

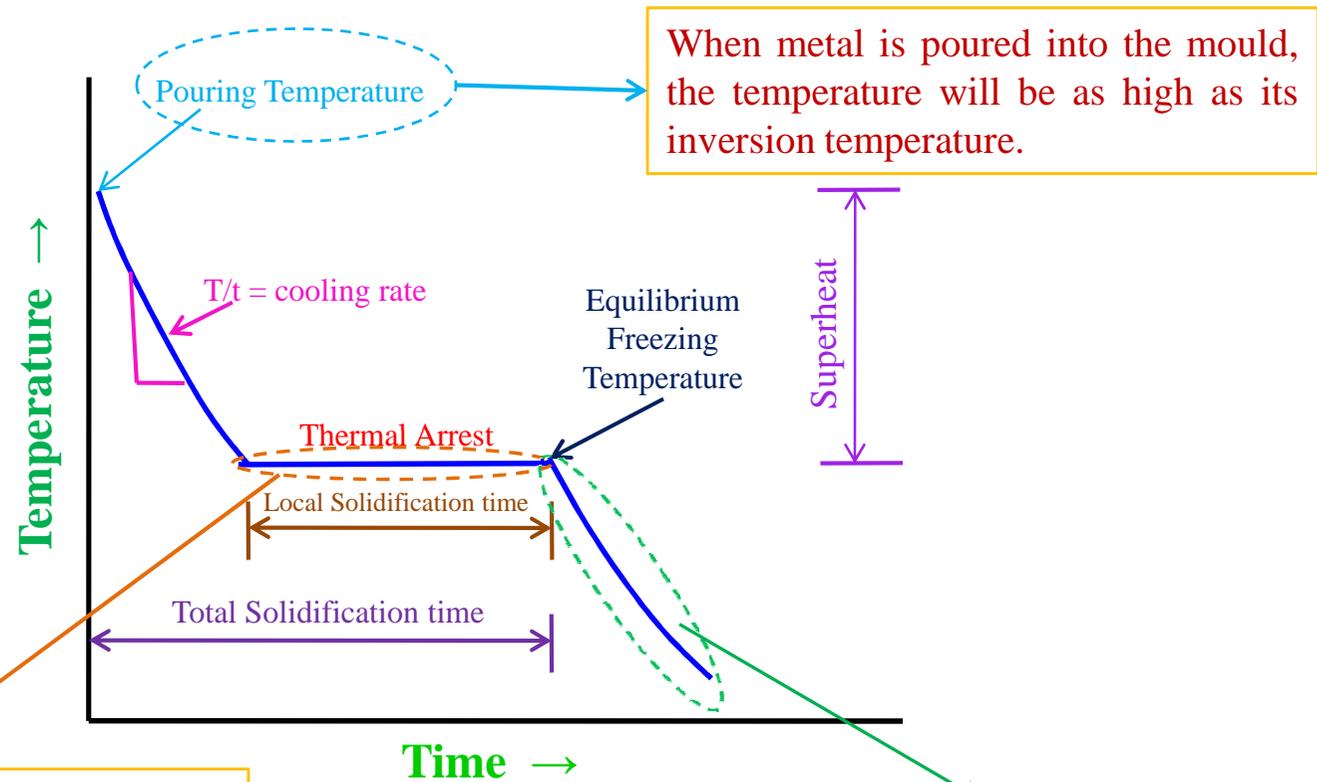
Introduction

- ❑ Three states of matter are distinguishable: gas, liquid, and solid
- ❑ In the gaseous state the metal atoms occupy a great deal of space because of their rapid motion. The atoms move independently and are usually widely separated so that the attractive forces between atoms are negligible. The arrangement of atoms in a gas is one of complete disorder.
- ❑ At some lower temperature, the kinetic energy of the atoms has decreased so that the attractive forces become large enough to bring most of the atoms together in a liquid. And there is a continual interchange of atoms between the vapor and liquid across the liquid surface.
- ❑ The attractive forces between atoms in a liquid may be demonstrated by the application of pressure. A gas may be easily compressed into a smaller volume, but it takes a high pressure to compress a liquid. There is, however, still enough free space in the liquid to allow the atoms to move about irregularly.
- ❑ As the temperature is decreased, the motions are less vigorous and the attractive forces pull the atoms closer together until the liquid solidifies. Most materials contract upon solidification, indicating a closer packing of atoms in the solid state.
- ❑ The atoms in the solid are not stationary but are vibrating around fixed points, giving rise to the orderly arrangement of crystal structures.

Mechanism of Crystallization

- ❑ Crystallization is the transition from the liquid to the solid state and occurs in two stages:
 - Nuclei formation
 - Crystal Growth
- ❑ Although the atoms in the liquid state do not have any definite arrangement, it is possible that some atoms at any given instant are in positions exactly corresponding to the space lattice they assume when solidified.
- ❑ These chance aggregates or groups are not permanent but continually break up and reform at other points.
- ❑ The higher the temperature, the greater the kinetic energy of the atoms and the shorter the life of the group. When the temperature, of the liquid is decreased, the atom movement decreases, lengthening the life of the group, and more groups will be present at the same time.
- ❑ Atoms in a material have both kinetic and potential energy. *Kinetic energy is related to the speed at which the atoms move and is strictly a function of temperature.* The higher the temperature, the more active are the atoms and the greater is their kinetic energy. *Potential energy, on the other hand, is related to the distance between atoms.* The greater the average distance between atoms, the greater is their potential energy.

Solidification (or) Freezing



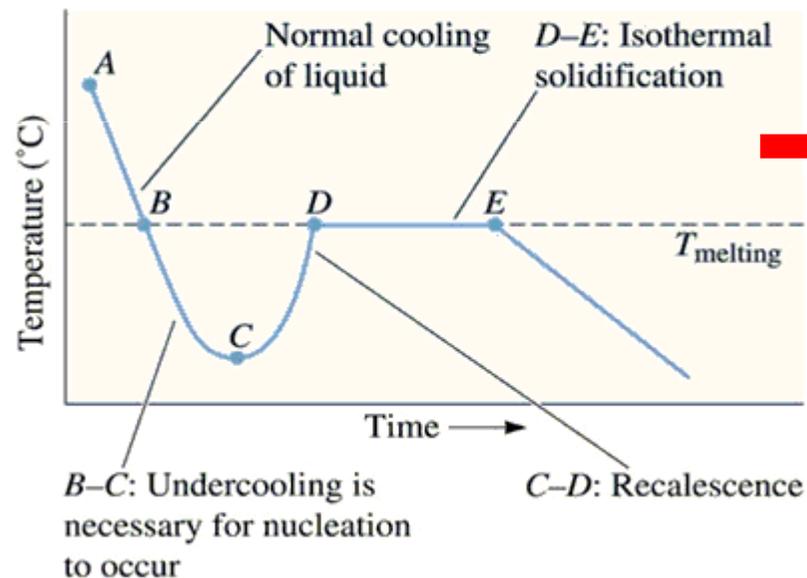
When metal is poured into the mould, the temperature will be as high as its inversion temperature.

It gets cooled when poured into the mould and molten metal in the liquid form will solidify. This time is called local solidification time

The solidified metal in the mould (called casting) gets cooled in the mould to the temperature of the surroundings

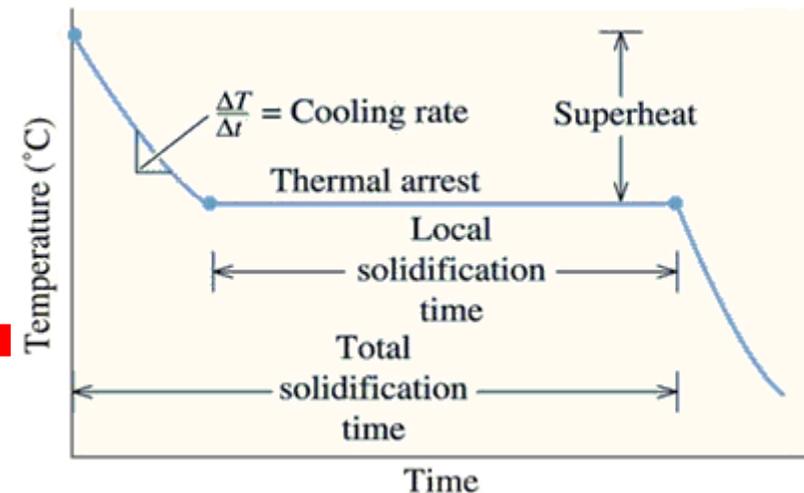
Cooling Curves

- ❑ **Recalescence** : The increase in temperature of an undercooled liquid metal as a result of the liberation of heat during nucleation.
- ❑ **Thermal Arrest** : A plateau on the cooling curve during the solidification of a material caused by the evolution of the latent heat of fusion during solidification.
- ❑ **Total Solidification Time** : The time required for the casting to solidify completely after the casting has been poured.
- ❑ **Local Solidification Time** : The time required for a particular location in a casting to solidify once nucleation has begun.



Cooling curve for a pure metal that has not been well inoculated. Liquid cools as specific heat is removed (between points A and B). Undercooling is thus necessary (between points B and C). As the nucleation begins (point C), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point C to point D). Metal continues to solidify at a constant temperature (T_{melting}). At point E, solidification is complete. Solid casting continues to cool from the point.

Cooling curve for a well inoculated, but otherwise pure metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature

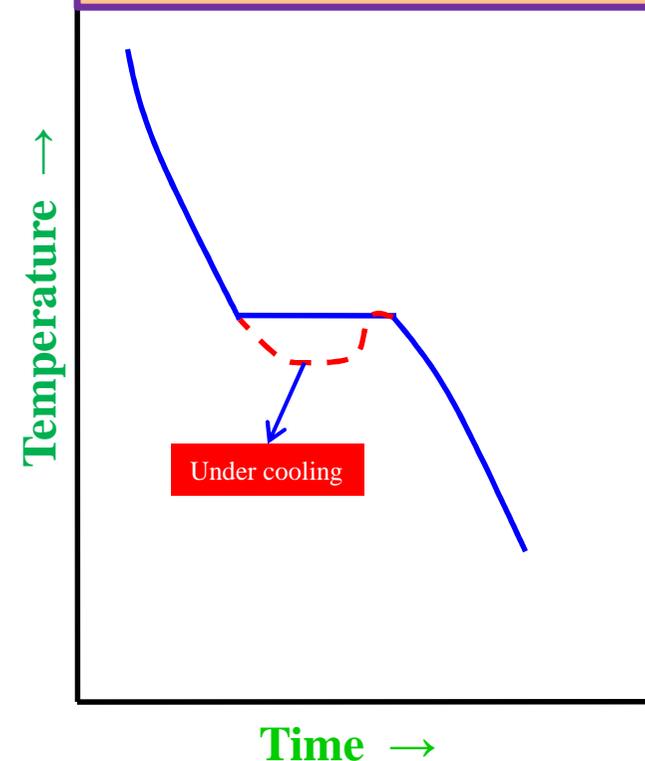


Solidification of pure metal : Super cooling

- ❑ In a pure metal at its freezing point where both the liquid and solid states are at the same temperature. The kinetic energy of the atoms in the liquid and the solid must be the same, but there is a significant difference in potential energy.
- ❑ The atoms in the solid are much closer together, so that solidification occurs with a release of energy. This difference in potential energy between the liquid and solid states is known as the *latent heat of fusion*.

- ❑ However, energy is required to establish a surface between the liquid and solid. In pure materials at the freezing point insufficient energy is released by the heat of fusion to create a stable boundary, and some under cooling is always necessary to form stable nuclei.
- ❑ Subsequent release of the heat of fusion will raise the temperature to the freezing point. The amount of undercooling required may be reduced by the presence of solid impurities which reduce the amount of surface energy required.

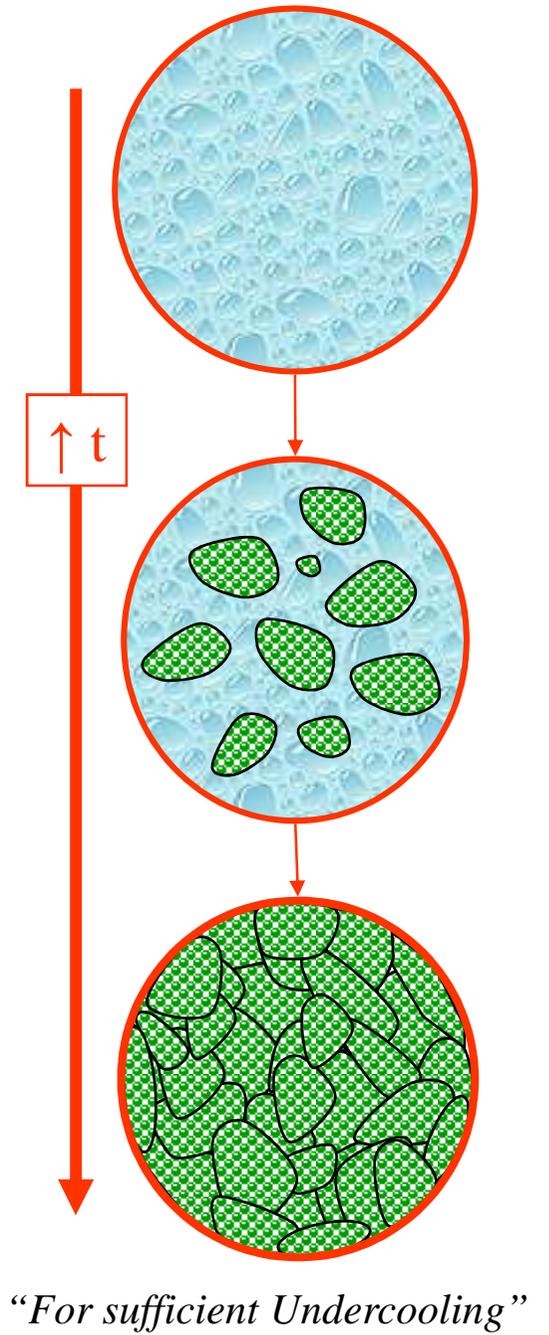
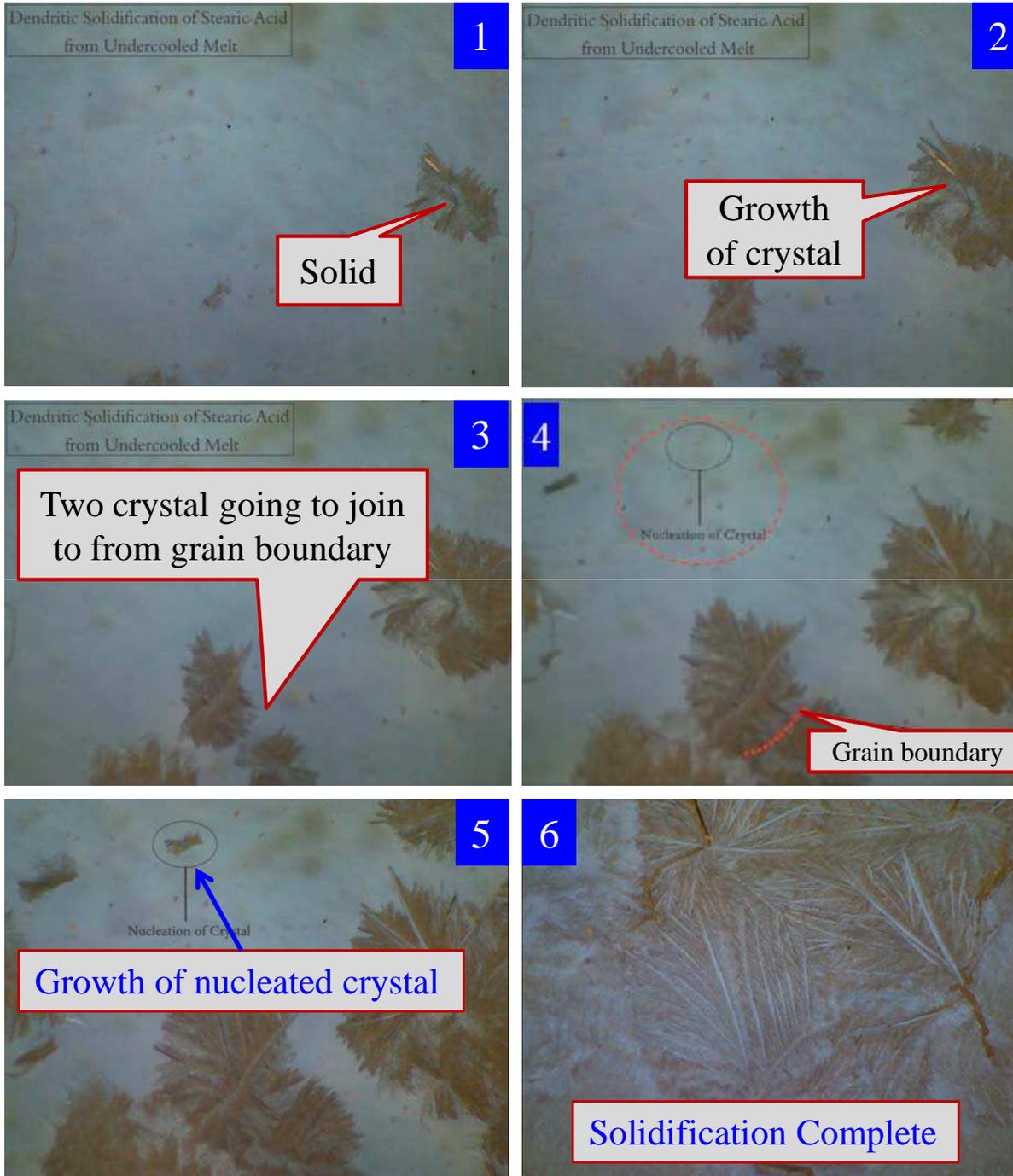
Cooling Curve for a pure metal



Solidification of pure metal

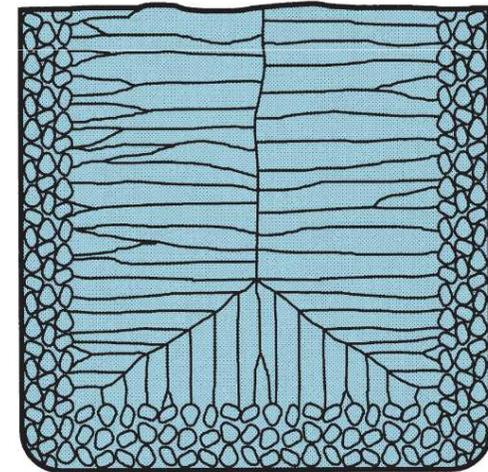
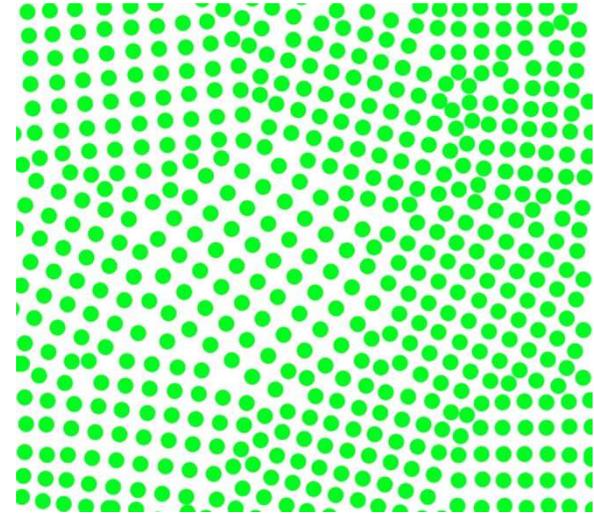
- ❑ When the temperature of the liquid metal has dropped sufficiently below its freezing point, stable aggregates or nuclei appear spontaneously at various points in the liquid. These nuclei, which have now solidified, act as centers for further crystallization.
- ❑ As cooling continues, more atoms tend to freeze, and they may attach themselves to already existing nuclei or form new nuclei of their own. Each nucleus grows by the attraction of atoms from the liquid into its space lattice.
- ❑ Crystal growth continues in three dimensions, the atoms attaching themselves in certain preferred directions, usually along the axes of the crystal this gives rise to a characteristic treelike structure which is called a **dendrite**.
- ❑ Since each nucleus is formed by chance, the crystal axes are pointed at random and the dendrites growing from them will grow in different directions in each crystal. Finally, as the amount of liquid decreases, the gaps between the arms of the dendrite will be filled and the growth of the dendrite will be mutually obstructed by that of its neighbors. This leads to a very irregular external shape.
- ❑ The crystals found in all commercial metals are commonly called **grains** because of this variation in external shape. The area along which crystals meet, known as the **grain boundary**, is a region of mismatch.

Liquid to Solid Phase Transformation : Solidification



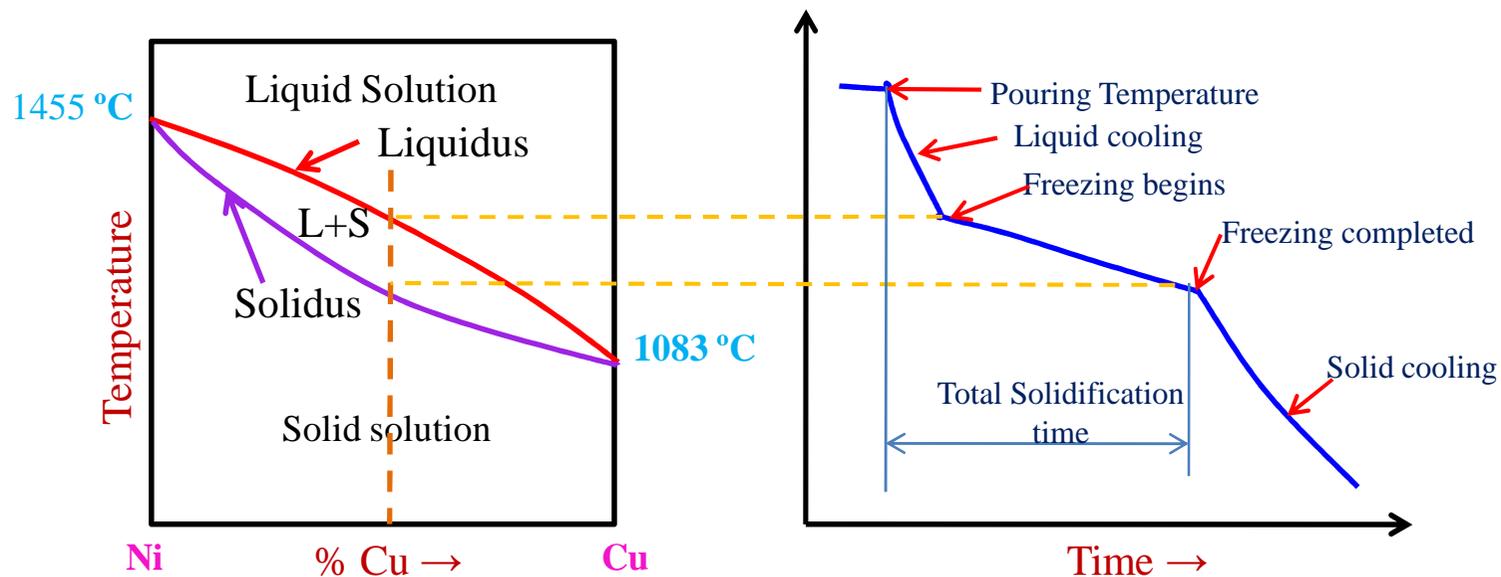
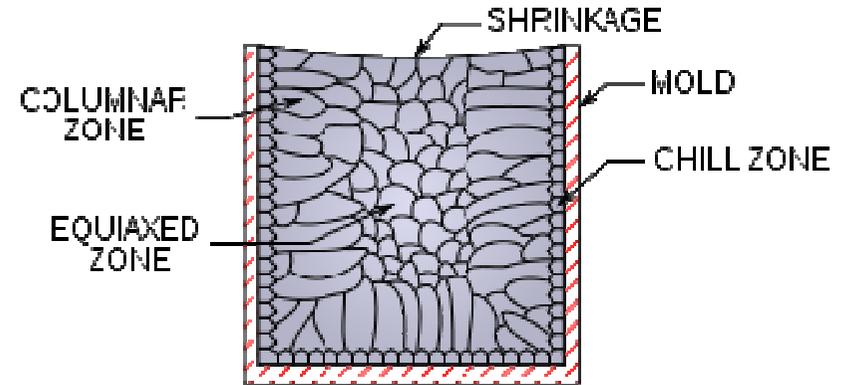
Solidification of pure metal

- ❑ This mismatch leads to a noncrystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- ❑ Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. Figure (previous page) shows schematically the process of crystallization from nuclei to the final grains.
- ❑ Due to chilling action of mold wall, a thin skin of solid metal is formed at the wall surface immediately after pouring.
- ❑ Grain structure in a casting of a pure metal, showing randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting.

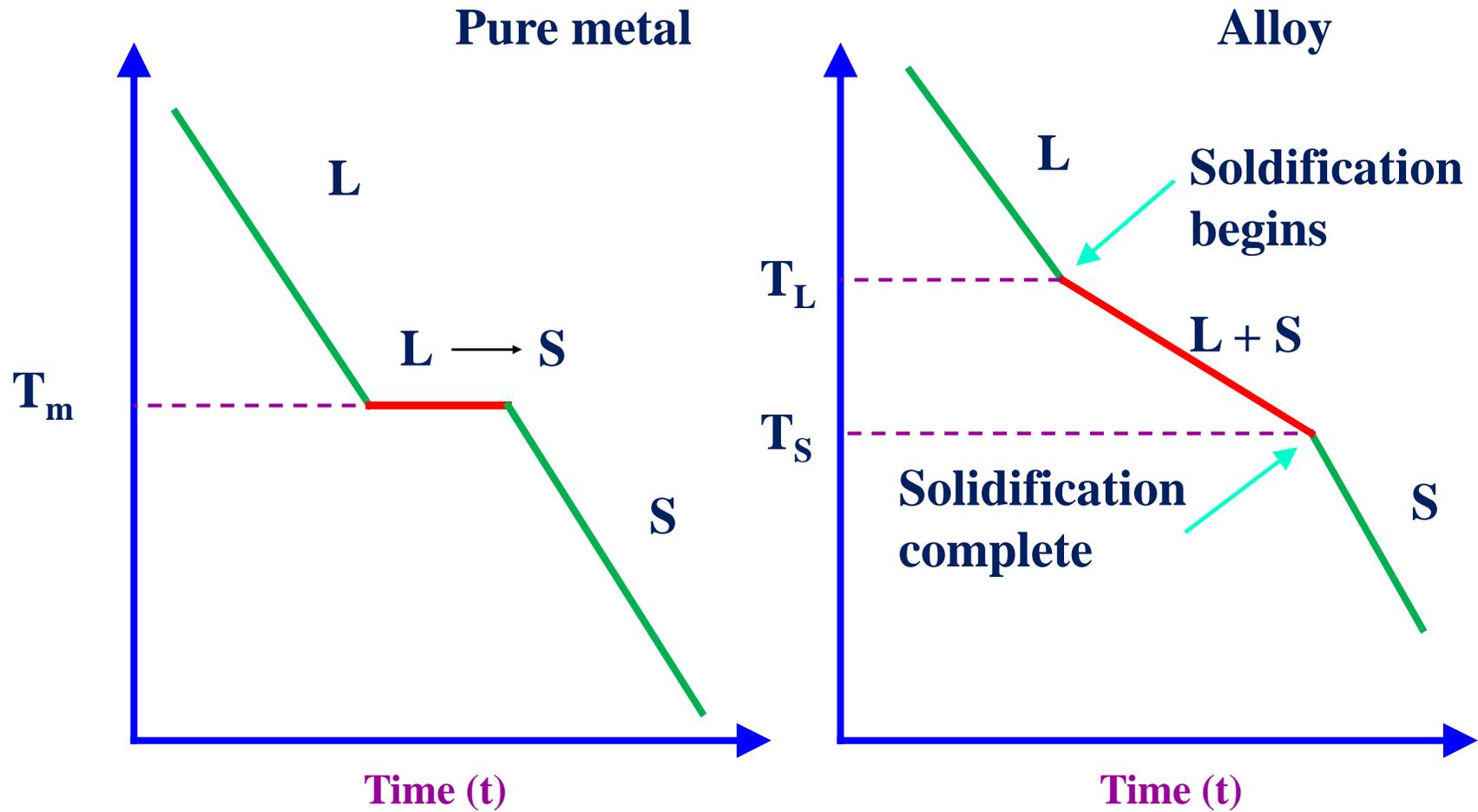


Solidification of Alloys

- ❑ Most alloys freeze over a temperature range
- ❑ Phase diagram for a Cu-Ni alloy system and cooling curve for different alloy systems.
- ❑ Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting.

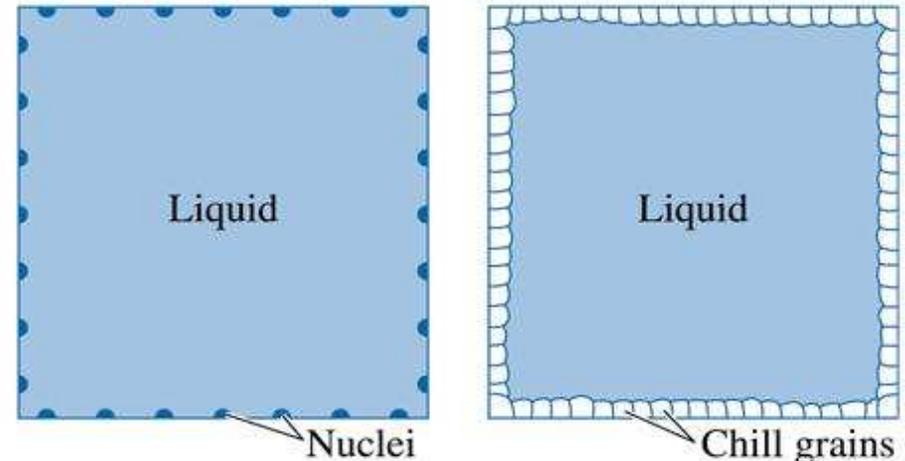


Comparison of cooling curves



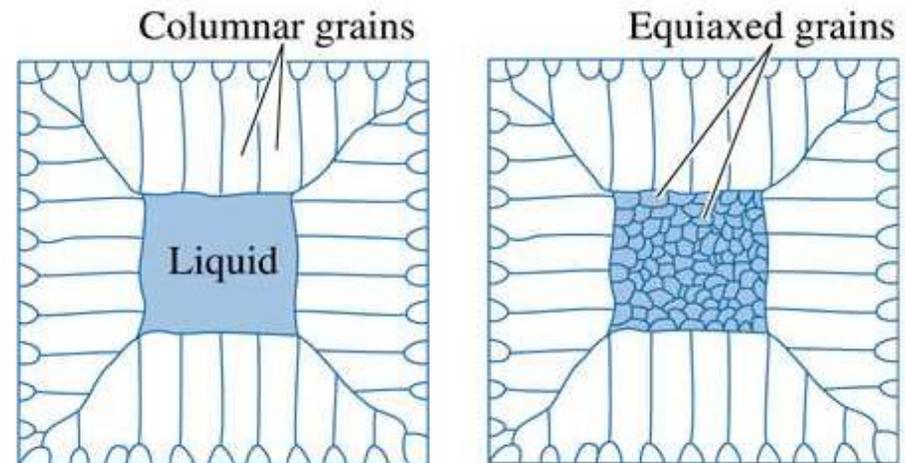
Cast Structure

- ❑ **Chill Zone:** A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- ❑ **Columnar Zone:** A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of a casting.
- ❑ **Equiaxed Zone:** A region of randomly oriented grains in the center of a casting produced as a result of widespread nucleation.



Nucleation begins

Chill zone forms



preferred growth produces the columnar zone

additional nucleation creates the equiaxed zone

Figure: Development of the ingot structure of a casting during solidification:

Nucleation

Solidification



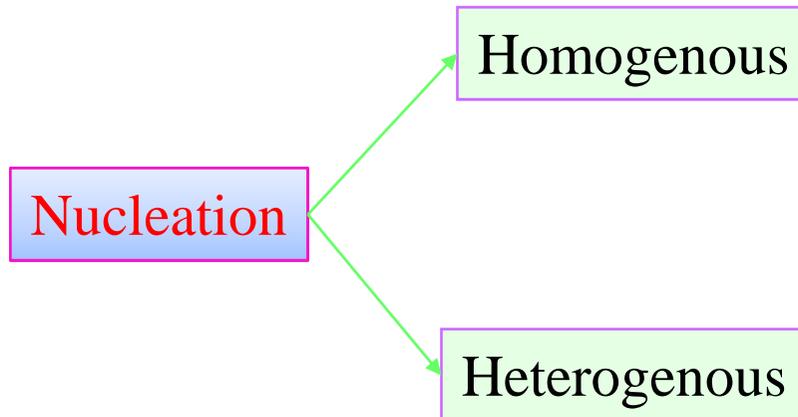
Nucleation



Growth

- ❑ Nucleation: localized formation of a distinct thermodynamic phase.
- ❑ Nucleation can occur in a gas, liquid or solid phase. Some examples of phases that may form via nucleation include:
 - In gas-creation of liquid droplets in saturated vapor
 - In liquid-formation of gaseous bubbles crystals (e.g., ice formation from water) or glassy regions.
 - In solid-Nucleation of crystalline, amorphous and even vacancy clusters in solid materials. Such solid state nucleation is important, for example, to the semiconductor industry.
- ❑ Most nucleation processes are physical, rather than chemical.
- ❑ There are two types of nucleation : **homogeneous** and **heterogeneous**. This distinction between them is made according to the site at which nucleating events occur. For the **homogeneous** type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the **heterogeneous** type, nuclei form preferentially at structural inhomogeneities such as container surfaces insoluble impurities grain boundaries, dislocations and so on

Nucleation



- *It occurs spontaneously and randomly, but it requires superheating or supercooling of the medium.*

- **Liquid → solid**
walls of container, inclusions

- **Solid → solid**
inclusions, grain boundaries, dislocations, stacking faults

- ❑ The probability of nucleation occurring at point in the parent phase is same throughout the parent phase
- ❑ In heterogeneous nucleation there are some preferred sites in the parent phase where nucleation can occur

Nucleation

- ❑ Compared to the heterogeneous nucleation (which starts at nucleation sites on surfaces) homogeneous nucleation occurs with much more difficulty in the interior of a uniform substance. The creation of a nucleus implies the formation of an interface at the boundaries of a new phase.
- ❑ Liquids cooled below the maximum heterogeneous nucleation temperature (melting temperature) but which are above the homogeneous nucleation temperature. (pure substance freezing temperature) are cooled super cooled.
- ❑ An example of supercooling: pure water freezes at -42°C rather than at its freezing temperature $^{\circ}\text{C}$.

***Nucleation** - The physical process by which a new phase is produced in a material.*

***Critical radius (r^*)** - The minimum size that must be formed by atoms clustering together in the liquid before the solid particle is stable and begins to grow.*

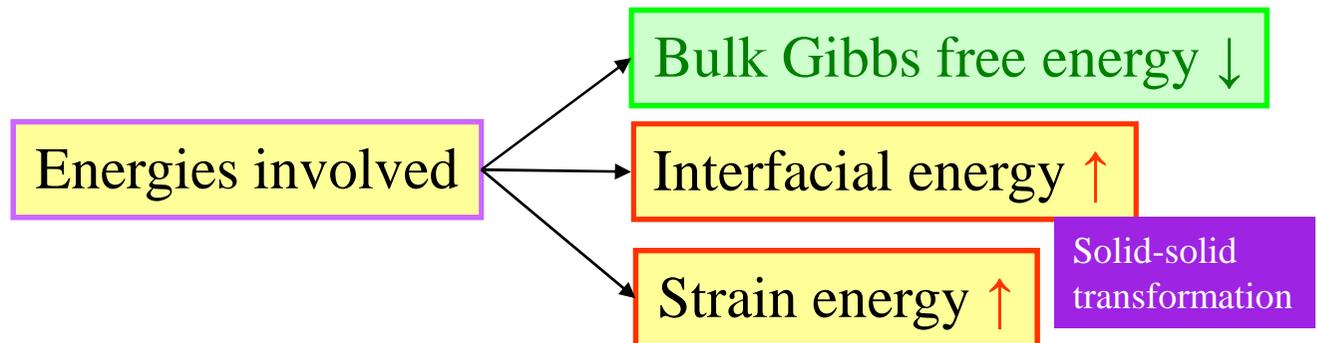
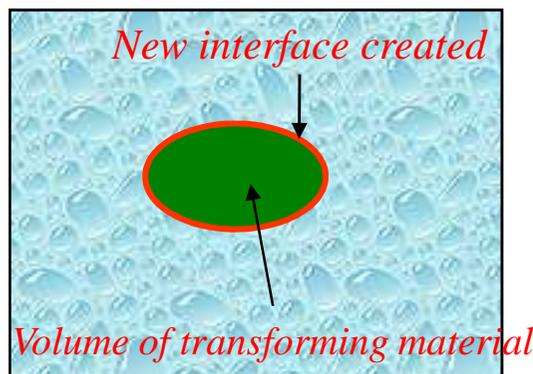
***Undercooling** - The temperature to which the liquid metal must cool below the equilibrium freezing temperature before nucleation occurs.*

***Homogeneous nucleation** - Formation of a critically sized solid from the liquid by the clustering together of a large number of atoms at a high undercooling (without an external interface).*

***Heterogeneous nucleation** - Formation of a critically sized solid from the liquid on an impurity surface.*

Nucleation

- ❑ There is no change in composition involved as we are considering a pure metal. If we solidify an alloy this will involve long range diffusion.
- ❑ When a volume of material (V) transforms three energies have to be considered :
 - ✓ reduction in G (assume we are working at constant T & P),
 - ✓ increase in γ (interface free-energy),
 - ✓ increase in strain energy.
- ❑ In a liquid to solid phase transformation the strain energy term can be neglected as the liquid melt can flow to accommodate the volume change (assume we are working at constant T & P).
- ❑ The process can start only below the melting point of the liquid (as only below the melting point the $G_{\text{Liquid}} < G_{\text{Solid}}$). I.e. we need to Undercool the system. As we shall note, under suitable conditions (e.g. container-less solidification in zero gravity conditions), melts can be undercooled to a large extent without solidification taking place.



Solidification of Pure Metal : Homogeneous Nucleation

- ❑ Consider a pure melt which is cooled below its melting temperature such a liquid is known as undercooled.
- ❑ Let a small volume V_s of the liquid turn into solid. If G_s is the free energy per unit volume of the solid and G_l that of the liquid, if A_{ls} is the liquid- solid interfacial area, and if γ_{ls} is interfacial free energy, then the total free energy of the system is given by

$$G_F = V_s G_s + V_l G_l + \gamma_{ls} A_{ls}$$

- ❑ Before the small volume of solid formed, the free energy of the system is given by

$$G_l = (V_s + V_l) G_l$$

- ❑ Thus, the total free energy change associated with the transformation of a small volume of liquid vs. into solid is given by

$$\delta G = G_F - G_l$$

$$= V_s (G_s - G_l) + \gamma_{ls} A_{ls}$$

$$\delta G = V_s \Delta G + \gamma_{ls} A_{ls}$$

Solidification of Pure Metal : Homogeneous Nucleation

Free energy change on nucleation =

Reduction in bulk free energy + increase in surface energy + increase in strain energy

$$\delta G = (\text{Volume}).(\Delta G) + (\text{Surface}).(\gamma)$$

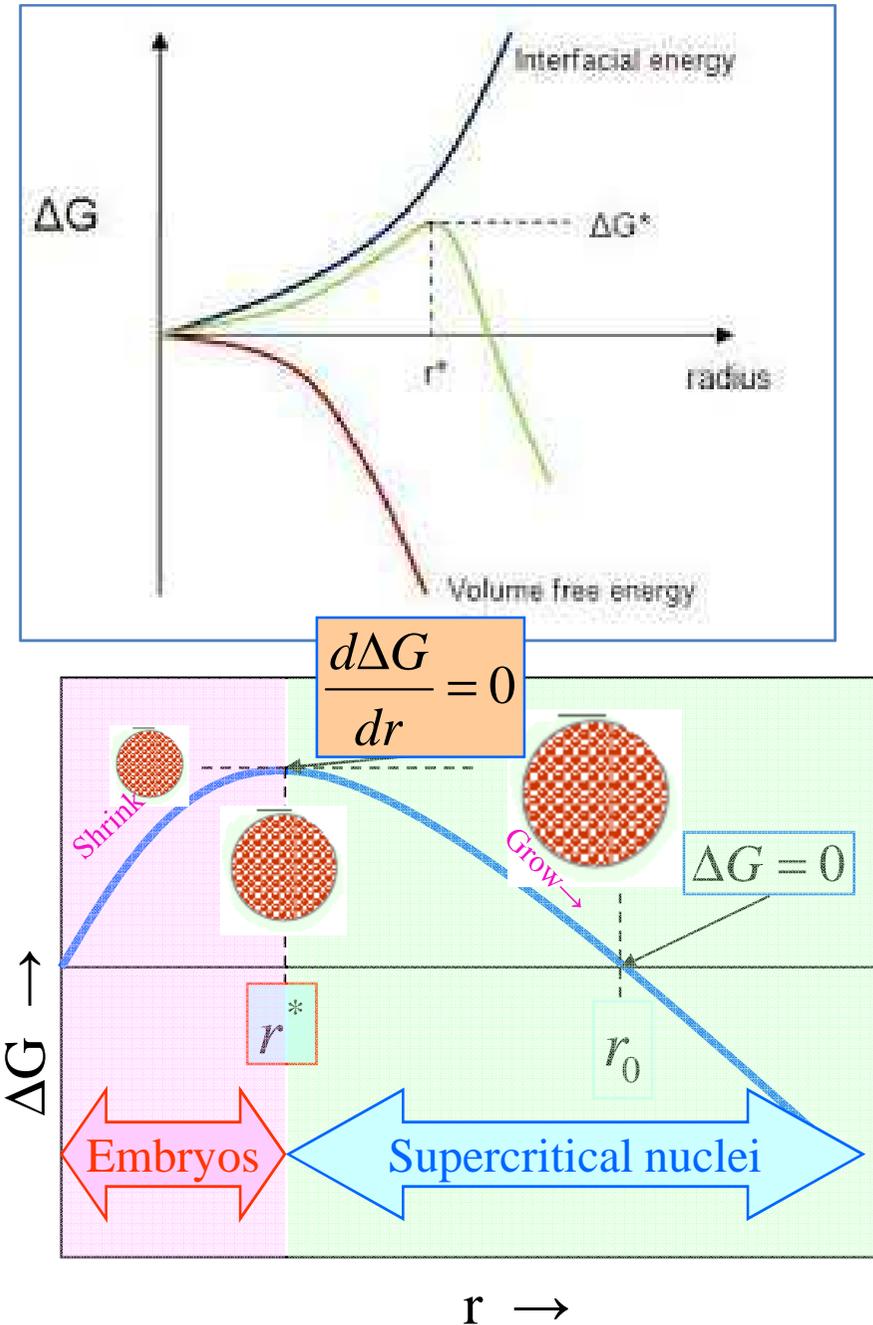
- ❑ Note that the interfacial energy is always positive. Hence the contribution from the second term is always positive.
- ❑ However, depending on whether the liquid is above or below the melting temperature, ΔG is positive or negative.
- ❑ Hence, in an under cooled liquid, where ΔG is negative, the system will try to minimize the shape in such a way that the overall interfacial energy is reduced so that the maximum reduction in free energy can be achieved.
- ❑ If we assume interfacial energy to be isotropic, then the volume transformed is a sphere of radius r (since the maximum volume is enclosed for the minimal surface area for a sphere), we get

$$\delta G = \left(\frac{4}{3} \pi r^3 \right).(\Delta G_v) + \left(4 \pi r^2 \right).(\gamma_{ls})$$

Solidification of Pure Metal : Homogeneous Nucleation

- ❑ In figure, we show the variation of the volume free energy, interfacial energy and overall free energy change as a function of r .
- ❑ Since the interfacial contribution goes as r^2 and that of bulk free energy as r^3 , at smaller r , interfacial energy always dominates and being a positive energy, it actually suppresses the formation of solid.
- ❑ Unless the size of the solid is above some size where in the (negative) bulk free energy change can more than compensate for the (+ve) interfacial energy, the solid will not be stable (even if it forms).
- ❑ Thus one can identify the critical radius of the solid that is stable when formed in the under cooled liquid by minimizing δG with respect to 'r'.

$$\left[\frac{d\delta G}{dr} \right]_{r=r^*} = 0$$



Solidification of Pure Metal : Homogeneous Nucleation

$$\delta G = \left(\frac{4}{3} \pi r^3 \right) \cdot (\Delta G_v) + (4\pi r^2) \cdot (\gamma_{ls}) \Rightarrow \left[\frac{d\delta G}{dr} \right]_{r=r^*} = 0$$

$$\frac{d}{dr} \left[\frac{4}{3} \pi r^3 \Delta G + 4\pi r^2 \gamma_{ls} \right]_{r=r^*} = 0$$

$$\left[4\pi r^2 \Delta G + 8\pi r \gamma_{ls} \right]_{r=r^*} = 0$$

$$\left[4\pi r^2 \Delta G = -8\pi r \gamma_{ls} \right]_{r=r^*} \Rightarrow r^* = \frac{-2\gamma_{ls}}{\Delta G}$$

$$\delta G^* = \frac{4}{3} \pi \left(\frac{-2\gamma_{ls}}{\Delta G} \right)^3 \Delta G + 4\pi \left(\frac{-2\gamma_{ls}}{\Delta G} \right)^2 \gamma_{ls}$$

$$= -\frac{4}{3} \pi \times \frac{8\gamma_{ls}^3}{\Delta G^3} \Delta G + 4\pi \times \frac{4\gamma_{ls}^2}{\Delta G} \gamma_{ls}$$

$$= \left(-\frac{32\pi}{3} + \frac{48\pi}{3} \right) \frac{\gamma_{ls}^3}{\Delta G^2}$$

$$\delta G^* = \frac{16\pi\gamma_{ls}^3}{3\Delta G^2}$$

Rate of Nucleation

- There is an energy barrier of ΔG^* for formation of a solid nucleus of critical size r^* . The probability of energy fluctuation of size ΔG^* is given by the Arrhenius equation and the rate of homogeneous nucleation is

$$N^* = V_d \exp\left(-\frac{\Delta G^*}{KT}\right)$$

- Where V_d is the frequency with which atoms from liquid attach to the solid nucleus. The rearrangement of atoms needed for joining the solid nucleus typically follows the same temperature dependence as the diffusion co-efficient.

Questions..?

1. Differentiate between a crystal, dendrite, and a grain.
2. Why is grain boundary irregular?
3. Is there any difference in the kinetic energy of the atoms in the liquid and the gas at the boiling point? explain
4. What is supercooling and explain the mechanism of crystallization?
5. Define homogeneous nucleation and heterogeneous nucleation? And derive the expression for homogeneous nucleation.
6. Calculate the critical free energy of nucleation of ice from water at (i) 0°C, (ii)-5°C, and (iii)-40°C. Also calculate the critical radius at each temperature. The enthalpy of fusion of ice is 6.02kJ/mol. The energy of the ice-water interface, 0.076 J m⁻², can be taken to be independent of temperature. [molar volume of ice = 19 cm³]
7. **(a)** For the solidification of pure gold, calculate the critical radius r^* and the activation free energy ΔG^* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are -1.16×10^9 J/m³ and 0.132 J/m², respectively, assume supercooling value of gold is 230°C. **(b)** And also calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.413 nm for solid gold at its melting temperature.
8. Name the two stages involved in the formation of particles of a new phase. Briefly describe each.

Questions..?

9. Rewrite the expression for the total free energy change for nucleation for the case of a cubic nucleus of edge length a (instead of a sphere of radius r). Now differentiate this expression with respect to a and solve for both the critical cube edge length, a^* , and also free energy ΔG^* . Is ΔG^* greater for cube or sphere?
10. Assume for the solidification of nickel that nucleation is homogeneous, and the number of stable nuclei is 10^6 nuclei per cubic meter. Calculate the critical radius and the number of stable nuclei that exist at the following degrees of supercooling: 200 K and 300 K. and What is significant about the magnitudes of these critical radii and the numbers of stable nuclei? [$r_{Ni} = 0.255 \text{ J/m}^2$, $\Delta H_f = -2.53 \times 10^9 \text{ J/m}^3$, Super cooling value for Ni = 319°C]

Introduction

- ❑ *You have been introduced to the lattice structures and types of bonding in crystalline solids in earlier lectures.*
- ❑ You know that the behavior of electrons determine the way the atoms interact- the type of bonding (metallic, ionic, covalent and vanderwaals), that holds atoms in a solid together.
 - ✓ But is the knowledge of bonding and crystal structure is sufficient to predict the macroscopic properties of materials?
- ❑ So far in our study of crystalline solids, we have assumed a correspondence between the abstract three-dimensional lattice and the actual structure of solids. This implies that crystals are perfect.
- ❑ **Perfect Crystal** : A crystal, in which all the atoms are at rest on their correct lattice position in the crystal.
- ❑ Such perfect crystals could only exist at absolute zero, and thermal vibrations can be treated as a form of defect in crystal structures.
 - ✓ For $T > 0K$, defects always exist in the structure.

REAL CRYSTALS ARE NEVER PERFECT, THERE ARE ALWAYS DEFECTS

Introduction

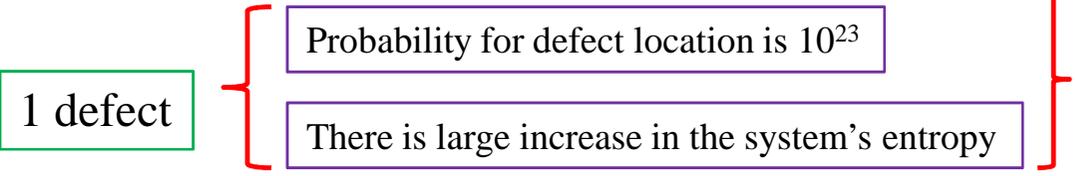
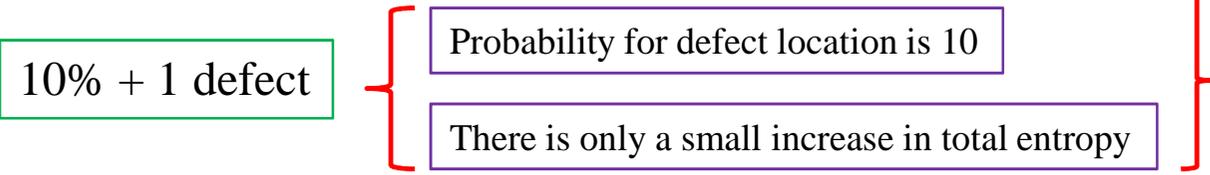
- ❑ *For example* : If a bulk metal (i.e., steel) were a single perfect crystal, it would have a strength far exceeding the strongest steel ever produced from metallurgical research. May be this is one of the limitation, in the strength of a metal comes from the number and type of defect, rather than from the nature of the ideal crystal lattice.
- ❑ *Many other important properties of materials are due to the imperfections caused by crystal defects (may be...!)*
- ❑ In this topic we will discuss different types of imperfections or defects in the ideal arrangement of atoms in a crystal.
- ❑ **For example** : When/If you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size.
- ❑ **Another example** : Forging a metal tool introduces defects! and increases strength and elasticity of the tool. Note, that in the case the required properties are achieved without changes in composition of the material, but just by manipulating the crystal defects.

“Crystals are like people, it is the defects in them which tend to make them interesting”

- Colin Humphreys

Thermodynamic cause of crystal imperfections

- ❑ Crystal defects are thermodynamically-controlled phenomena.
 - ✓ To understand how defects come about, consider the effect of probability on entropy in the following two examples.
- ❑ A typical single crystal of a large gemstone contains about 1 mole of atoms. Now compare the effect of adding a single additional defect to

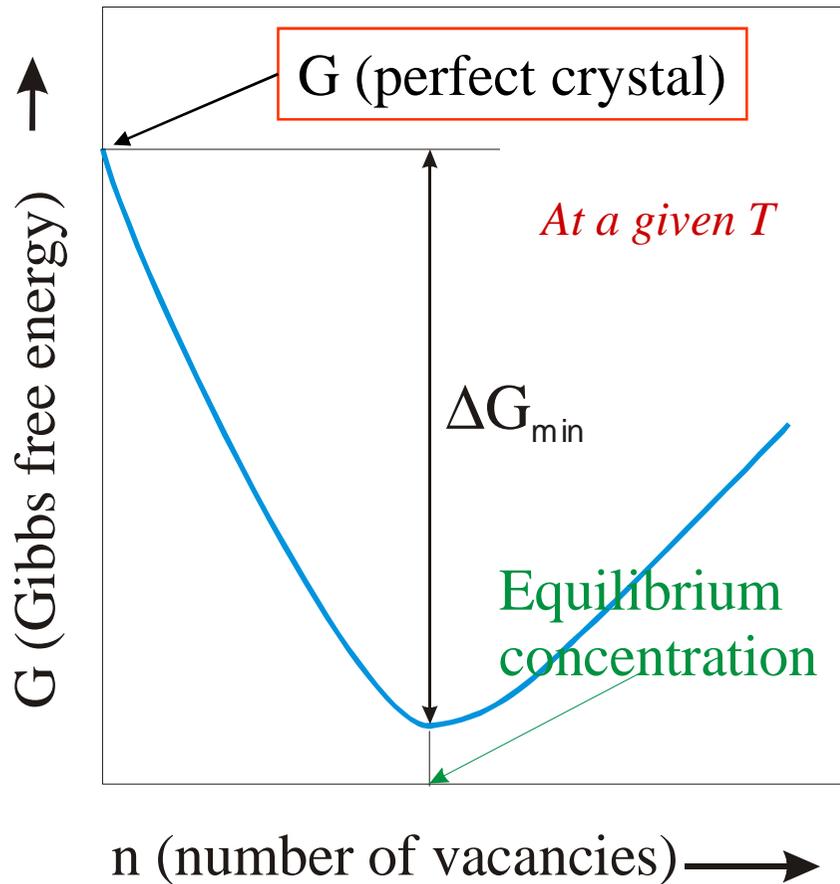
- ❑ An ideal crystal → 1 defect 
- ❑ A lattice which already has 10% defects → 10% + 1 defect 

- ❑ This kind of entropy is called configurational entropy. It is given by the equation

$$S = K \ln(\omega) \quad K = \text{Boltzmann constant}$$
$$\omega = \text{Probability}$$

- ❑ So far the effect of entropy; however, the creation of any kind of defect costs energy, since the total lattice energy will be reduced. The competing effects of the energy required to disturb the lattice and the initial large gain in entropy causes a minimum in the free energy.

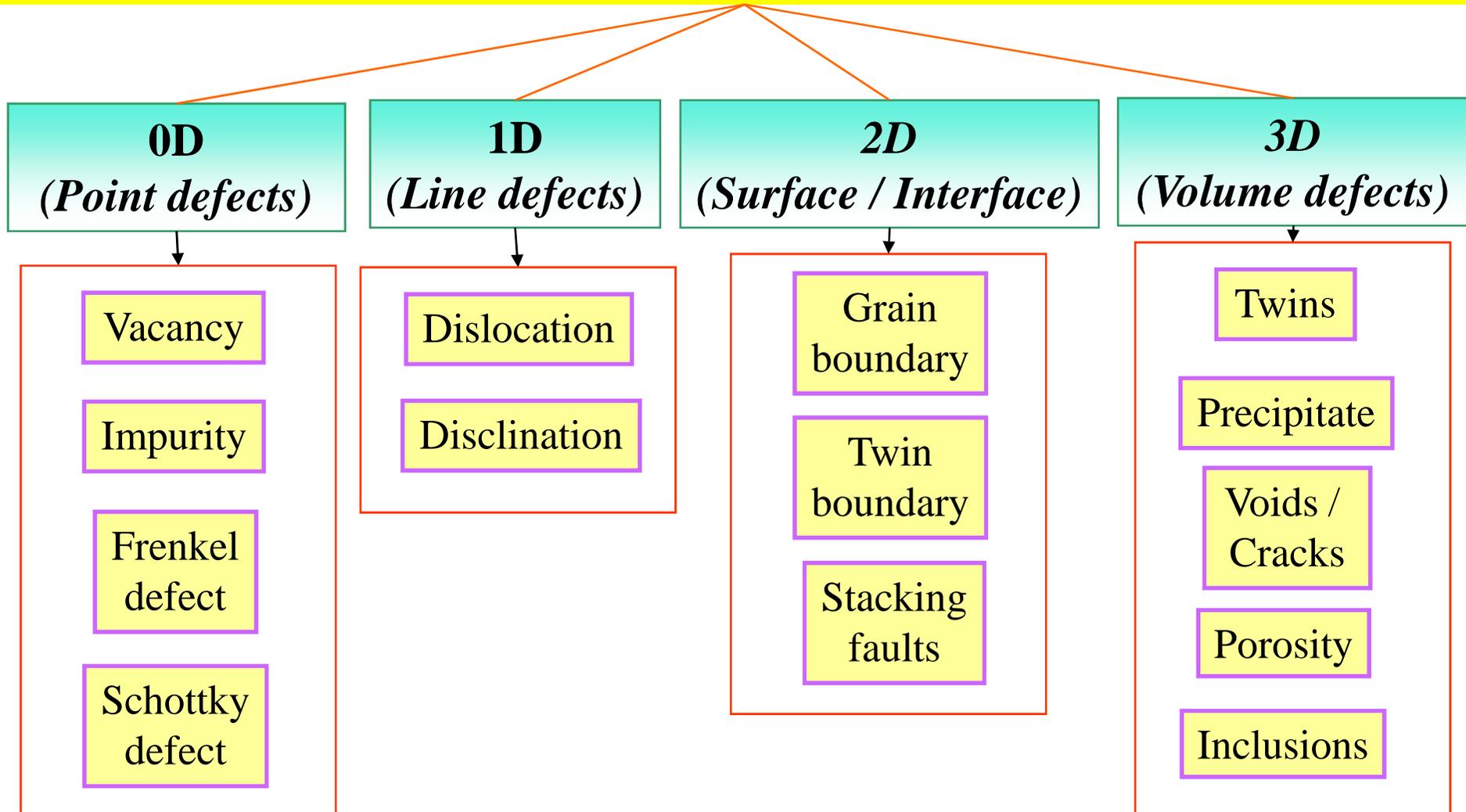
Thermodynamic cause of crystal imperfections



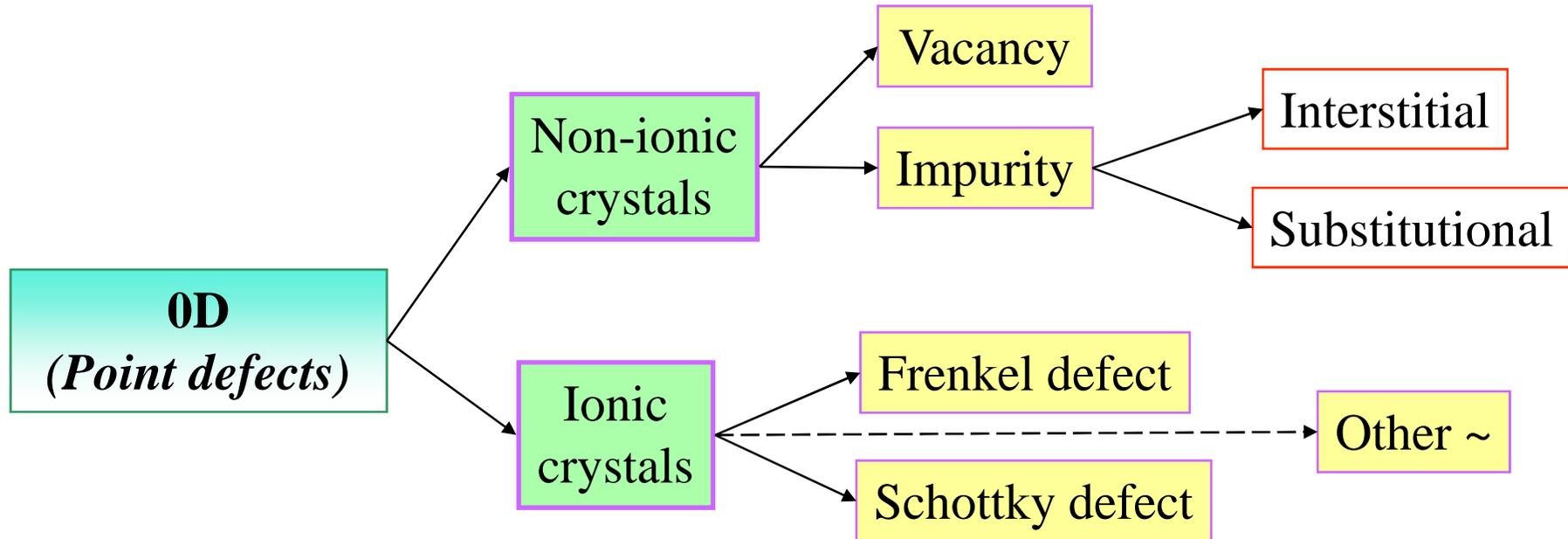
T ($^{\circ}\text{C}$)	n/N
500	1×10^{-10}
1000	1×10^{-5}
1500	5×10^{-4}
2000	3×10^{-3}
$\Delta H_f = 1 \text{ eV/vacancy}$ $= 0.16 \times 10^{-18} \text{ J/vacancy}$	

❑ Certain equilibrium number of vacancies are preferred at $T > 0\text{K}$

CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY



Point Defects



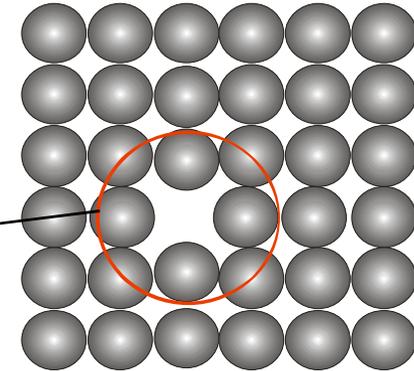
- ❑ Imperfect point-like regions in the crystal about the size of 1-2 atomic diameters

Point Defects : Non-ionic crystals

Vacancy

- ❑ Missing atom from an atomic site
- ❑ Atoms around the vacancy displaced
- ❑ Tensile stress field produced in the vicinity

Tensile Stress Fields ?



Impurity

Interstitial

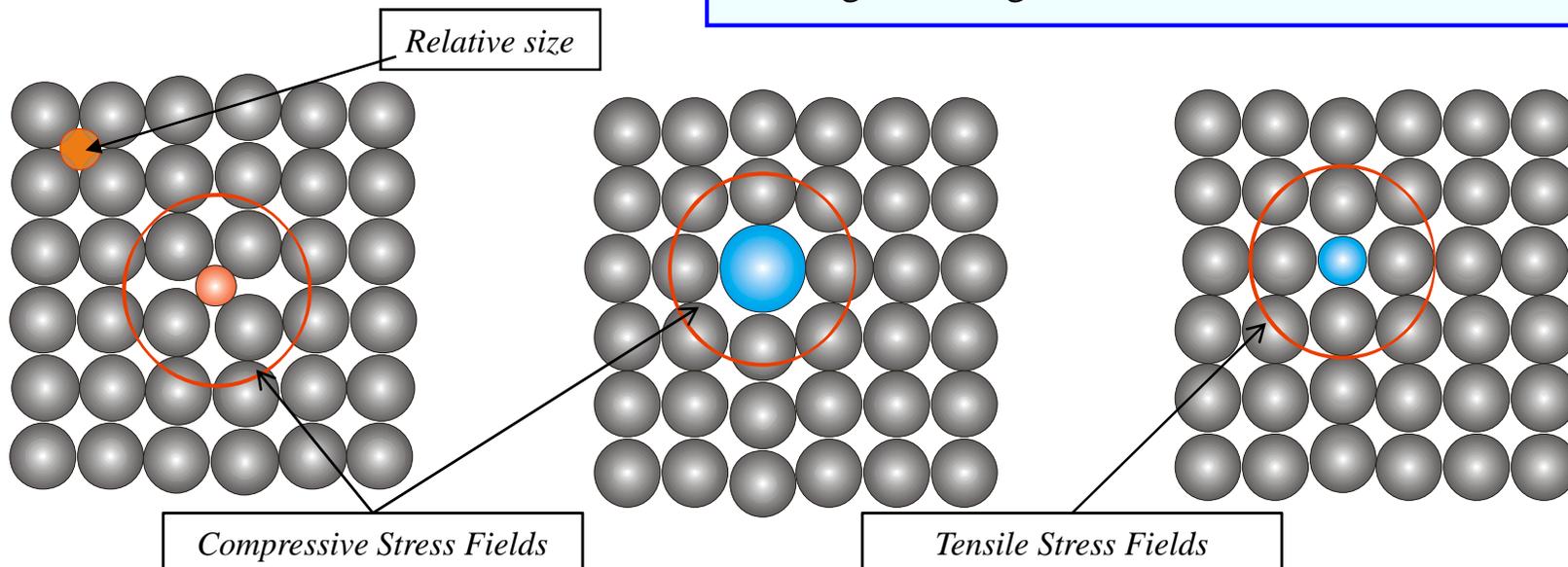
Substitutional

❑ Substitutional Impurity

- Foreign atom replacing the parent atom in the crystal
- E.g. **Cu** sitting in the lattice site of FCC-**Ni**

❑ Interstitial Impurity

- Foreign atom sitting in the void of a crystal
- E.g. **C** sitting in the octahedral void in HT FCC-**Fe**



Point Defects : Ionic crystals

❑ Overall electrical neutrality has to be maintained

Frenkel defect

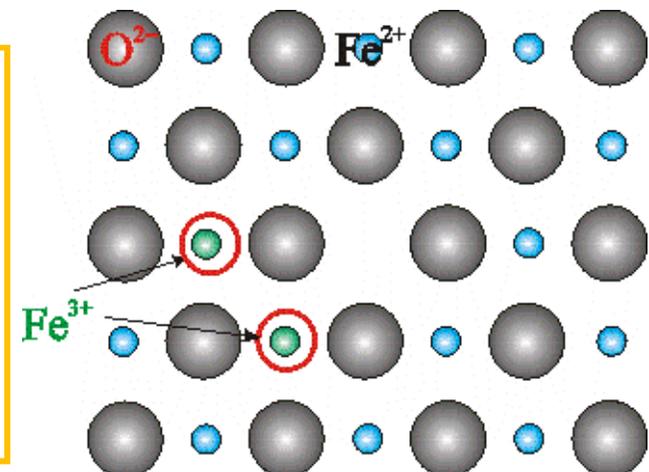
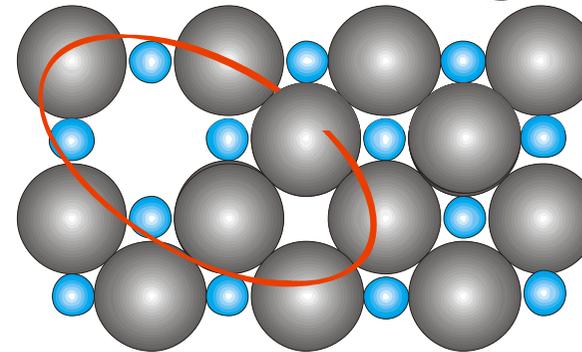
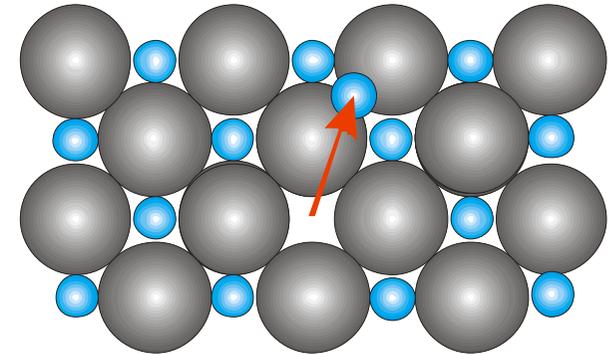
- Cation (being smaller get displaced to interstitial voids
- E.g. AgI, CaF₂

Schottky defect

- Pair of anion and cation vacancies
- E.g. Alkali halides

Other defects due to charge balance

- ❑ FeO heated in oxygen atmosphere → Fe_xO ($x < 1$)
- ❑ Vacant cation sites are present
- ❑ Charge is compensated by conversion of ferrous to ferric ion:
$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^{-}$$
- ❑ For every vacancy (of Fe cation) two ferrous ions are converted to ferric ions → provides the 2 electrons required by excess oxygen



How many vacancies are present?

- ❑ The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v , increases exponentially with the absolute temperature, T and can be estimated using the equation:

$$N_v = N_s \exp\left(\frac{-E_v}{K_B T}\right)$$

N_s = Number of regular lattice sites

K_B = Boltzman constant

E_v = Energy needed to form a vacant lattice site in a perfect crystal

- ❑ Using this simple equation we can estimate vacancy per 10^n lattice atoms.

Solved Example -1

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.4 g/cm³ respectively.

This problem may be solved by using following equations

It is first necessary, however, to determine the value of N_s , the number of atomic sites per cubic meter for copper,

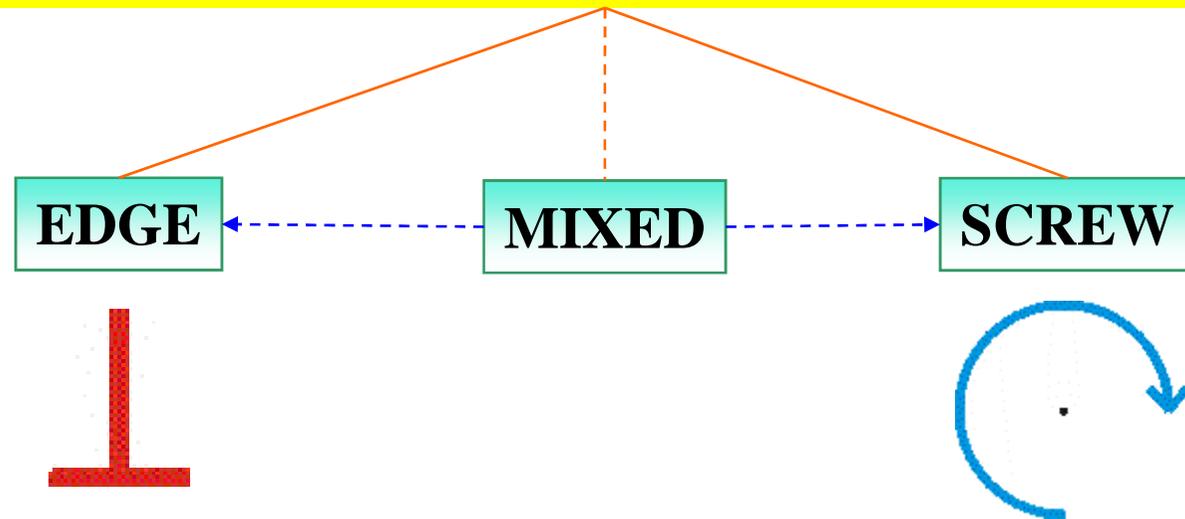
from its atomic weight A_{Cu} , its density ρ and Avogadro's number N_A , according to

$$\begin{aligned} N_s &= \frac{N_A \rho}{A_{Cu}} \\ &= \frac{(6.023 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\ &= 8.0 \times 10^{28} \text{ atoms/m}^3 \end{aligned}$$

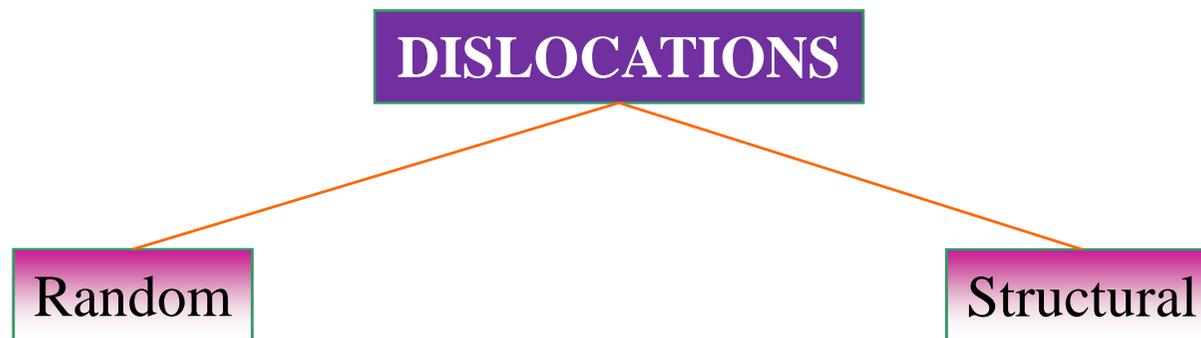
Thus the number of vacancies at 1000°C is equal to $N_v = N_s \exp\left(\frac{-E_v}{K_B T}\right)$

$$\begin{aligned} &= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[\frac{-0.9 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\ &= 2.2 \times 10^{25} \text{ vacancies/m}^3 \end{aligned}$$

1D Defects : DISLOCATIONS



- Usually dislocations have a mixed character and *Edge* and *Screw* dislocations are the ideal extremes

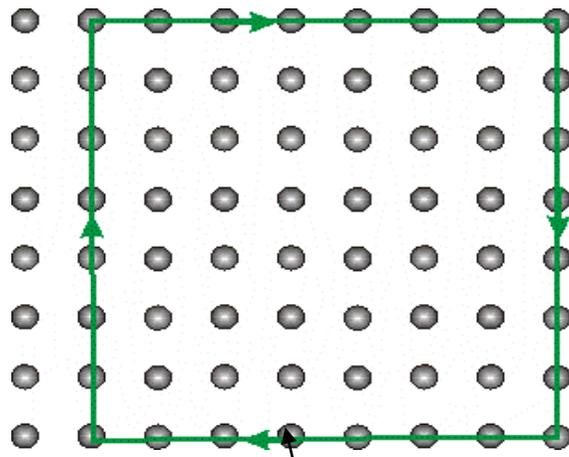


- Geometrically necessary dislocations

Introduction

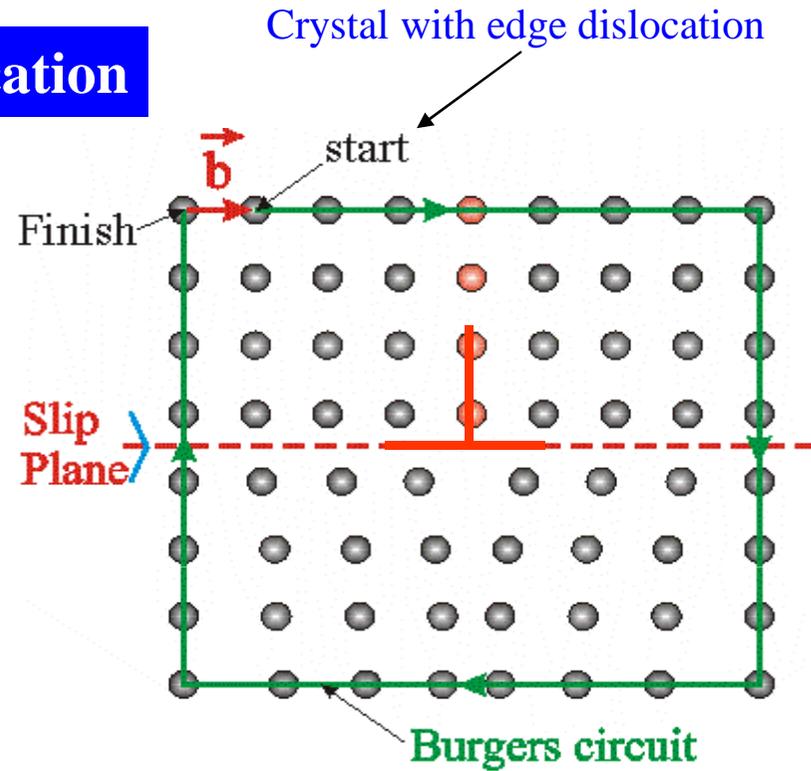
- ❑ Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane
- ❑ The intersection of the extra half-plane of atoms with the slip plane defines the dislocation line (*for an edge dislocation*)
- ❑ Direction and magnitude of slip is characterized by the Burgers vector of the dislocation (*A dislocation is born with a Burgers vector and expresses it even in its death!*)
- ❑ The Burgers vector is determined by the Burgers Circuit
- ❑ Right hand screw (finish to start) convention is used for determining the direction of the Burgers vector
- ❑ As the periodic force field of a crystal requires that atoms must move from one equilibrium position to another \Rightarrow **b** must connect one lattice position to another (*for a full dislocation*)
- ❑ Dislocations tend to have as small a Burgers vector as possible
- ❑ The edge dislocation has compressive stress field above and tensile stress field below the slip plane.
- ❑ Dislocations are non-equilibrium defects and would leave the crystal if given an opportunity

Burgers Vector

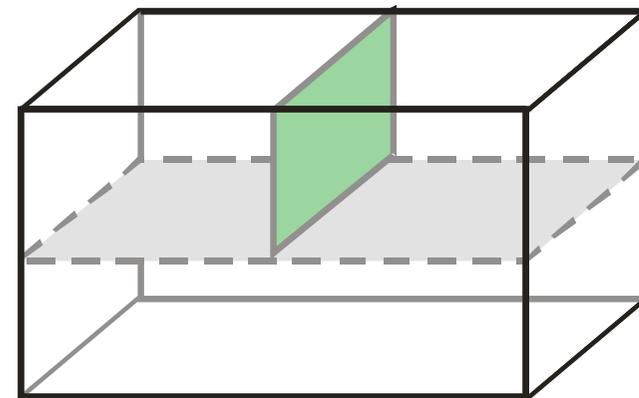
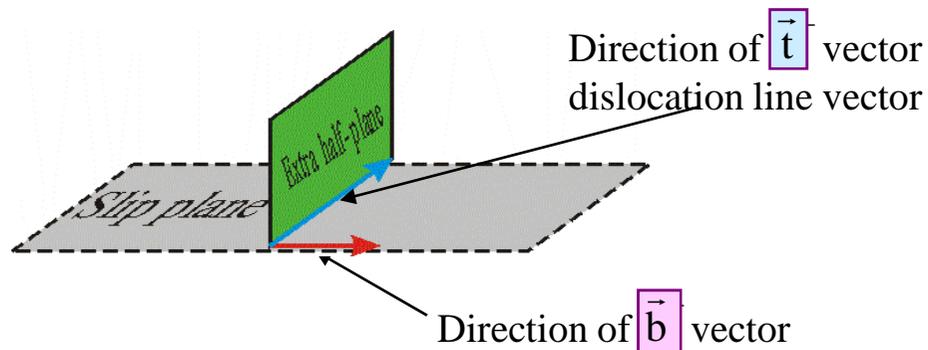


Perfect crystal

Edge dislocation



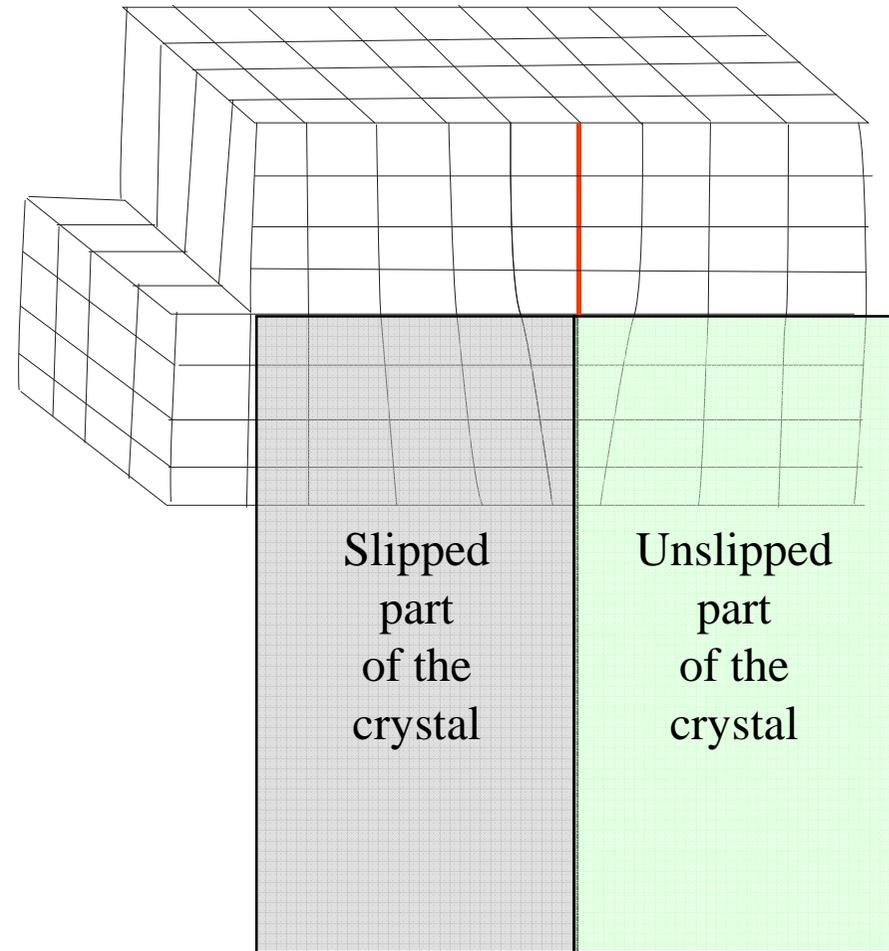
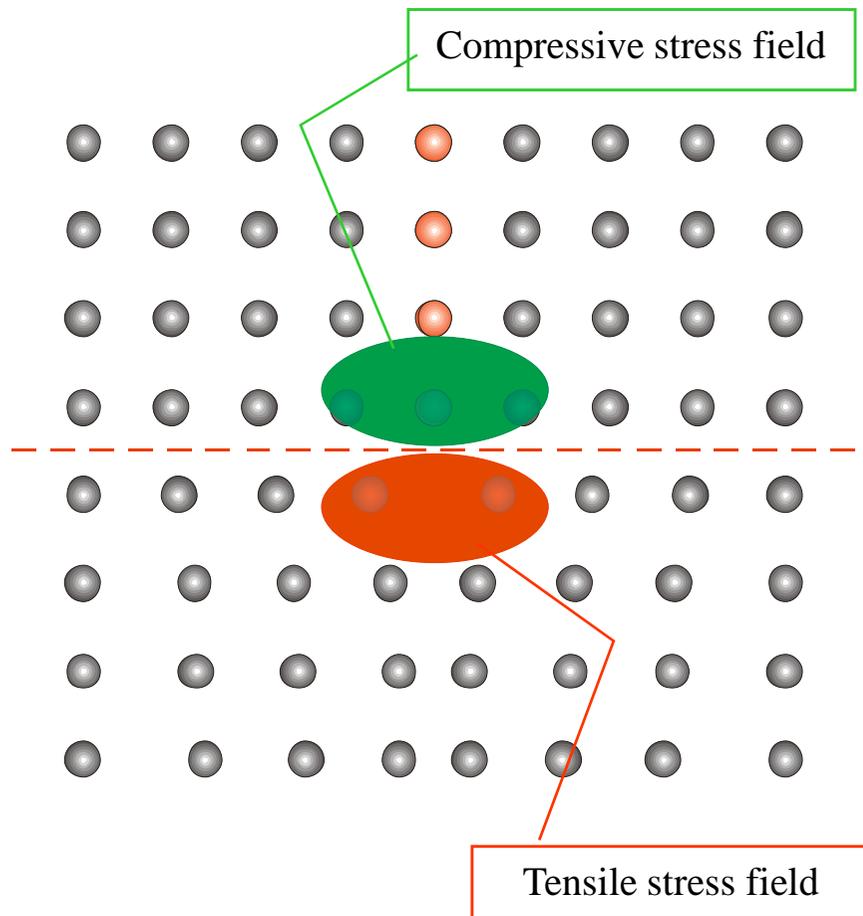
RHFS:
Right Hand Finish to Start convention



A dislocation has associated with it two vectors:

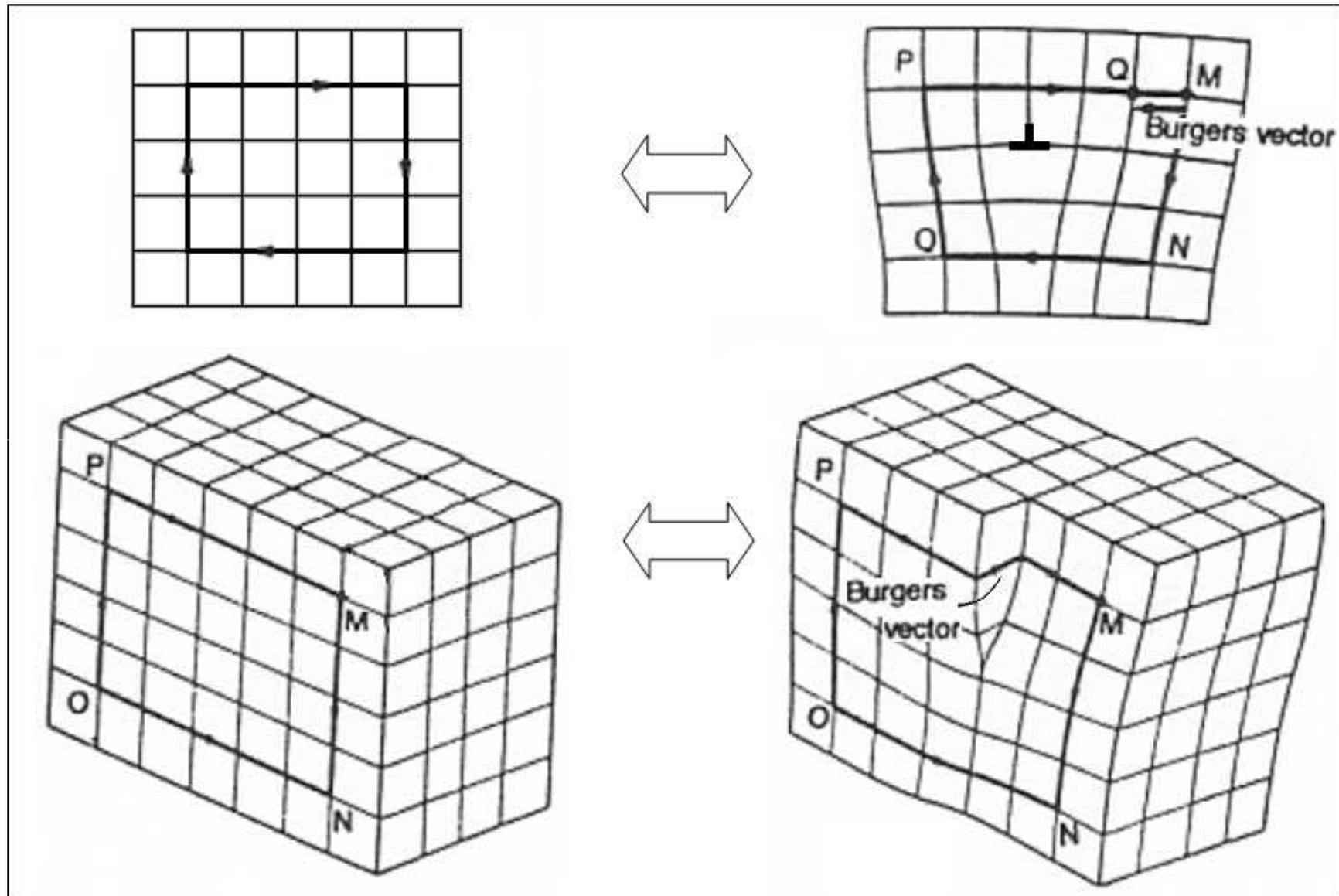
\vec{t} → A unit tangent vector along the dislocation line

\vec{b} → The Burgers vector



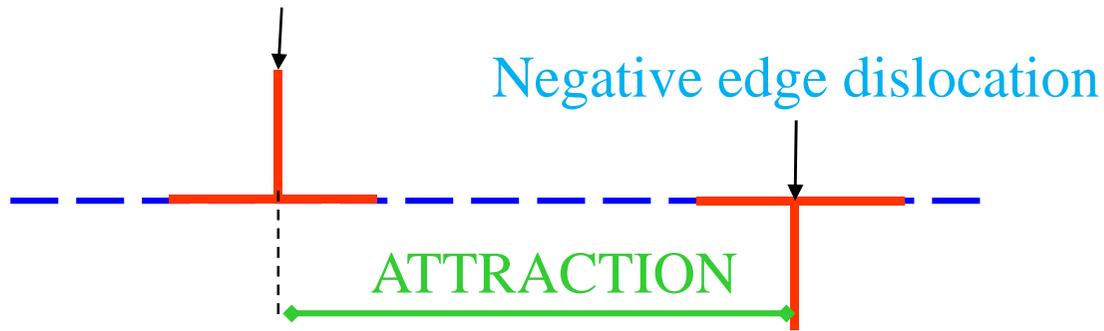
Dislocation is a boundary between the slipped and the unslipped parts of the crystal lying over a slip plane

Burgers Vector in Edge & Screw dislocations



+ve & -ve edge dislocations

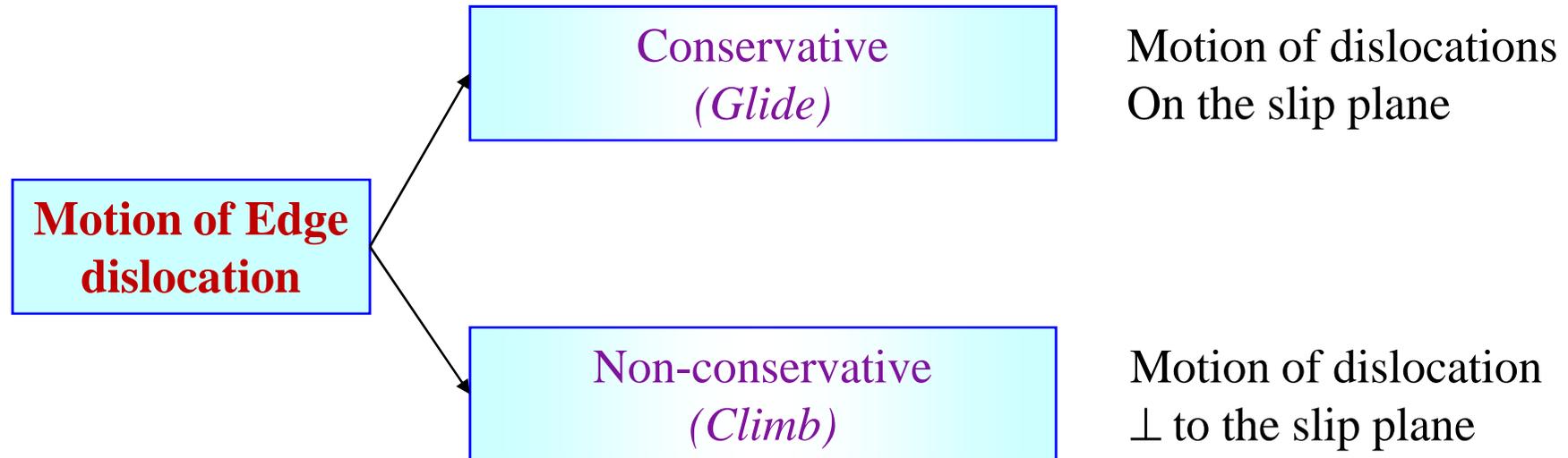
Positive edge dislocation



Can come together and cancel one another

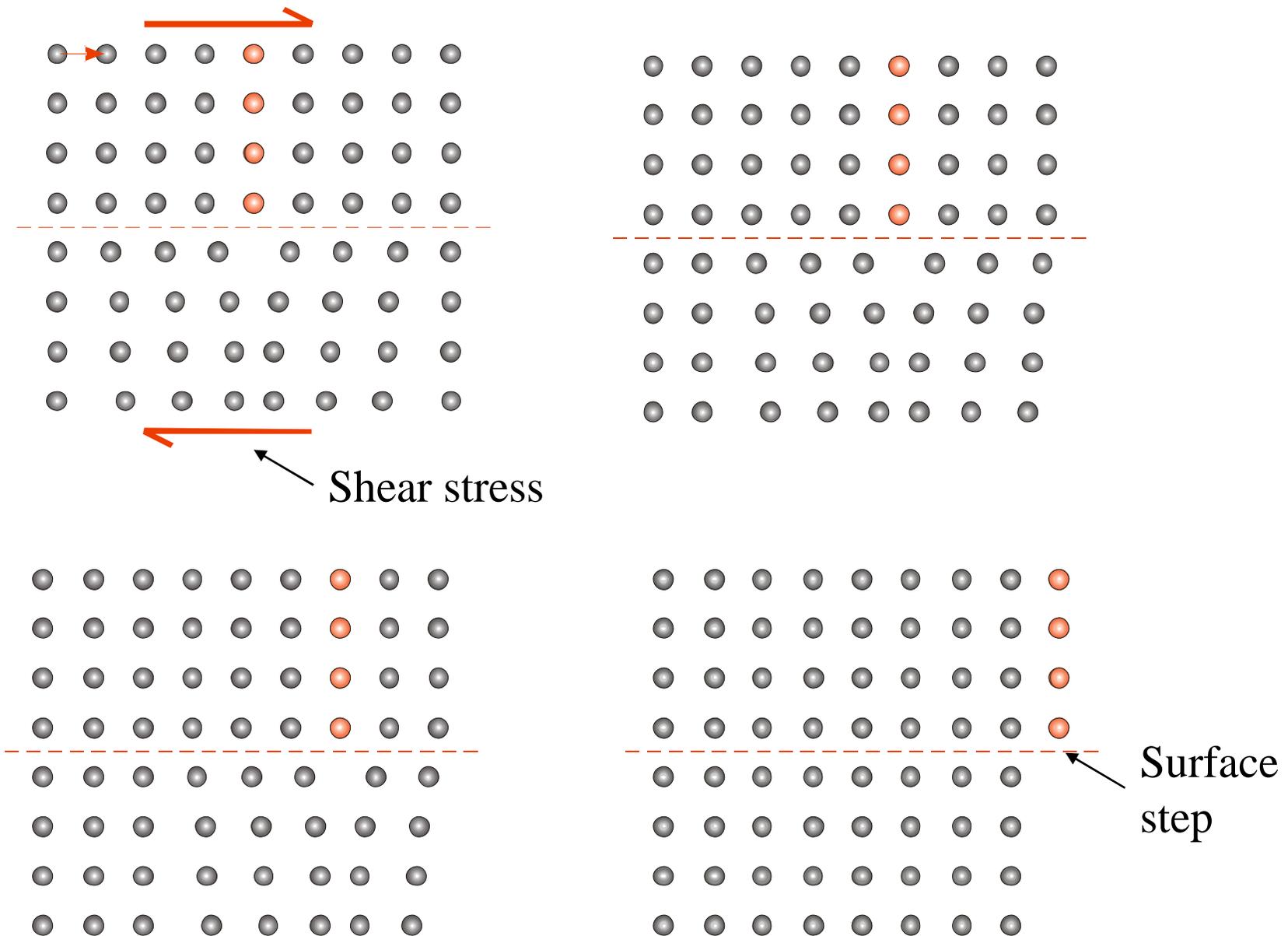


Motion of dislocations

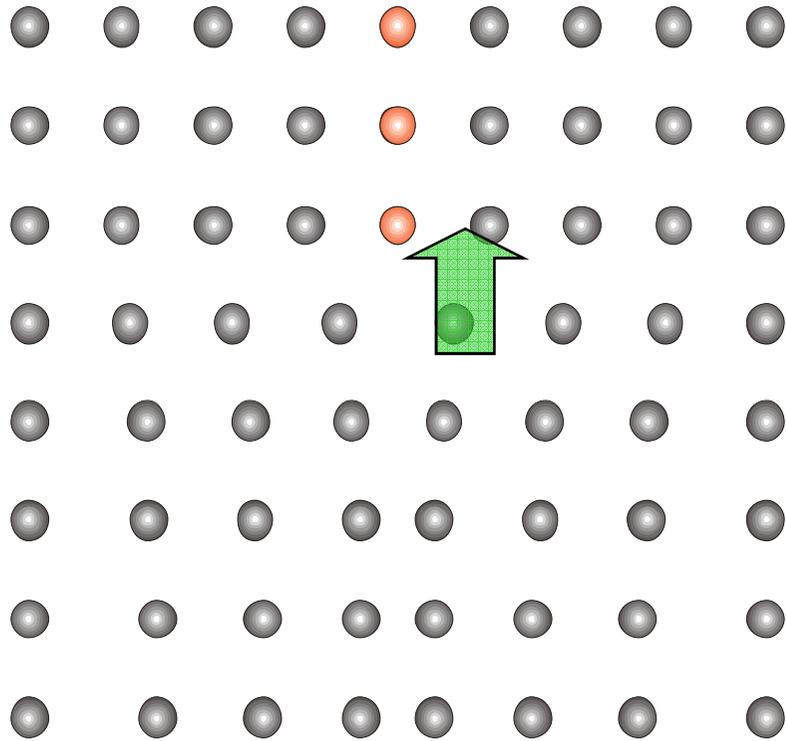


- ❑ For edge dislocation: as $\mathbf{b} \perp \mathbf{t} \rightarrow$ they define a plane \rightarrow *the slip plane*
- ❑ Climb involves addition or subtraction of a row of atoms below the half plane
 - ▶ +ve climb = climb up \rightarrow removal of a plane of atoms
 - ▶ -ve climb = climb down \rightarrow addition of a plane of atoms

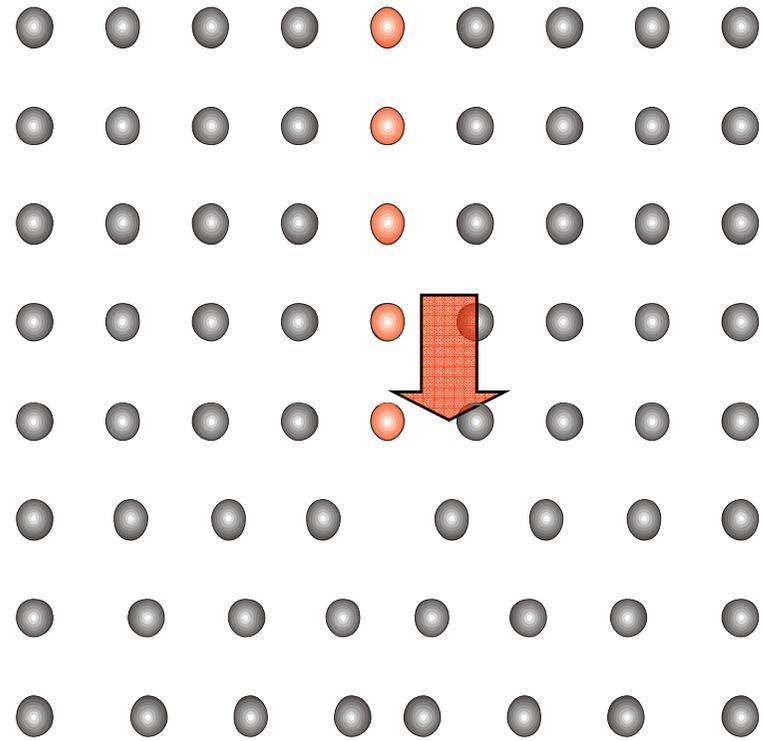
Edge Dislocation Glide



Edge Climb

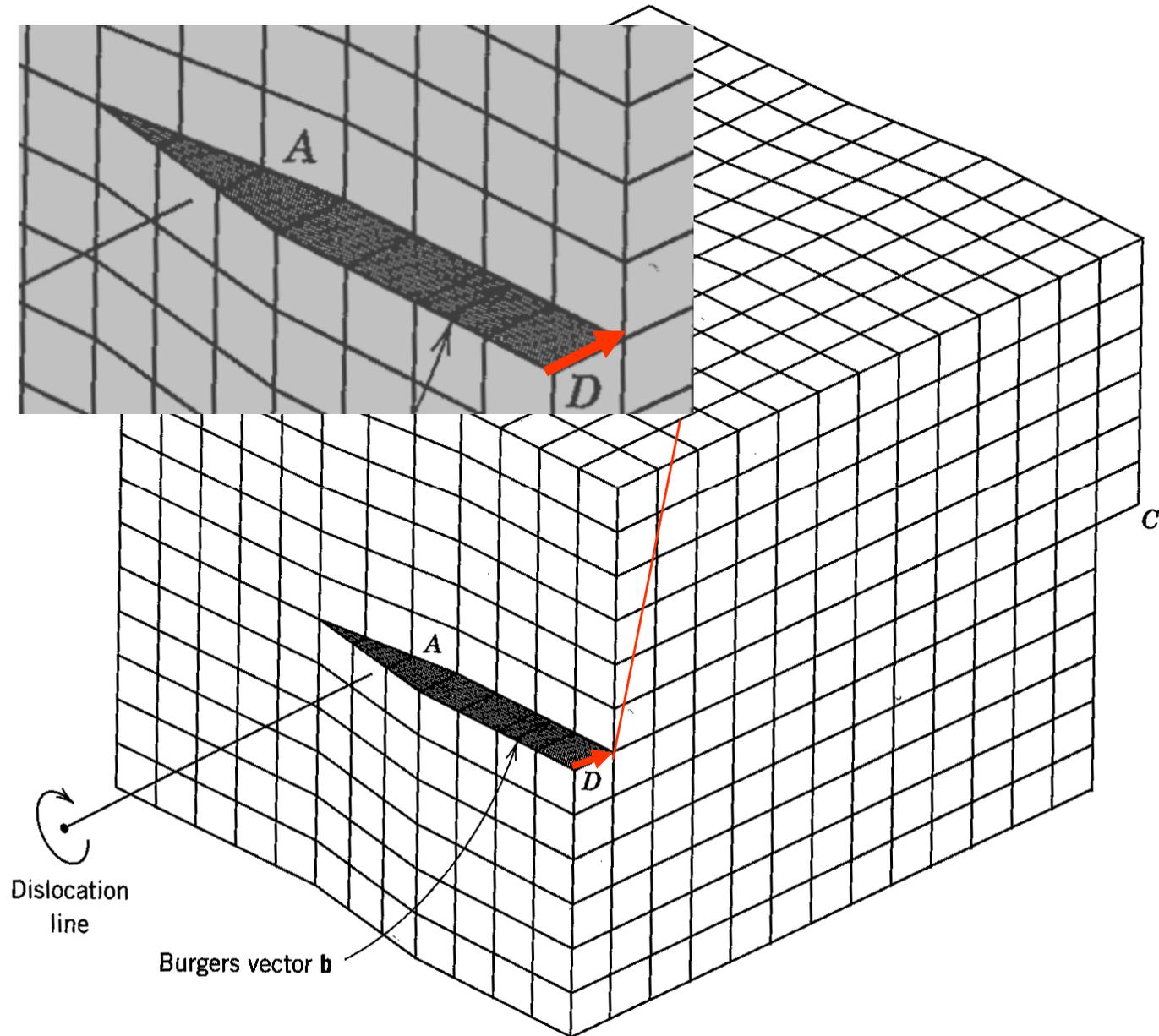


Positive climb
Removal of a row of atoms

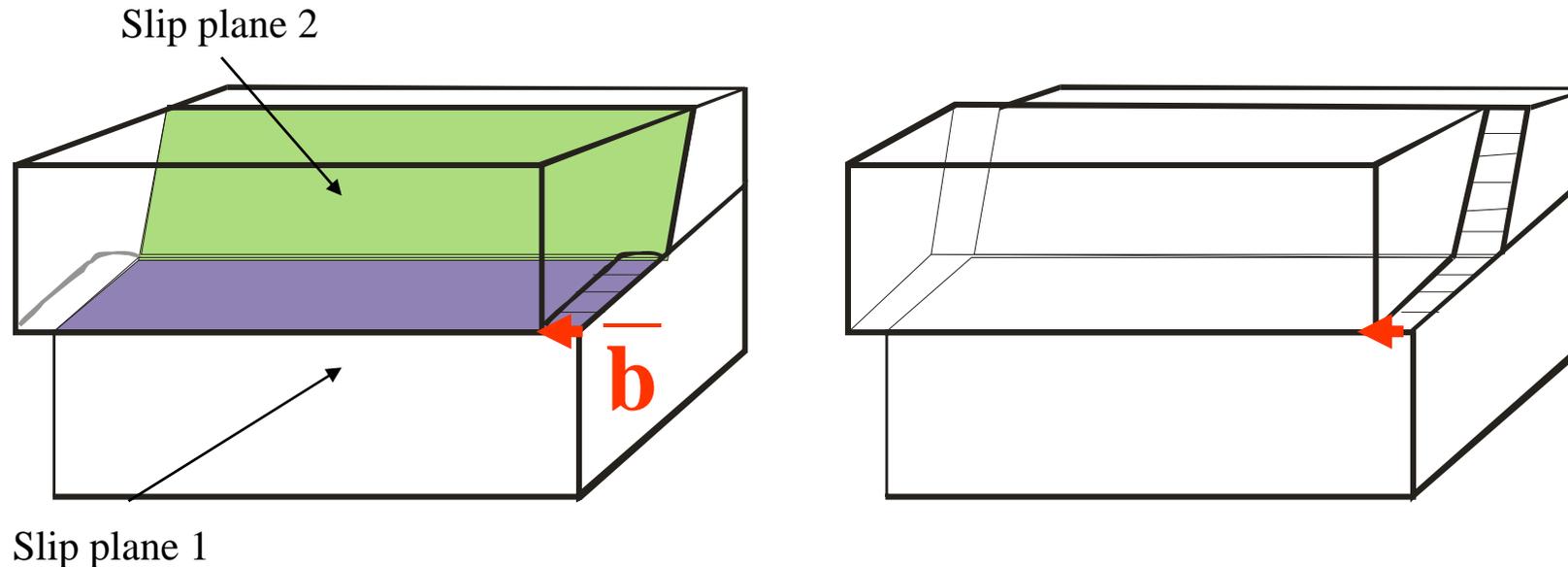


Negative climb
Addition of a row of atoms

Screw dislocation



Screw dislocation cross-slip



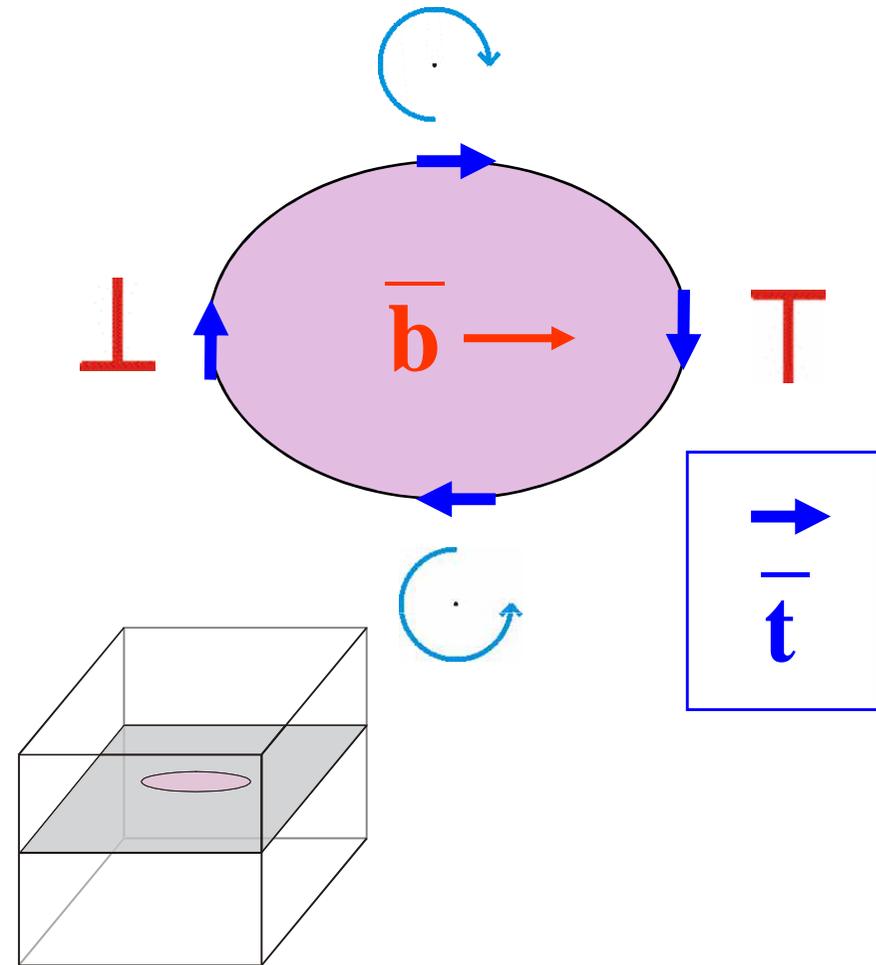
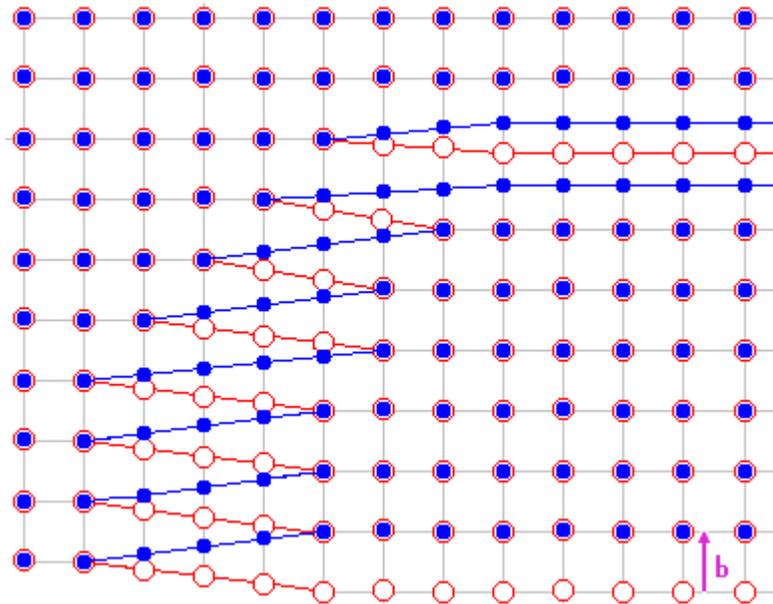
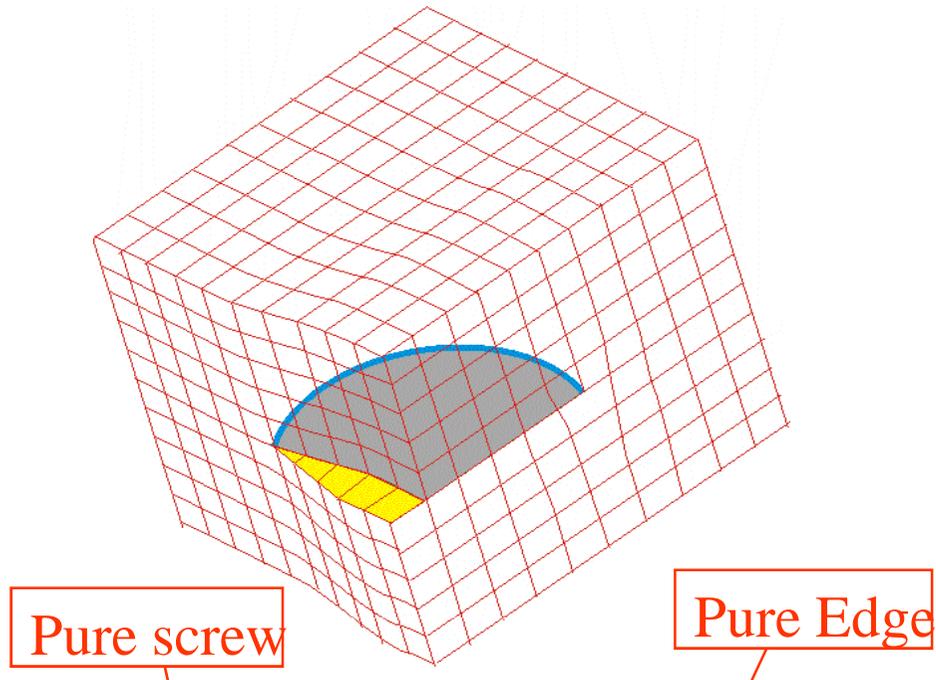
The dislocation is shown cross-slipping from the blue plane to the green plane

- The dislocation line ends on
 - ✓ The free surface of the crystal
 - ✓ Internal surface or interface
 - ✓ Closes on itself to form a loop
 - ✓ Ends in a node
- A node is the intersection point of more than two dislocations
- The vectoral sum of the Burgers vectors of dislocations meeting at a node = 0

Geometric properties of dislocations

Dislocation Property	Type of dislocation	
	Edge	Screw
Relation between dislocation line (\mathbf{t}) and \mathbf{b}	\perp	\parallel
Slip direction	\parallel to \mathbf{b}	\parallel to \mathbf{b}
Direction of dislocation line movement relative to \mathbf{b}	\parallel	\perp
Process by which dislocation may leave slip plane	Glide/Climb	Cross-slip

Mixed dislocations



We are looking at the plane of the cut (sort of a semicircle centered in the lower left corner). Blue circles denote atoms just below, red circles atoms just above the cut. Up on the right the dislocation is a pure edge dislocation on the lower left it is pure screw. In between it is mixed. In the link this dislocation is shown moving in an animated illustration.

Energy of dislocations

- ❑ Dislocations have distortion energy associated with them
- ❑ E per unit length
- ❑ Edge → Compressive and tensile stress fields
Screw → Shear strains

Energy of dislocation

Elastic

E

Non-elastic (*Core*)

~E/10

Energy of a dislocation / unit length

$$E \cong \frac{1}{2} G b^2$$

G → (μ) shear modulus
b → |**b**|

Dislocations will have as small **b** as possible

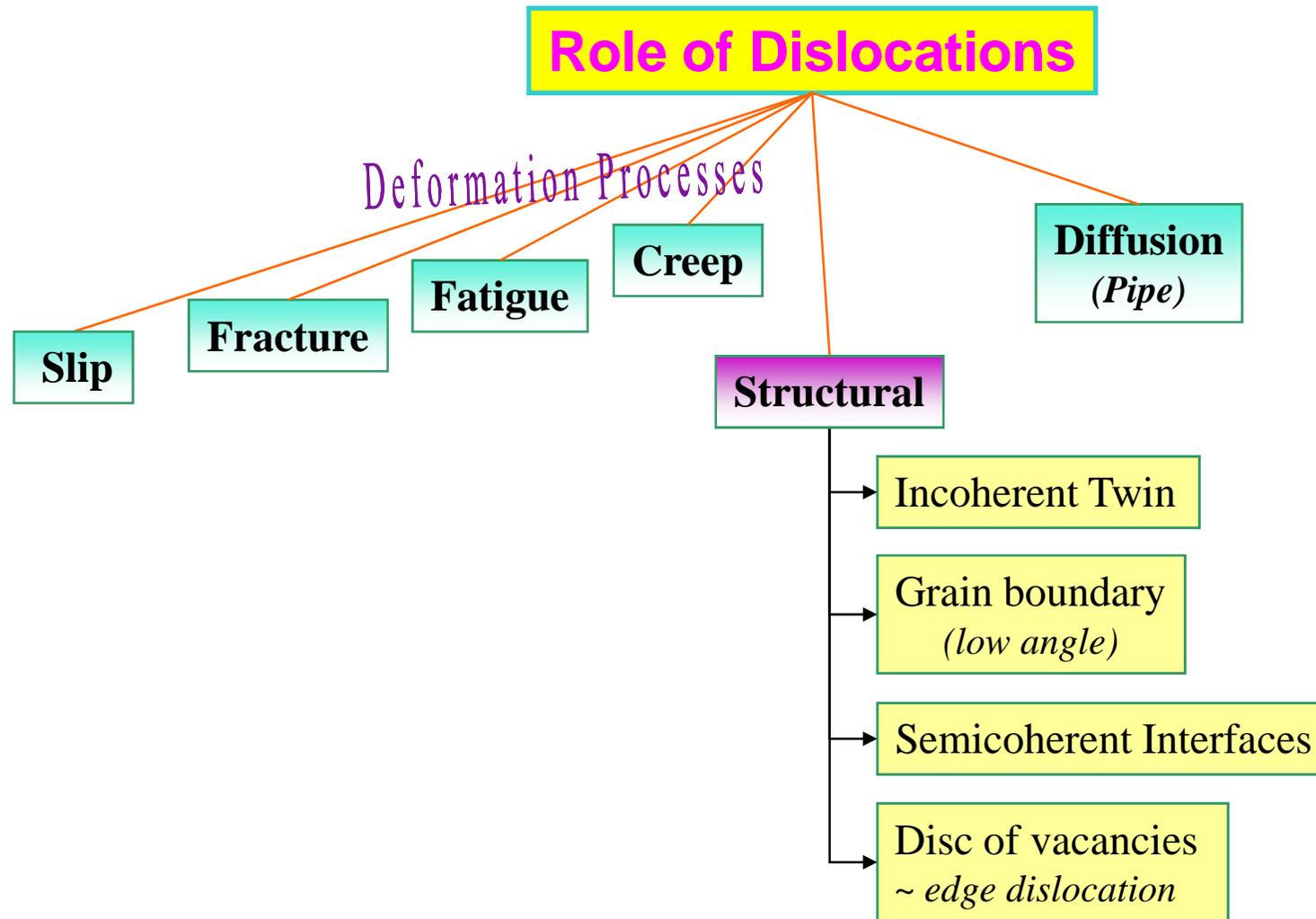
Dislocations
(in terms of lattice translation)

Full

b → Full lattice translation

Partial

b → Fraction of lattice translation

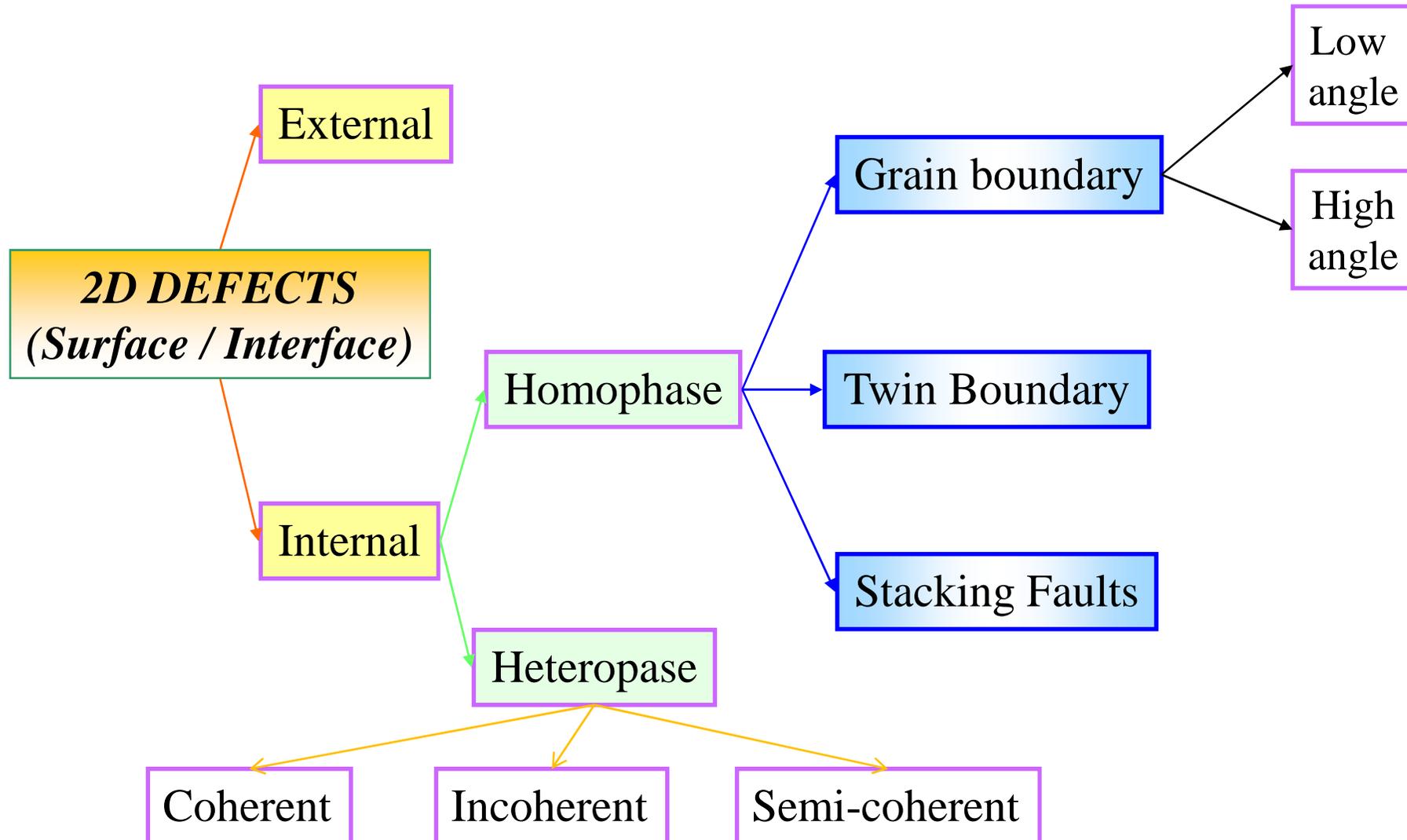


Formation of dislocations (in the bulk of the crystal)

- Due to accidents in crystal growth from the melt
- Mechanical deformation of the crystal

2D Defects : Surface defects

- ❑ 2D in a mathematical sense
- ❑ The region of distortion is ~ few atomic diameters in thickness

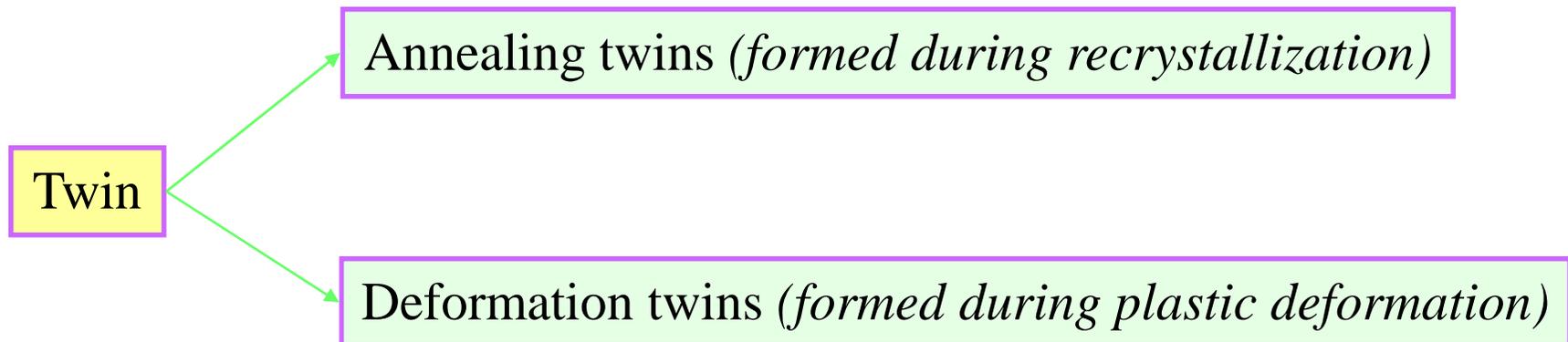


Grain Boundary

- ❑ The grain boundary region may be distorted with atoms belonging to neither crystal
- ❑ The thickness may be of the order of few atomic diameters
- ❑ The crystal orientation changes abruptly at the grain boundary
- ❑ In an low angle boundary the orientation difference is $< 15^\circ$
- ❑ In the low angle boundary the distortion is not so drastic as the high-angle boundary \rightarrow can be described as an array of dislocations
- ❑ Grain boundary energy is responsible for grain growth on heating $\sim (>0.5T_m)$
- ❑ Large grains grow at the expense of smaller ones
- ❑ The average no. of nearest neighbours for an atom in the grain boundary of a close packed crystal is 11

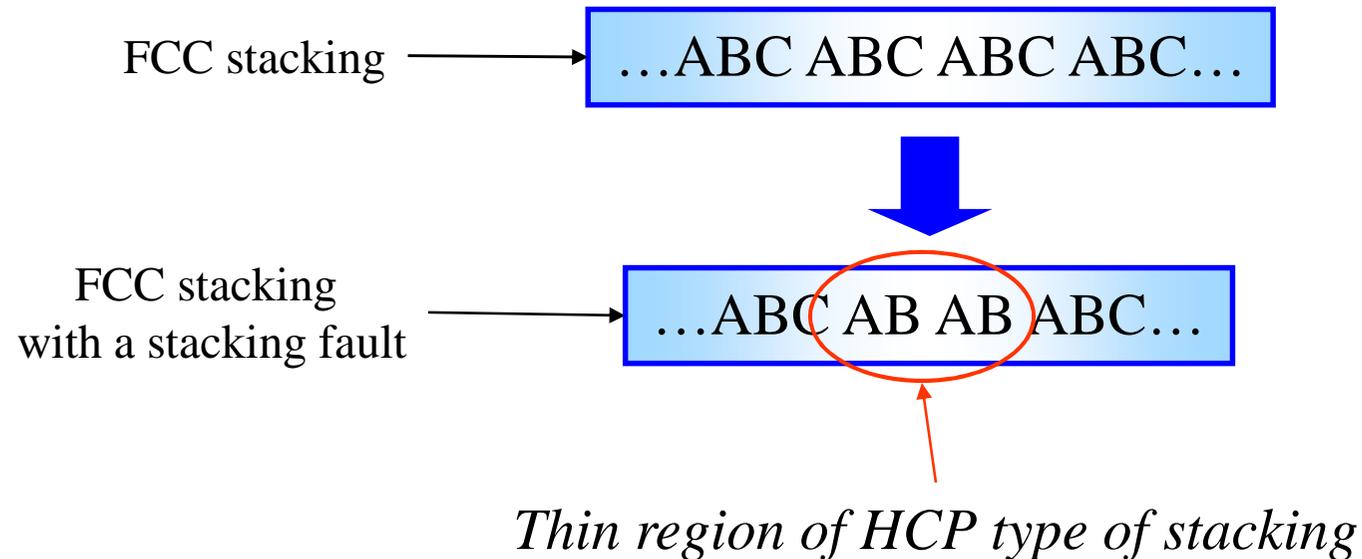
Twin Boundary

- ❑ The atomic arrangement on one side of the twin boundary is related to the other side by a symmetry operation (usually a mirror)
- ❑ Twin boundaries usually occur in pairs such that the orientation difference introduced by one is restored by the other
- ❑ The region between the regions is called the twinned region



Stacking Fault

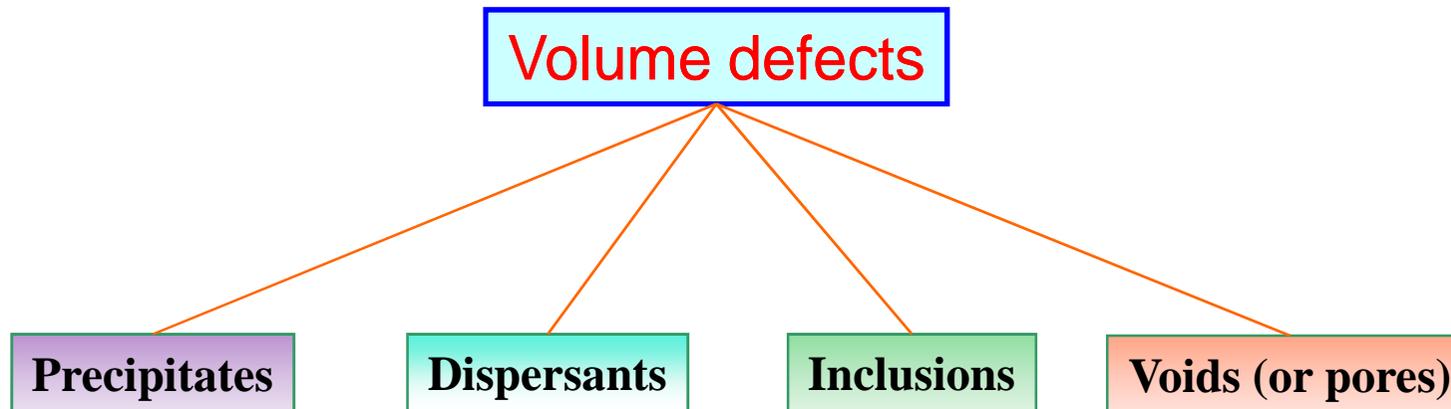
- ❑ Error in the sequence of stacking atomic planes → Stacking fault
- ❑ Defined by a shift vector



- ❑ In above the number of nearest neighbours remains the same but next-nearest neighbours are different than that in FCC
- ❑ Stacking fault energy $\sim 0.01 - 0.05 \text{ J/m}^2$
- ❑ Stacking fault in HCP can lead to thin region of FCC kind of stacking

3D Defects : volume defects

Volume defects in crystals are three dimensional aggregates of atoms or vacancies



PRECIPITATES

Precipitates are small particles that are introduced into the matrix by solid state reactions. While precipitates are used for several purposes, their most common purpose is to increase the strength of structural alloys by acting as obstacles to the motion of dislocations. Their efficiency in doing this depends on their size, their internal properties, and their distribution through the lattice. However, their role in the microstructure is to modify the behavior of the matrix rather than to act as separate phases in their own right.

3D Defects : volume defects

DISPERSANTS

Dispersants are larger particles that behave as a second phase as well as influencing the behavior of the primary phase. They may be large precipitates, grains, or polygranular particles distributed through the microstructure. When a microstructure contains dispersants such properties as mechanical strength and electrical conductivity are some average of the properties of the dispersant phase and the parent.

INCLUSIONS

Inclusions are foreign particles or large precipitate particles. They are usually undesirable constituents in the microstructure. For example, inclusions have a deleterious effect on the useful strength of structural alloys since they are preferential sites for failure. They are also often harmful in microelectronic devices since they disturb the geometry of the device by interfering in manufacturing, or alter its electrical properties by introducing undesirable properties of their own.

VOIDS (OR PORES)

Voids (or pores) are caused by gases that are trapped during solidification or by vacancy condensation in the solid state. They are almost always undesirable defects. Their principal effect is to decrease mechanical strength and promote fracture at small loads.

Questions..?

1. Differentiate Frenkel and Schottky defects.
2. Find the equilibrium concentration of vacancies in aluminium (eV/vacancy = 0.70, $\Delta H_f = 68$ KJ/mol) and nickel (eV/vacancy = 1.74, $\Delta H_f = 168$ KJ/mole) at 0K, 300K, and 900K.
3. Why point defects are called “ Equilibrium defects”. State your reasons
4. Compute the line energy of dislocations in BCC iron. The Burgers vector in iron is of the $\frac{1}{2}\langle 111 \rangle$ type. The shear modulus of iron is 80.2 GN m^{-2} [$a_{\text{BCC Fe}} = 2.87 \text{ \AA}$]
5. The surface of copper crystal is of the $\{111\}$ type. Calculate the surface energy (enthalpy) of copper. [$a_{\text{FCC Fe}} = 3.61 \text{ \AA}$]
6. The surface energy of a single crystal depends on crystallographic orientation. Does this surface energy increase or decrease with an increase in planar density. Why?
7. Calculate the energy for vacancy formation in silver, given that the equilibrium number of vacancies at 800°C (1073K) is $3.6 \times 10^{23} \text{ m}^{-3}$. The atomic weight and density (at 800°C) for silver are respectively, 107.9 g/mol and 9.5 g/cm^3 .
8. Cite the relative Burgers vector–dislocation line orientations for edge, screw, and mixed dislocations.
9. For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?

Questions..?

10. The grain boundary energy of a small angle grain boundary is less than for a high angle one. Why is this so?
11. For a BCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (110) plane? Why?
12. If there are 10^{10} m^{-2} of edge dislocations in a simple cubic crystal, how much would each of these climb down on an average when the crystal is heated from 0 to 1000K? The enthalpy of formation of vacancies is 100 KJ mol^{-1} . The lattice parameter is 2 \AA . The volume of one mole of the crystal is $5.5 \times 10^{-6} \text{ m}^3$
13. What is the geometry of edge dislocation? How did the concept arise? What is the geometry of the screw dislocation? Differentiate Edge and Screw dislocations
14. Write short note on Volume defects
15. What is the Burgers vector of a dislocation? How is the Burgers circuit used to define the Burgers vector ?