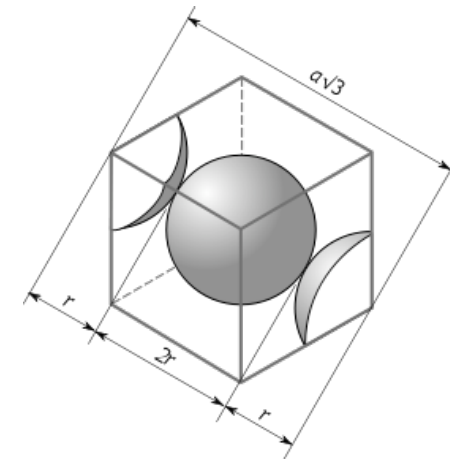
$$\text{Atomic Packing Factor} = \frac{\text{Volumen of atoms in a unit cell}}{\text{Total unit cell volume}} = \frac{4 \cdot \left( \frac{4\pi R^3}{3} \right)}{\left( \frac{4}{\sqrt{2}} R \right)^3} = 0,74$$

**74 % of the volume of the cell is occupied**

## BODY-CENTERED CUBIC STRUCTURE (BCC)



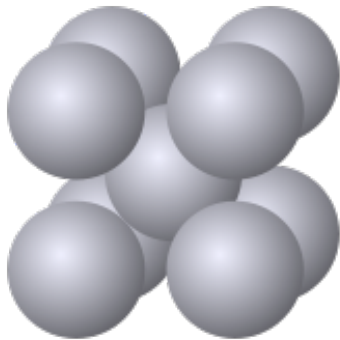
- Coordination Number : **8**
- N° atoms per cell =  **$8 \cdot \frac{1}{8} + 1 = 2$**
- **$V_{\text{cell}} = a^3$  as  $4R = a\sqrt{3}$**



[http://commons.wikimedia.org/wiki/File:Geometrie\\_cubique\\_centre.svg](http://commons.wikimedia.org/wiki/File:Geometrie_cubique_centre.svg)

$$V_{\text{cell}} = \left[ \frac{4R}{\sqrt{3}} \right]^3$$

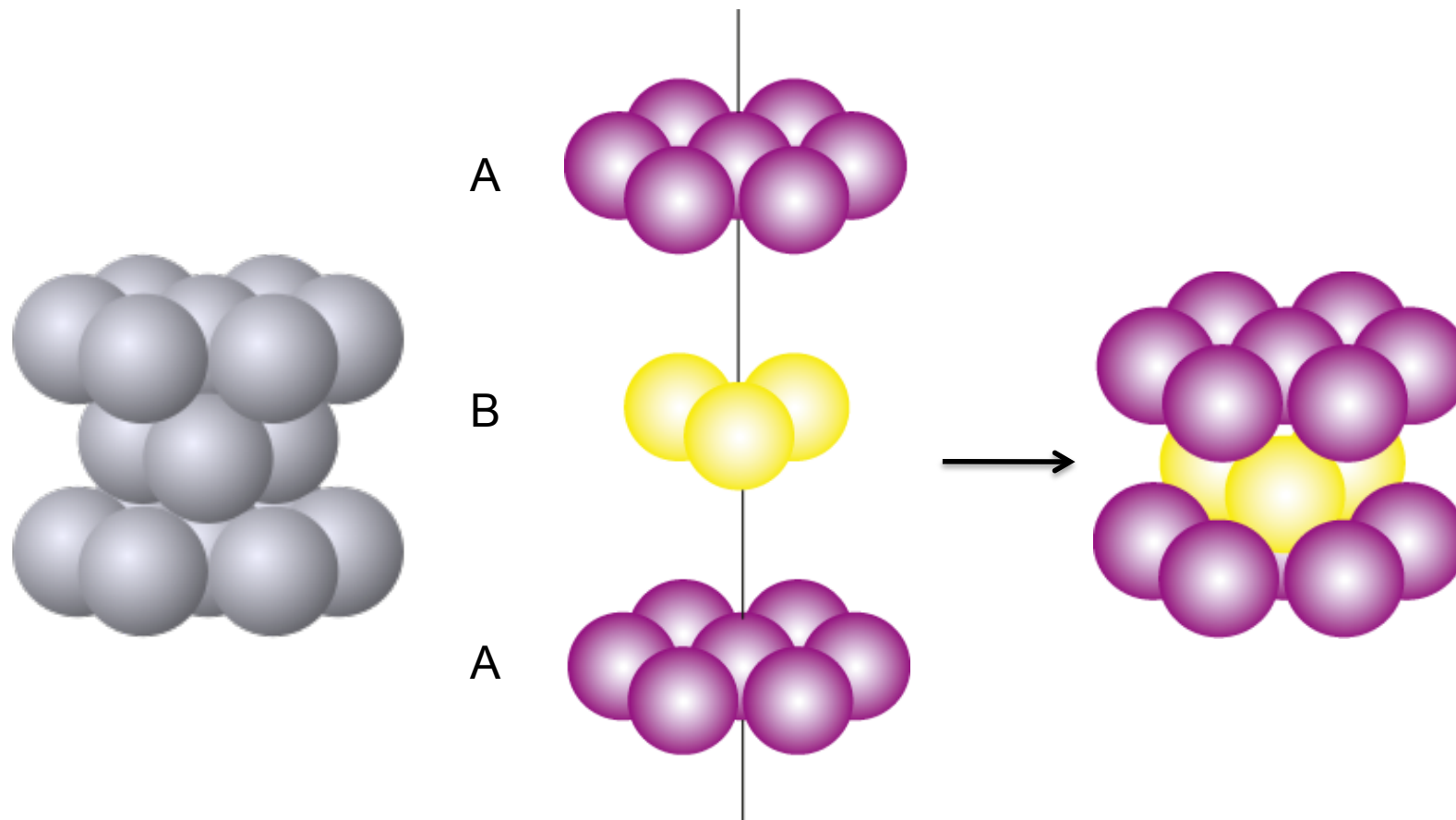
$$V_{\text{atoms}} = \left[ \frac{4}{3} \pi \cdot R^3 \right] \cdot 2$$



$$\text{Atomic Packing Factor} = \frac{\text{Volumen of atoms in a unit cell}}{\text{Total unit cell volume}} = \frac{2 \cdot \left( \frac{4\pi R^3}{3} \right)}{\left( \frac{4}{\sqrt{3}} R \right)^3} = 0,68$$

**68 % of the volume of the cell is occupied**

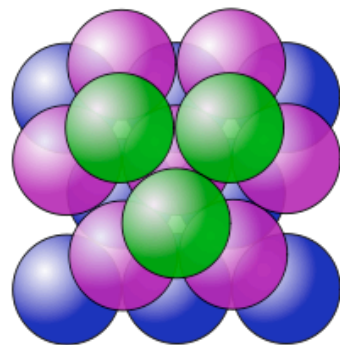
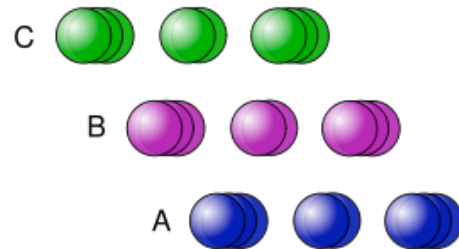
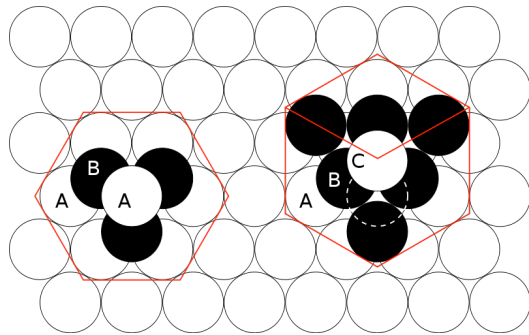
## HEXAGONAL CLOSED- PACKED STRUCTURE (HCP)



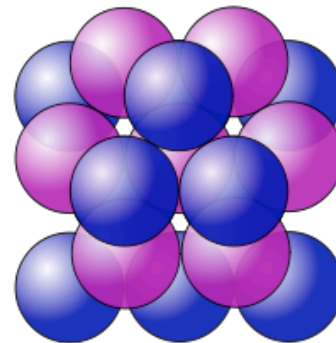
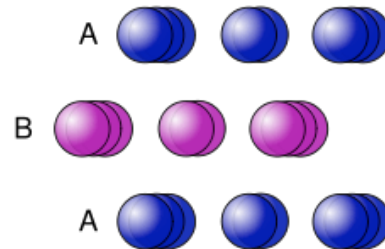
Atom in third layer lies over atom on first layer

- N<sup>o</sup> of atoms in the cell =  $12 \cdot \frac{1}{6} + 2 \cdot \frac{1}{2} + 3 = 6$
- Coordination Number: **12**
- Packing factor: **0,74**

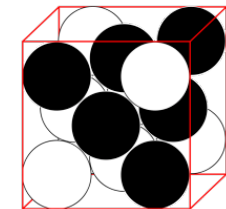
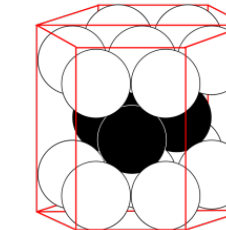
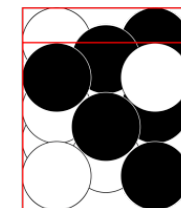
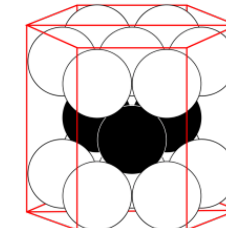
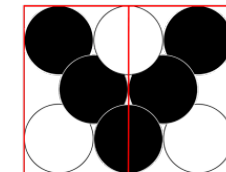
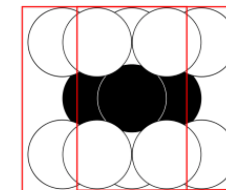
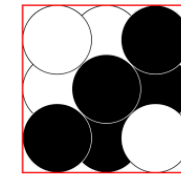
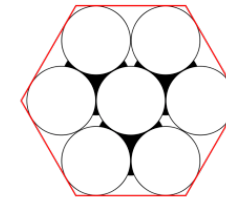
# PACKING SYSTEMS



**FCC: ABCABC...**



**HCP: ABAB...**



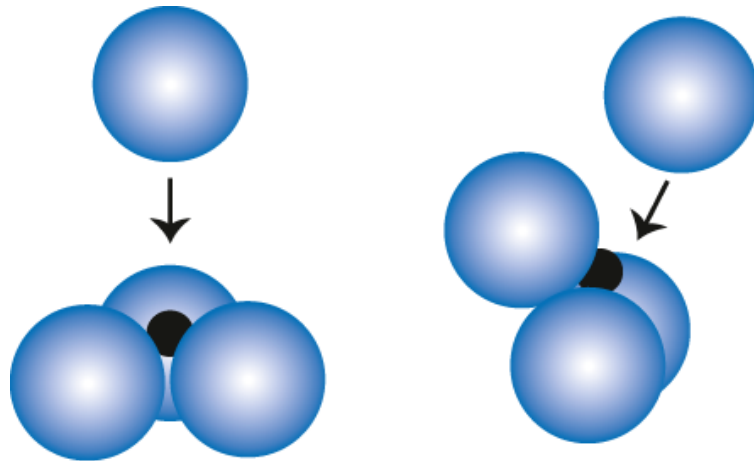
**HCP**

**FCC**

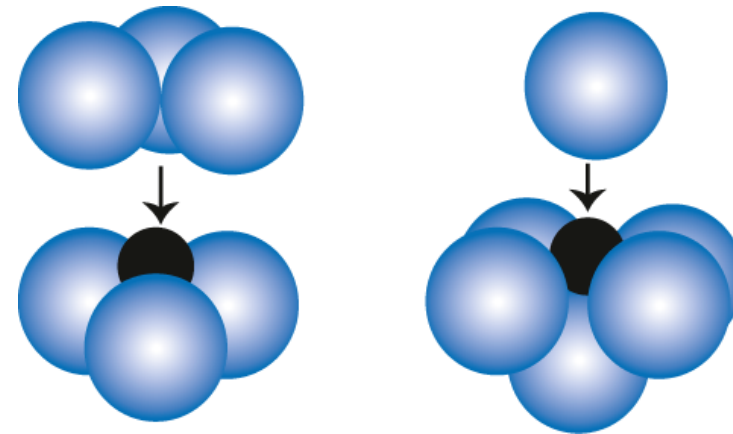
## INTERSTITIAL SITES

There are 2 types of interstitials sites:

- **TETRAHEDRAL** (Coord. N° 4)
- **OCTAHEDRAL** (Coord. N° 6)



**TETRAHEDRAL**

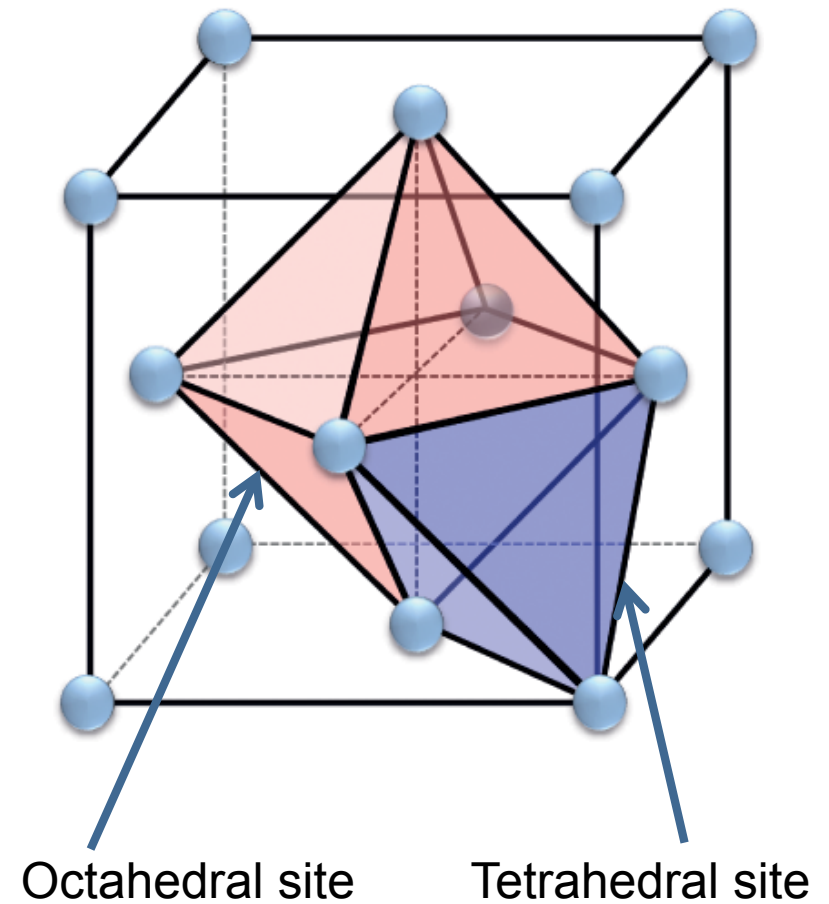
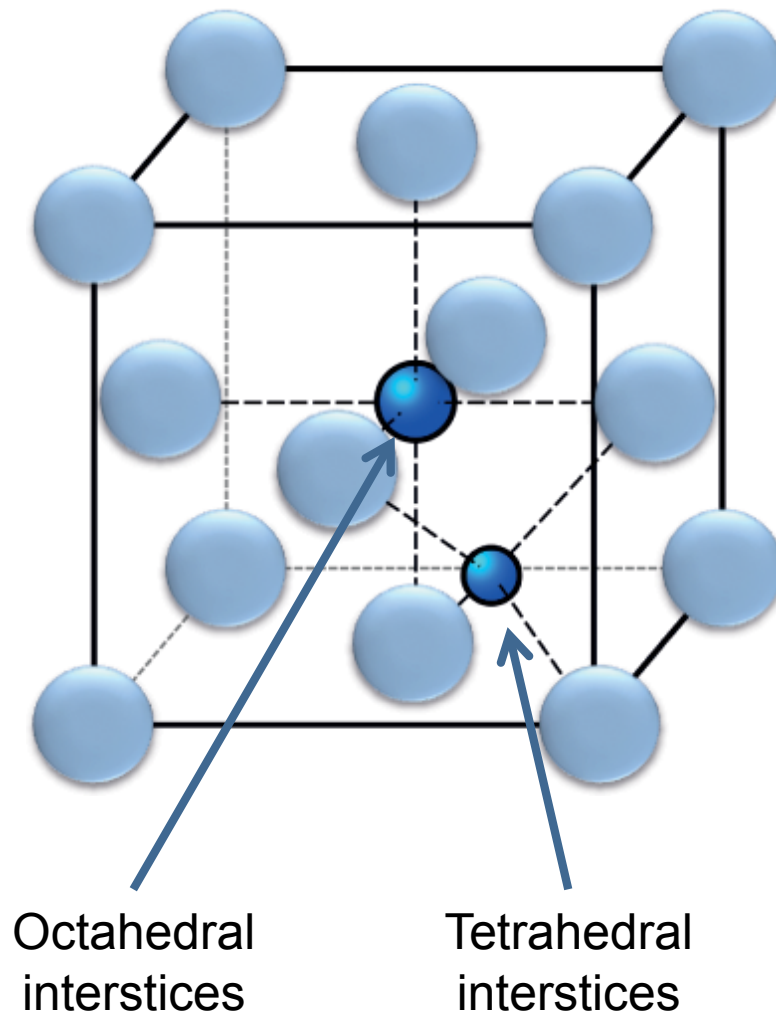


**OCTAHEDRAL**

In compact structures is certain that:

- **N° of tetrahedral sites =  $2n$**
- **N° of octahedral sites =  $n$**
- **$n$  = N° atoms in the cell**

## INTERSTITIAL SITES : IN FCC STRUCTURE





## INTERSTICES: SOLUBILITY OF C IN IRON

- Different packing factors:  $f_{\text{bcc}}=0.68$  and  $f_{\text{fcc}}=0.74$

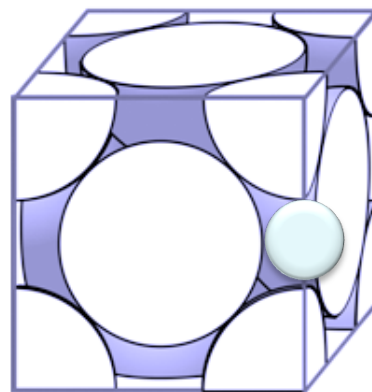
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$V_{\text{interstices}}(\text{fcc}) < V_{\text{interstices}}(\text{bcc})$ , but  $\text{No.}_{\text{interstices}}(\text{fcc}) > \text{No.}_{\text{interstices}}(\text{bcc})$

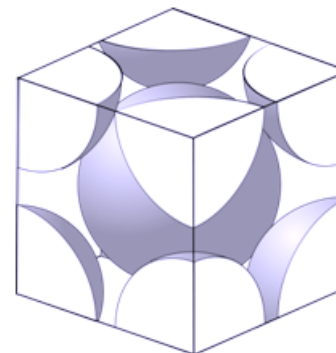
- This fact allows us to explain the solubility of C in Fe:

$T_{\text{room.}} \Rightarrow \text{Fe}_\alpha(\text{bcc}) \text{ } 0.02\text{-}0.05\%\text{C} \Rightarrow \text{ferrite}$

High T ( $>910^\circ\text{C}$ )  $\Rightarrow \text{Fe}_\gamma(\text{fcc}) \text{ } 2\%\text{C} \Rightarrow \text{austenite}$



**Fe- $\gamma$   
(fcc)**



**Fe- $\alpha$   
(bcc)**

## ELECTRONEUTRALITY IN IONIC CERAMICS

**Ionic structure** : packing of anions with cations in interstitials

The ions tend to pack densely in order to **reduce**  $E_{\text{total}}$

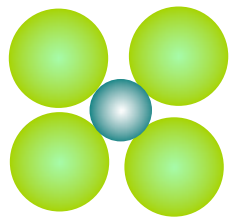
**Sizes**  $C^+ A^- \Rightarrow (r_{\text{cation}} < r_{\text{anion}})$

**Electroneutrality**

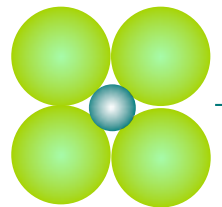
**Coordination Index** (By increasing C.I  $\Rightarrow$  increase stability)

**Sharing of polyhedral** (sharing vertices instead of edges or faces (increases the distance between cations))

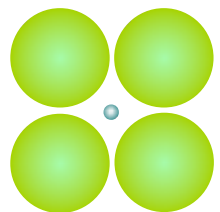
## PACKING OF IONS



STABLE



The relation between radius when  $A^-$  and  $C^+$  are in contact  $\Rightarrow$  **Relation of radius is critical (minimum)**



UNSTABLE

$\Rightarrow$  vibrates in its cage of  $A^-$

Arrangement of  $A^-$  around  $C^+$  central and C.I.

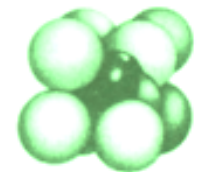
Cation/anion  
Radius ratio

$$r_C/r_A$$

C.I. 8

Corners of a cube

0.732-1.0



C.I. 6

Corners of an octahedron

0.414-0.732



C.I. 4

Corners of a tetrahedron

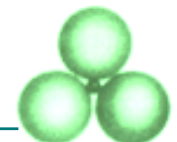
0.225-0.414



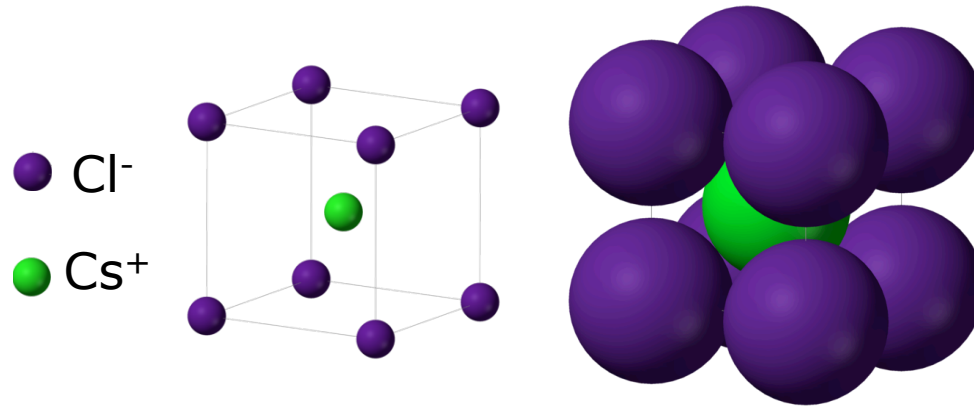
C.I. 3

Corners of a triangle

0.155-0.225



## SIMPLE CUBIC STRUCTURE: CsCl

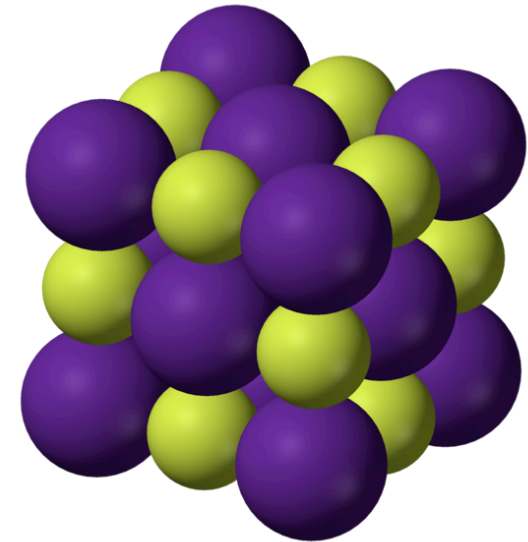
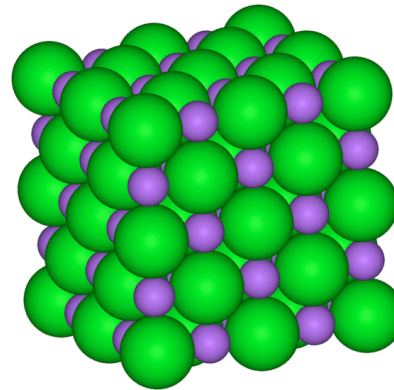
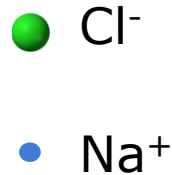
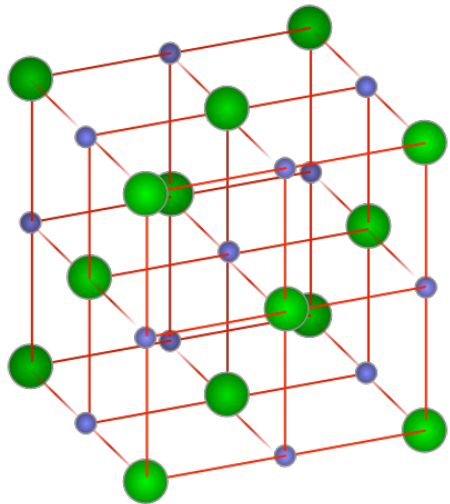


- Cl<sup>-</sup> : cubic
- Cs<sup>+</sup>: centre of the cube
- C.I.: 8

$$\frac{r_{Cs^+}}{r_{Cl^-}} = 0,94 > 0,732 \Rightarrow C.I. = 8 \Rightarrow \text{Cubic structure}$$

Ceramics that have this type of structure: **CsBr, TlCl, TlBr.**

## FCC STRUCTURE: NaCl

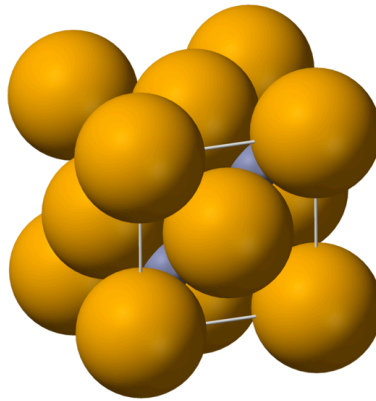
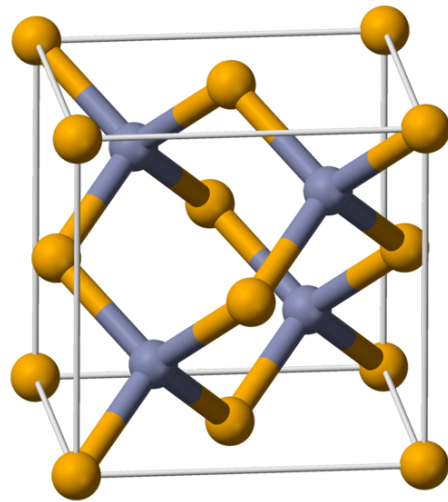


$$\frac{r_{Na^+}}{r_{Cl^-}} = 0,56 > 0,414 \Rightarrow C.I. = 6 \Rightarrow \text{Octahedral coord.}$$

- Cl<sup>-</sup>: FCC packing
- Na: all octahedral interstitials.
- 4 Na<sup>+</sup> and 4 Cl<sup>-</sup> per unit cell C.I.=6

Ceramics that have this type of structure: **MgO, CaO, FeO, NiO**

## FCC STRUCTURE: Zn Blende-ZnS



- $S^{2-}$ : FCC packing
- $Zn^{2+}$ :  $\frac{1}{2}$  tetrahedral interstitials
- 4  $Zn^{2+}$  and 4  $S^{2-}$  per unit cell

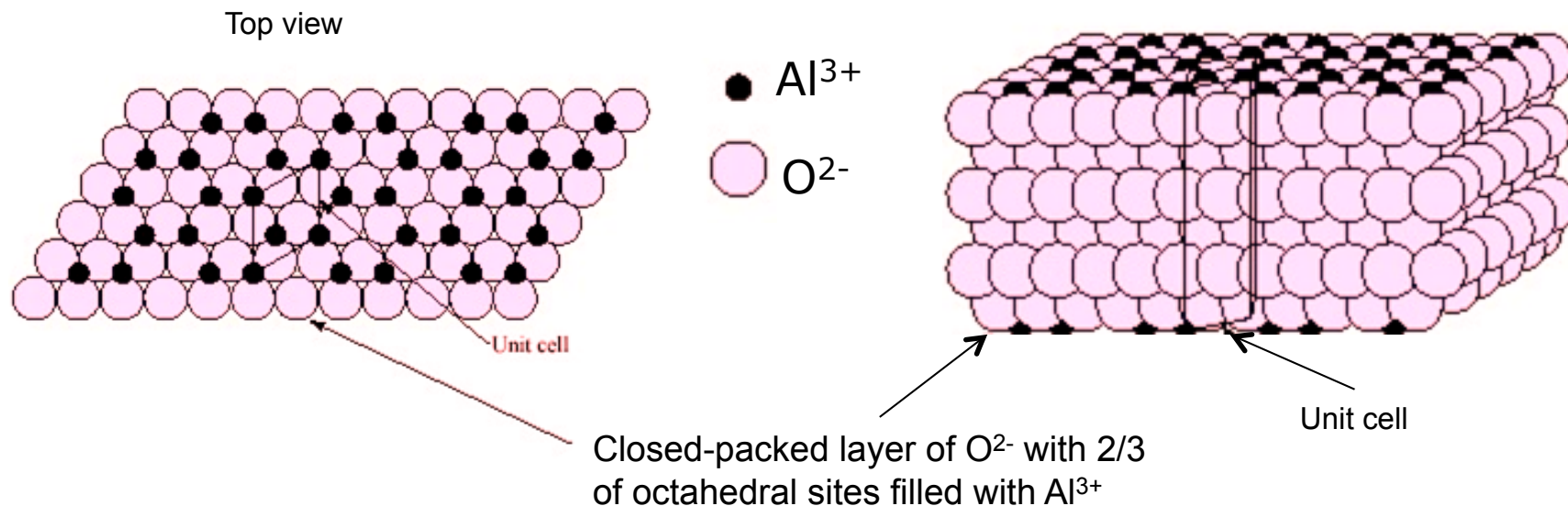
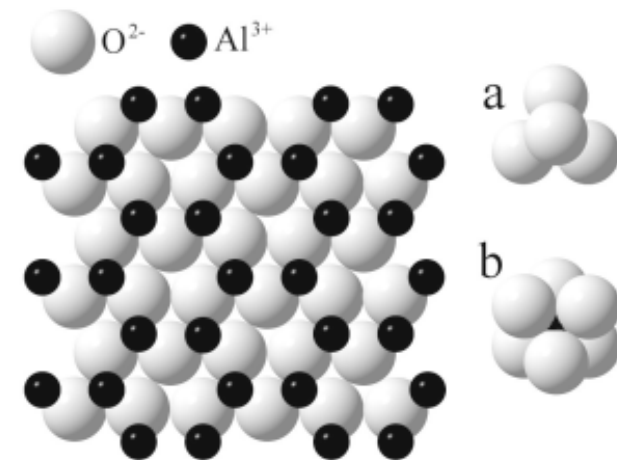
$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.345 \Rightarrow C.I. = 4$$

According to Pauling bond **Zn-S ~87% covalent**

Ceramics that have this type of structure: Typical semiconductors : **CdS, HgTe, NiAs, SiC, GaAs**

## HCP STRUCTURE: CORUNDUM (ALUMINA)

- $O^{2-}$ : HCP packing  $\rightarrow$  6 ions
- $Al^{3+}$ :  $2/3$  octahedral interstitials  $\rightarrow$  4 ions
- I.C.( $Al^{3+}$ ): 6 ; I.C.( $O^{2-}$ ): 6



Ceramics that have this type of structure:  **$Cr_2O_3$ ,  $Fe_2O_3$ ,  $Al_2O_3$  ...**

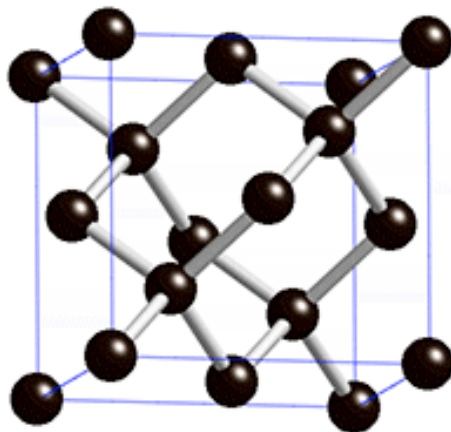
## POLYMORPHISM AND ALLOTROPY

**The same element or compound can exist in more than one crystalline state under  $\neq$  conditions of P and T.**

### Diamond-Graphite:

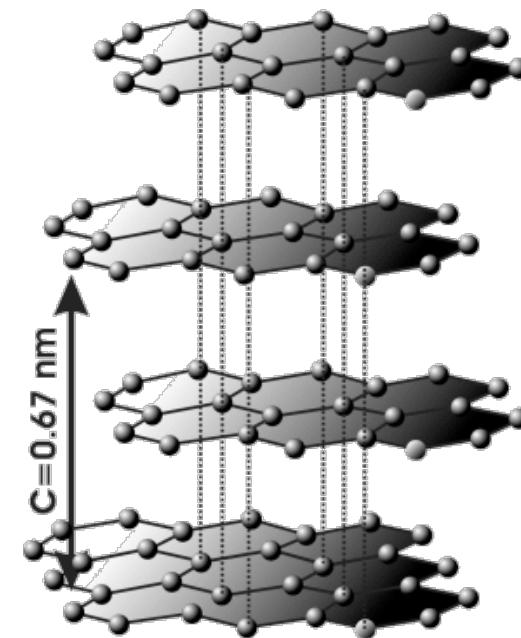
Diamond  $\Rightarrow$  3D covalent structure  $\Rightarrow$  hard, transparent, insulator

Graphite  $\Rightarrow$  Laminar structure  $\Rightarrow$  Secondary bonds between layers  $\Rightarrow$  soft, non transparent, conductor



C<sub>diamond</sub>

C<sub>graphite</sub>





## POLYMORPHISM AND ALLOTROPY

### Zirconia ( $\text{ZrO}_2$ ) :

- $\text{ZrO}_2$  in  $\text{Al}_2\text{O}_3 \Rightarrow$  increases the mechanical properties of alumina
- $\text{ZrO}_2(\text{cubic}) \rightarrow \text{ZrO}_2(\text{tetragonal}) \rightarrow \text{ZrO}_2(\text{monoclinic})$ 
  - $\Downarrow$   
structure  $\text{CaF}_2$ -fcc
  - $\Downarrow$   
dimensional deformation  
that consumes energy  $\Rightarrow \uparrow$  toughness

### Iron (steels):

BCC at room temperature; FCC from  $910^\circ\text{C} \Rightarrow$  possibility of thermal treatment

# AMORPHOUS MATERIALS AND SOLIDIFICATION

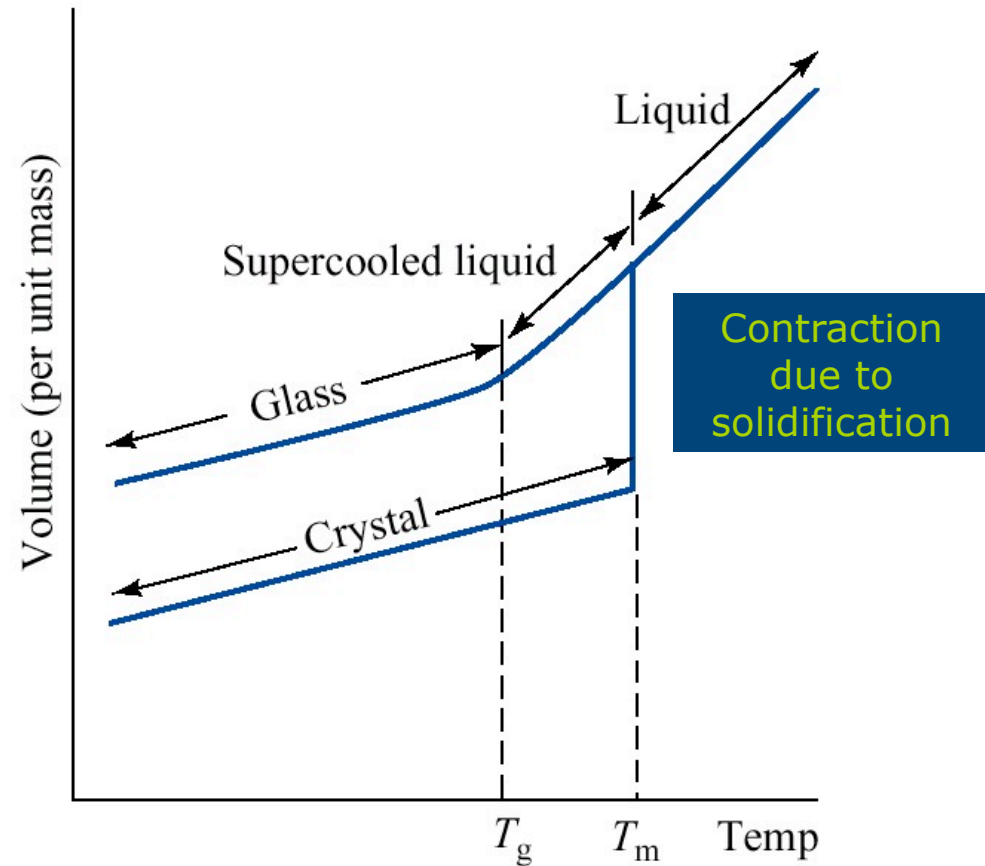
## Crystalline Solid

Starting from liquid state, lowering the temperature, solidifies at the melting/solidification temperature ( $T_m$ )

## GLASS

Starting from the liquid state, lowering the temperature, viscosity increases.

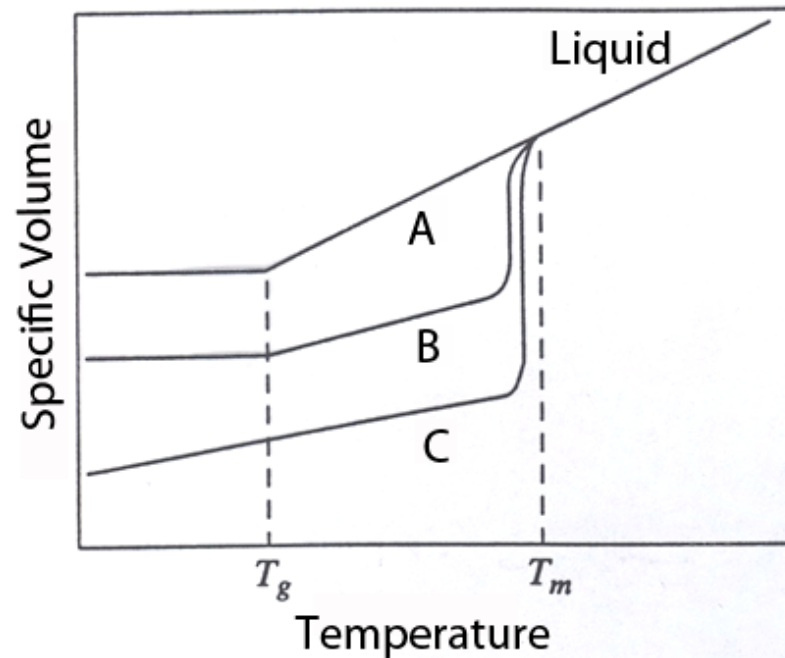
Plastic State  $\Leftrightarrow$  Rigid State



## GLASS TRANSITION TEMPERATURE

$T_m$  : Melting Temperature. Associated with crystalline zones

$T_g$  : **Glass Transition** Temperature. Associated with amorphous zones

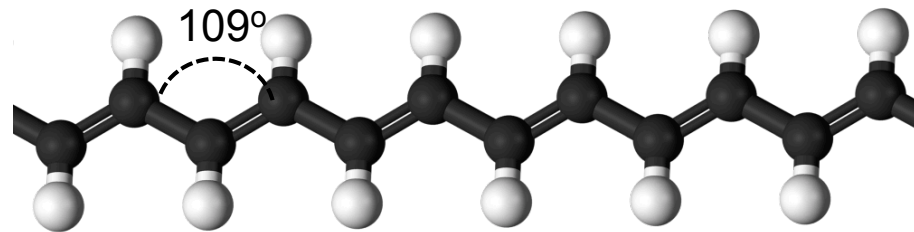


- A. Amorphous
- B. Semicrystalline
- C. 100% crystalline

$T < T_g \Rightarrow$  Glass state

$T > T_g \Rightarrow$  Rubbery or leathery state

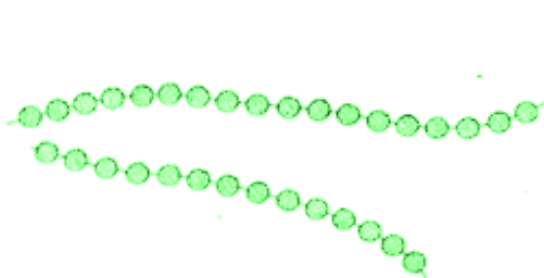
## POLYMERS: CHAIN STRUCTURES



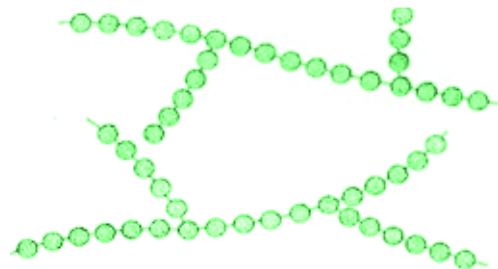
Chains of polymeric molecules NOT necessarily straight :



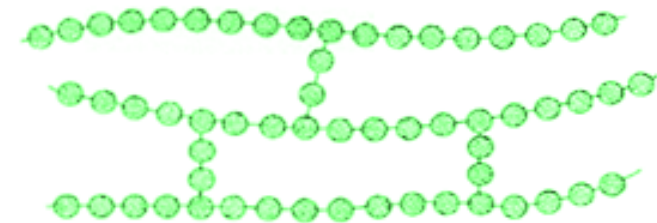
### MOLECULAR ARCHITECTURE



Linear



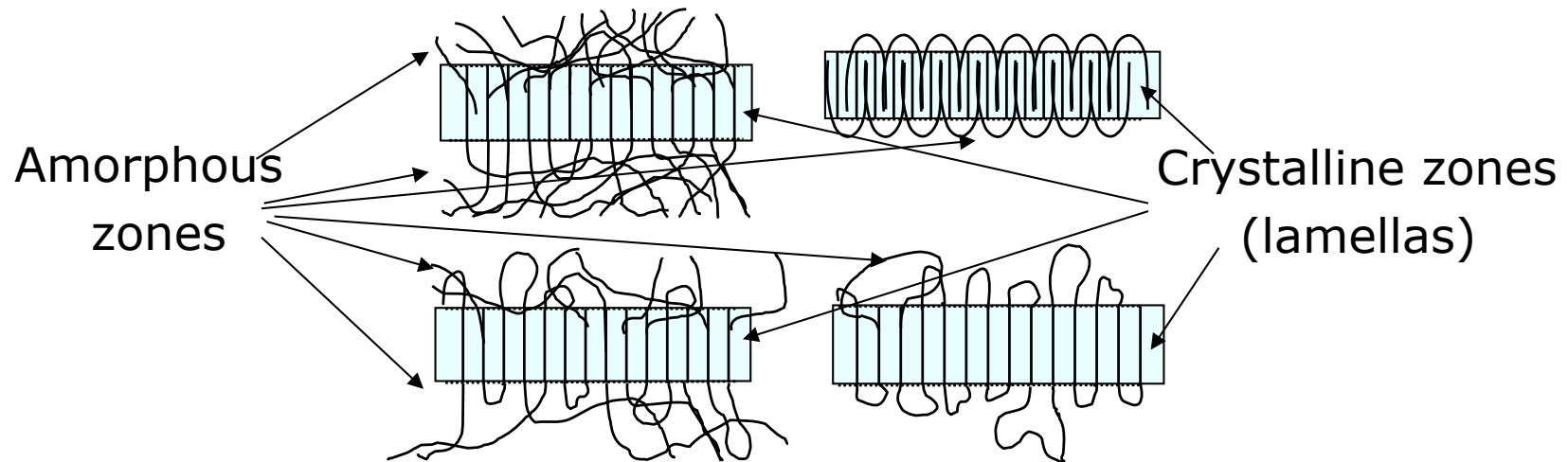
Branched



Crosslinked (branched polymer interconnected forming a network)

## POLYMERS: AMORPHOUS AND CRYSTALLINE

### Chain-folded model

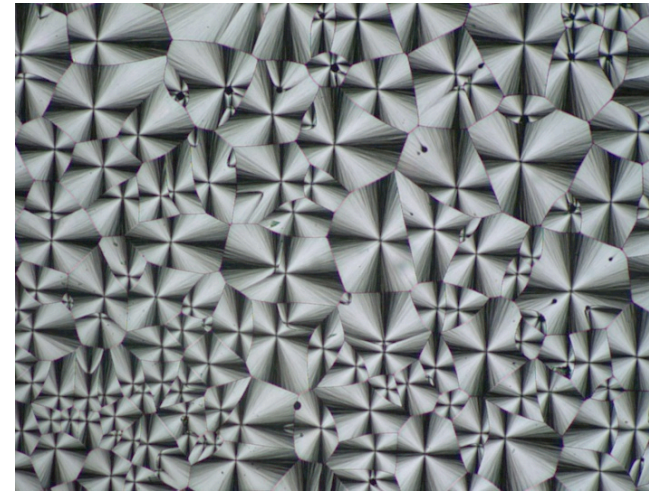
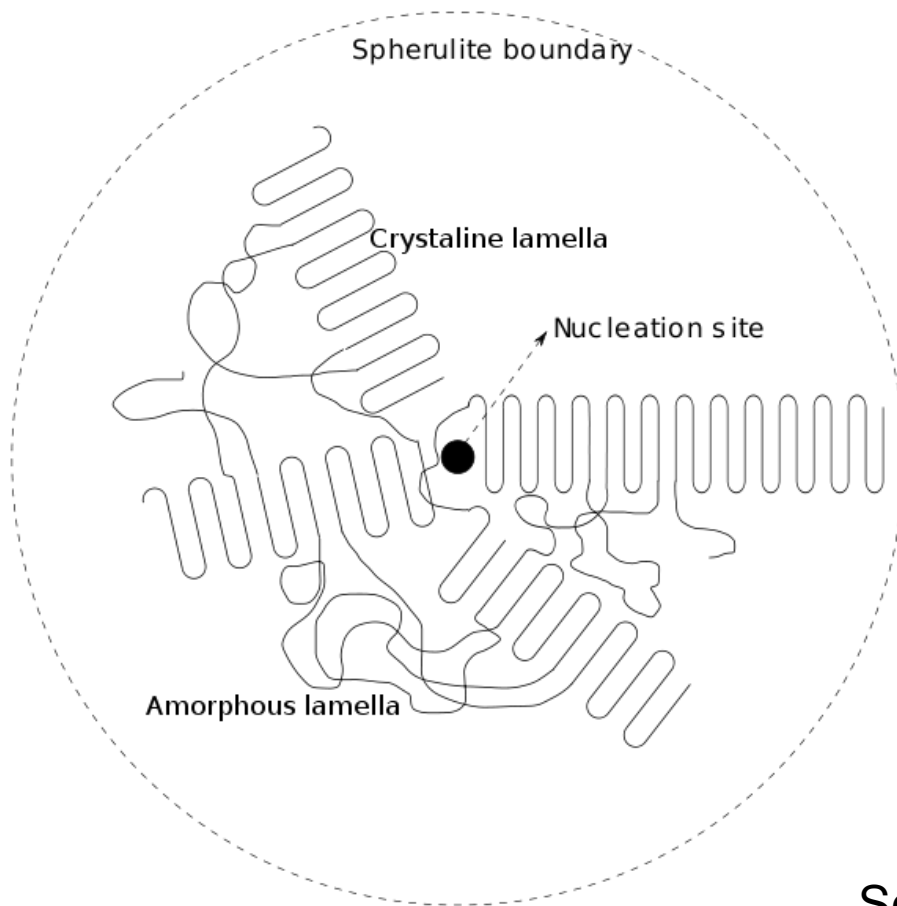


**Amorphous polymer:** Structure of disordered polymeric chains (as in liquid) but it behaves like a solid

**Semicrystalline polymer:** Amorphous regions (disordered chains) and crystalline regions (ordered chains)

## POLYMERS: AMORPHOUS AND CRYSTALLINE

### Spherulites



William D. Callister, Jr., Materials Science and Engineering  
An Introduction: John Wiley & Sons, Inc.

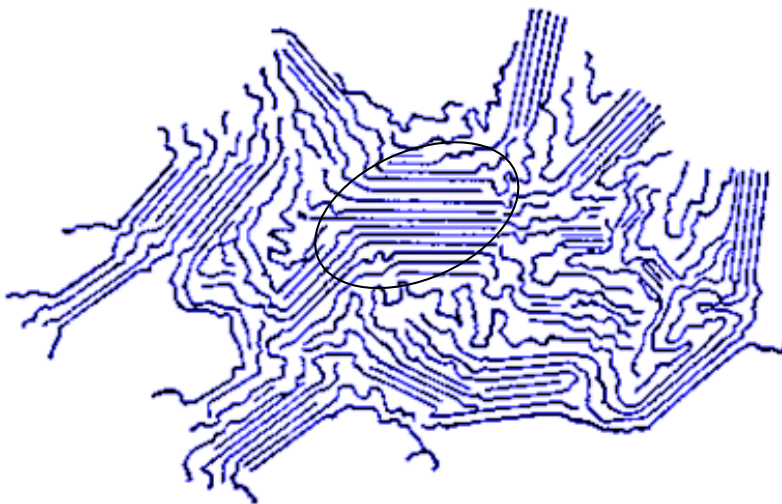
Some polymers that are crystallized from a melt form a **spherulite structure**.

## POLYMERS: AMORPHOUS AND CRYSTALLINE



Amorphous polymer

A semicrystalline polymer consists of crystalline regions (**crystallites**), which are interspersed with amorphous regions of randomly oriented molecules



Semicrystalline polymer

Fringed-micelle model  
of a semicrystalline polymer

## POLYMERS : STRUCTURE AND ISOTROPY



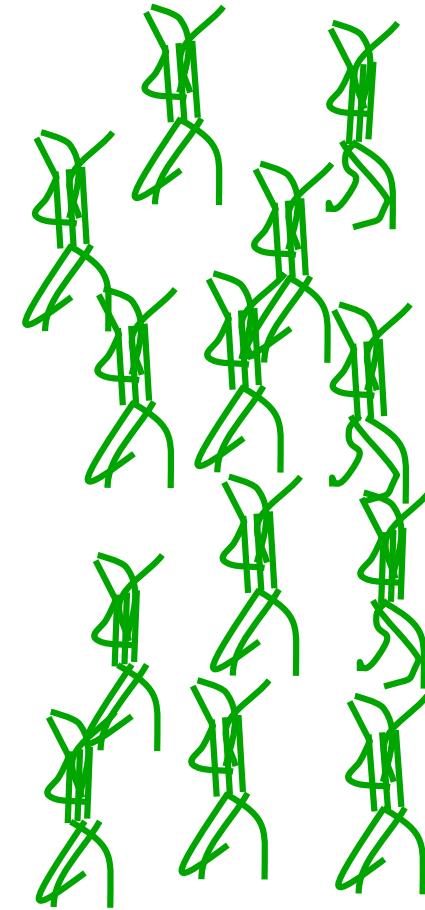
Amorphous solid

ISOTROPIC



Semicrystalline solid

ANISOTROPIC



Oriented semicrystalline solid