LECTURE NOTES ON

MM-15-036 : PHASE TRANSFORMATIONS

5th Semester, MME

MM-15-036

PHASE TRANSFORMATIONS

Course Coordinator

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PHASE TRANSFORMATIONS

Course Objective

The aim of this course is to gain an understanding of the role of phase transformations on the development of microstructure and properties of metallic materials. The course will highlight a number of commercially-significant applications where phase transformations are important.

Course Overview

Nucleation in the liquid and solid states; thermodynamics of phase transformations; solidification of pure metals and alloys; thermal supercooling; constitutional supercooling; interface stability; solute redistribution; Solid state transformations : nucleation and growth of phases; diffusion mechanisms; transformation kinetics; transformation diagrams. Diffusional and Diffusionless transformations: decomposition of solid solutions; ordering reactions, spinodal decomposition; eutectoid, bainitic and martensitic transformations. Aspects of ferrous metallurgy and common classes of low carbon and alloy steels to be taught illustrating some of the principles involved.

Learning Outcomes

Enhanced critical thinking, analytical and problem solving skills in materials science and engineering. An understanding of the principles underlying liquid-to solid and solid-state phase transformations in a range of materials. An understanding of the importance of phase transformations for controlling microstructure and properties in engineering alloys.

MM-15-036 : PHASE TRANSFORMATIONS

CONTENTS

INTRODUCTION TO PHYSICAL METALLURGY

REFERENCES

- Phase Transformations in Metals and Alloys (*This is the major reference for this course*)
  D.A.Porter, K.E. Easterling, and M.Y. Sharif
  CRC Press , Taylor & Francis Group
- Diffusion in solids
  Prof. Alok Paul , IISC Banglore
  NPTEL Web course
- Phase Transformations
  Prof. Anandh Subramaniam IIT Kanpur
- Phase Transformations & Heat Treatment
  Prof. M.P.Gururajan
  NPTEL web course
- Phase Transformations in Materials
  Romesh C. Sharma
  CBS Publishers & Distributors
- Introduction to Physical Metallurgy
  Sidney H. Avner
  McGraw Hill Education (India) Pvt Ltd

Introduction

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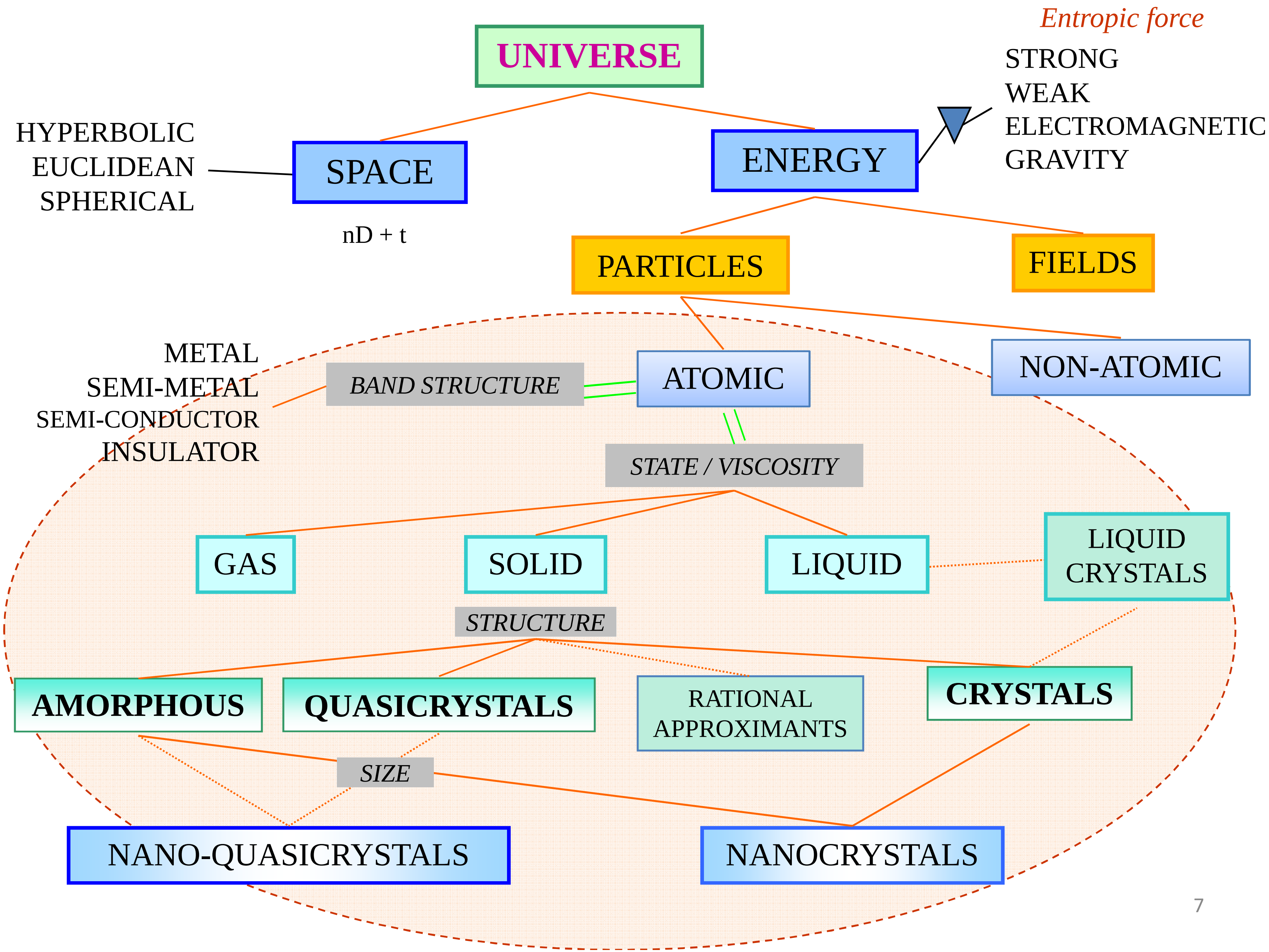


Entropic force

UNIVERSE

HYPERBOLIC
EUCLIDEAN
SPHERICAL

SPACE

nD + t

ENERGY

STRONG
WEAK
ELECTROMAGNETIC
GRAVITY

PARTICLES

FIELDS

ATOMIC

NON-ATOMIC

METAL
SEMI-METAL
SEMI-CONDUCTOR
INSULATOR

BAND STRUCTURE

STATE / VISCOSITY

GAS

SOLID

LIQUID

LIQUID CRYSTALS

STRUCTURE

AMORPHOUS

QUASICRYSTALS

RATIONAL APPROXIMANTS

CRYSTALS

SIZE

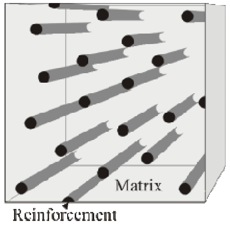
NANO-QUASICRYSTALS

NANOCRYSTALS

Classification of materials

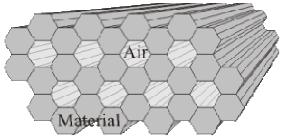
Materials

- Monolithic
  - Metals (& Alloys)
  - Ceramics & Glasses
  - Polymers (& Elastomers)
- Hybrids
  - Composite
  - Sandwich
  - Lattice
  - Segment

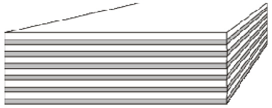


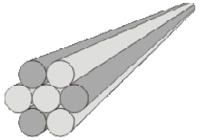
Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement

Sandwich structures: have a material on the surface (one or more sides) of a core material



Lattice* Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).



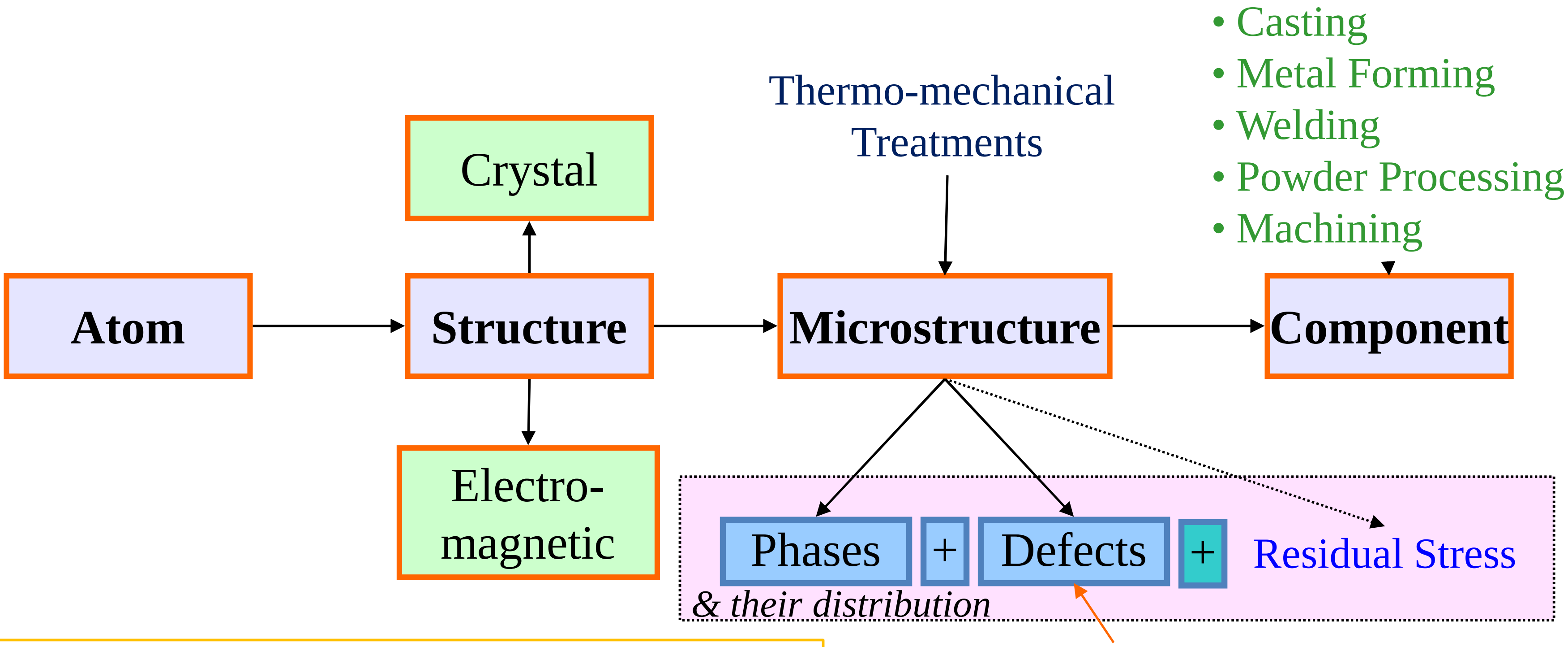


Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

Hybrids are designed to improve certain properties of monolithic materials

*Note: this use of the word 'lattice' should not be confused with the use of the word in connection with crystallography.

Length scales in metallurgy



- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Thermo-mechanical Treatments

Atom → **Structure** → **Microstructure** → **Component**

Crystal

Electro-magnetic

Phases + Defects + Residual Stress

& their distribution

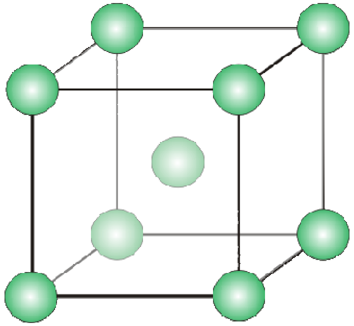
- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

- ❑ Structure could imply two types of structure:
  - ➢ Crystal structure
  - ➢ Electromagnetic structure
  - ▪ *Fundamentally these aspects are two sides of the same coin*
- ❑ Microstructure can be defined as: (Phases + Defect Structure + Residual Stress) *and their distributions*
- ❑ Microstructure can be 'tailored' by thermo-mechanical treatments

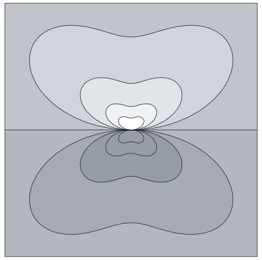
Processing determines shape and microstructure of a component

Length scales in metallurgy

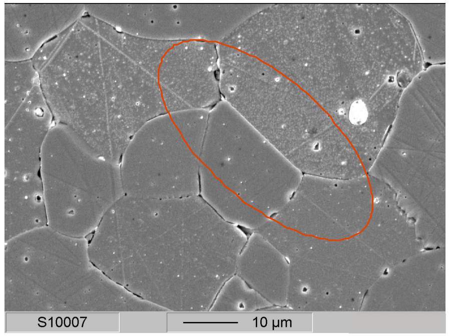
Let us start with a cursory look at the length scales involved in Materials Science



Angstroms



Dislocation Stress fields → Nanometers

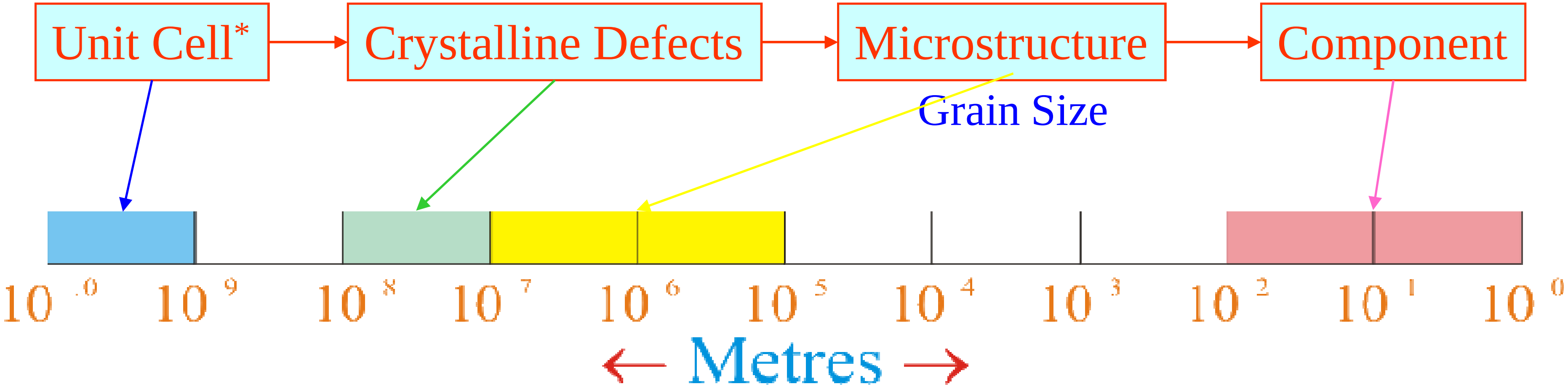


Microns

Centimeters

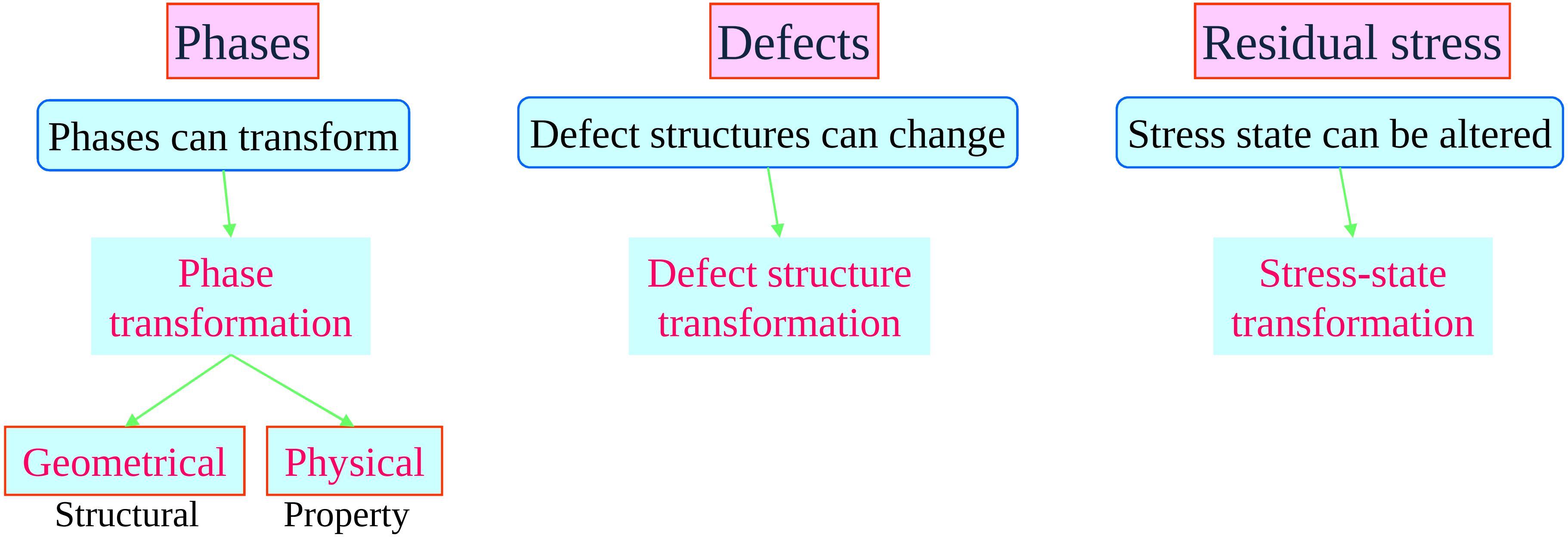
Unit Cell* → Crystalline Defects → Microstructure → Component

Grain Size



*Simple Unit Cells

Transformations in Materials



Phases

Phases can transform

Phase transformation

Geometrical

Structural

Physical

Property

Defects

Defect structures can change

Defect structure transformation

Residual stress

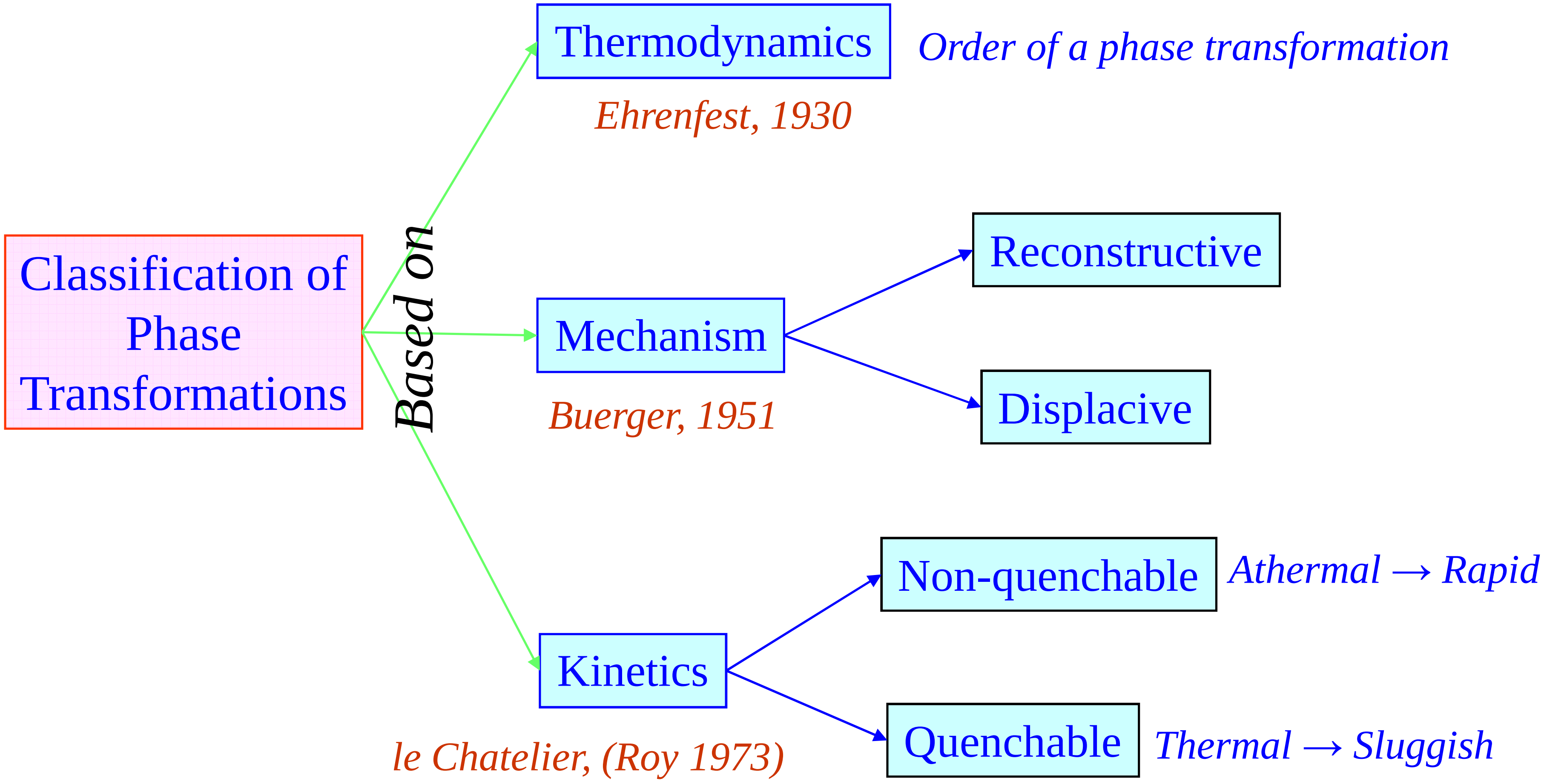
Stress state can be altered

Stress-state transformation

Phases → Microstructure

Phases Transformations → Microstructural Transformations

Classification of Transformations



Classification of Phase Transformations

Based on

- Thermodynamics — *Order of a phase transformation*
  - *Ehrenfest, 1930*
- Mechanism — *Buerger, 1951*
  - Reconstructive
  - Displacive
- Kinetics — *le Chatelier, (Roy 1973)*
  - Non-quenchable — *Athermal → Rapid*
  - Quenchable — *Thermal → Sluggish*

Classification of Transformations

- The thermodynamic characteristics associated with the phase transformations can be used to classify transformations; in this classification methodology, if the nth derivative of free energy (G) with respect to temperature (T) and pressure (P) is discontinuous, it is defined as the nth order transformation.
- As shown in Fig., in transformations such as melting, the first derivative has the discontinuity; hence, melting is a first order transformation; on the other hand, in some of the order/disorder transfor- mations, it is the second derivative which is discontinuous, making it the second order transformation.

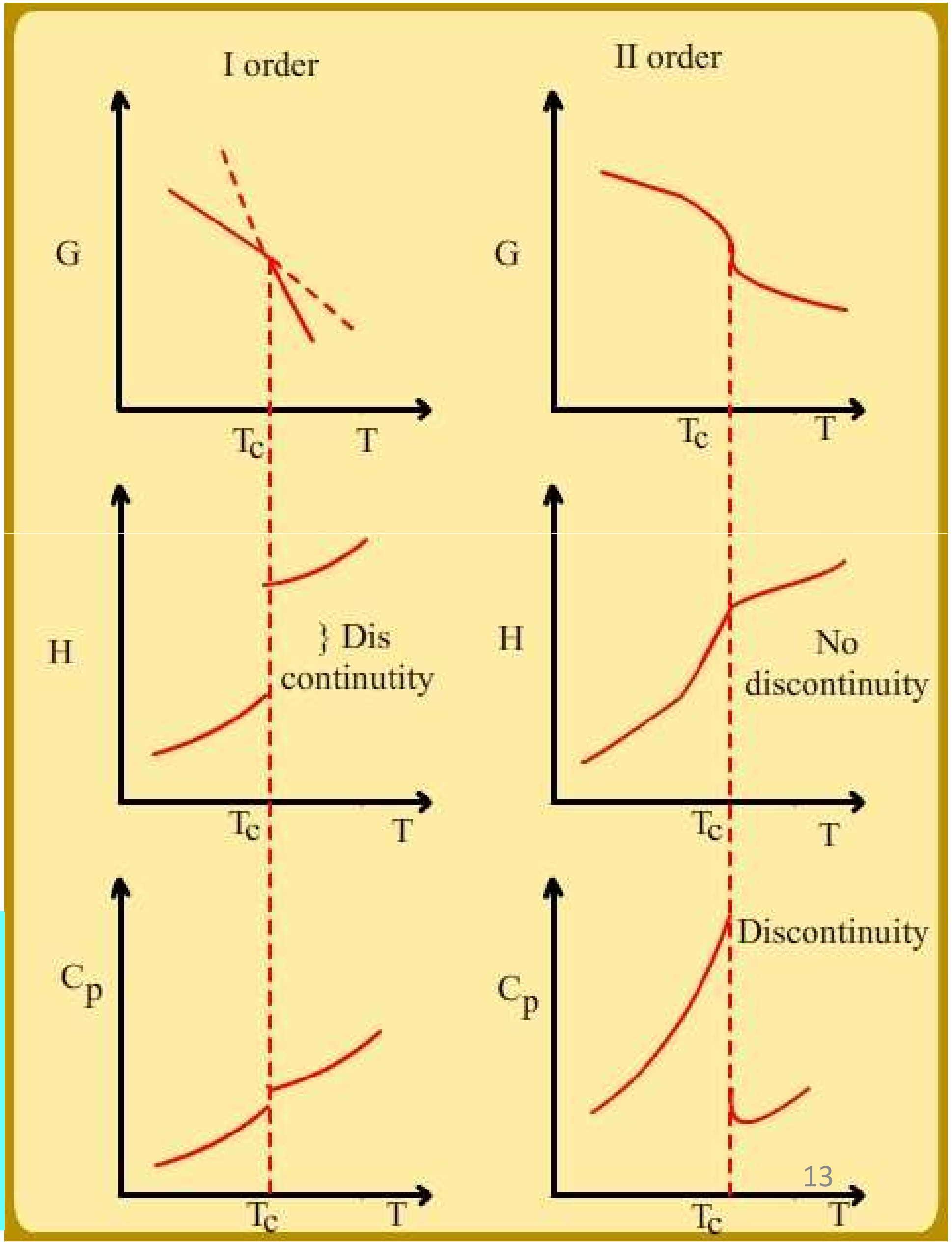
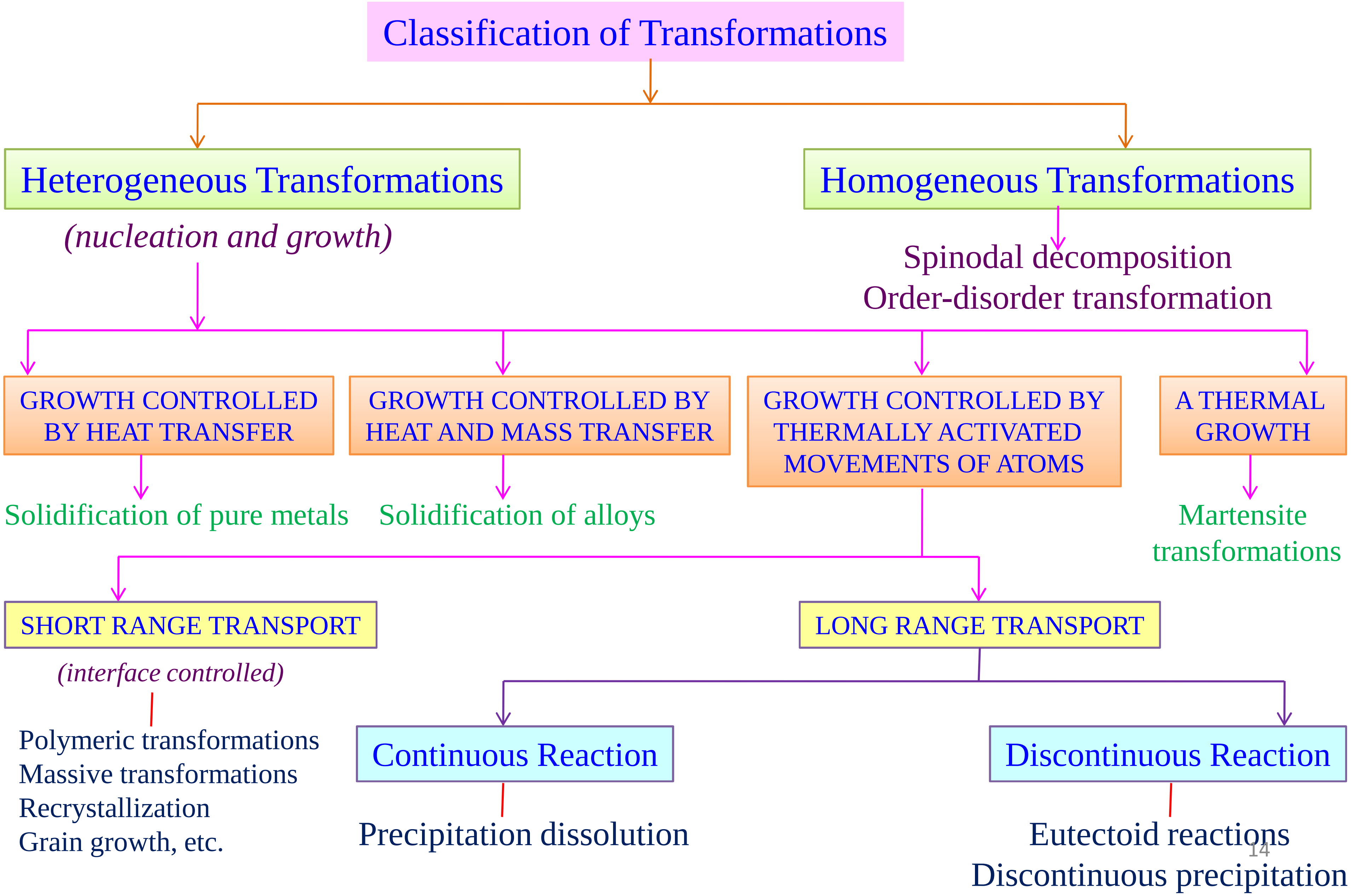


Figure: The thermodynamic classification of transformations: the first derivative of the free energy 'G' with respect to temperature 'T' , that is the enthalpy 'H' is discontinuous at the transformation temperature T_c as shown in the first column; the second derivative of the free energy with respective to temperature C_p is discontinuous while 'H' is not in the second column, making the order of transformation second.

Classification of Transformations



Classification of Transformations

Heterogeneous Transformations

(nucleation and growth)

Homogeneous Transformations

Spinodal decomposition
Order-disorder transformation

GROWTH CONTROLLED BY HEAT TRANSFER

Solidification of pure metals

GROWTH CONTROLLED BY HEAT AND MASS TRANSFER

Solidification of alloys

GROWTH CONTROLLED BY THERMALLY ACTIVATED MOVEMENTS OF ATOMS

A THERMAL GROWTH

Martensite transformations

SHORT RANGE TRANSPORT

(interface controlled)

Polymeric transformations
Massive transformations
Recrystallization
Grain growth, etc.

LONG RANGE TRANSPORT

Continuous Reaction

Precipitation dissolution

Discontinuous Reaction

Eutectoid reactions
Discontinuous precipitation

Classification of Transformations

- Phase transformations can be classified as homogeneous (transformations which take place through spinodal mechanism in which transformation takes place throughout the material) and heterogeneous (transformations which take place through nucleation and growth mechanism in which transformation takes place heterogeneously at a few places in the material at the start of the transformation).
- Transformations can also be classified as diffusional (or, so called, \`civilian') and diffusionless (or, so called \`military') depending on the mechanism. In civilian transformations, the nucleation and growth take place via diffusion assisted atomic motion. On the other hand, in the military transformation, the nucleation and growth is by shear and shuffle of atoms by less than one atomic displacement and the movement of all the participating atoms is coordinated.
- There are transformations which are thermally activated (which typically are based on diffusion) while there are others which are athermal.
- The transformations can also be diffusion controlled or interface controlled.
- Transformations can also be differentiated based on whether the interfaces formed are glissile or nonglissile.
- In some transformations there are compositional changes while in some other there are no composition changes.
- Further, transformations which are diffusional can either involve long range diffusion or short range diffusion.

Thermodynamics & Kinetics

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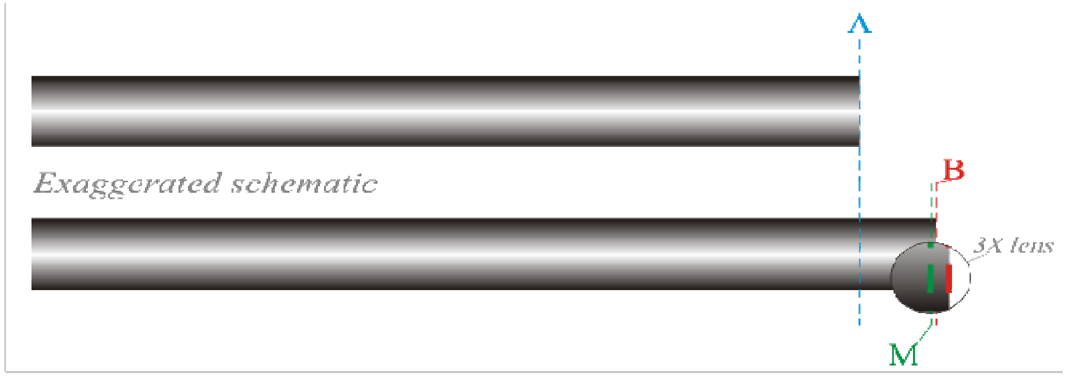
Introduction

- The fields of Thermodynamics and Kinetics are vast oceans and this chapter will introduce the bare essentials required to understand the remaining chapters.
- Let us start by performing the following (thought) experiment:
  Heat a rod of Al from room temperature to 500°C → As expected the rod will expand *(A → B in figure below).*
- The expansion occurs because of two reasons:
  1➢ Vibration of atoms (leading to an increase in average spacing between atoms→ the usual reason) *(A → M in figure below).*
- 2➢ Increase in the concentration of vacancies* (a vacancy is created when a Al atom goes to the surface and for every 4 vacancies created the volume equal to 1 unit cell is added). *(M → B in figure below).* The 2nd reason is a smaller effect in terms of its contribution to the overall increase in length of the specimen



Metal expands on heating due to 2 different physical reasons!

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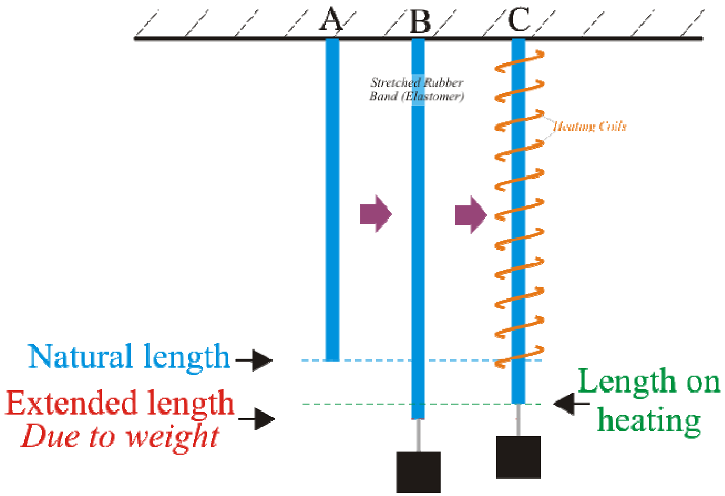
* *It costs energy for the system to put vacancies (broken bonds, distortion to the lattice)*
→ *then why does the system tolerate vacancies?*

Introduction

- Now let us perform another (thought) experiment to put in perspective the previous experiment:
  Heat a elastomer (cut rubber band) which has been stretched by a small weight by about 20°C (room temperature + 20°C) → the stretched rubber band will *contract*!
- The 2nd reason for the expansion of the Al rod is closely related to the contraction of the stretched rubber band! → occurs because of thermodynamic reasons (quantities like Gibbs Free Energy (G) and Entropy (S)), which we shall learn in this chapter.
- In the case of the heating of the Al rod- "how the vacancies form" is an issue of *kinetics*. Kinetics will be dealt with in the topic of kinetics and chapter on Diffusion.



A 'stretched' elastomer contracts on heating!

Introduction

- ☐ Let us next consider the melting of a pure metal at its melting point (MP) (at constant T and P) → by supplying heat to the sample of metal (so that the metal sample is only partly molten). At the MP the liquid metal is in equilibrium with the solid metal.
- ☐ The liquid has higher potential energy as well as higher kinetic energy than the solid.
- ☐ Then why does the liquid co-exist with the solid?
- ☐ The answer to this question lies in the fact that internal energy is not the measure of stability of the system *(under the circumstances)*.
- ☐ We will learn in this chapter that it is the Gibbs Free Energy (G). The molten metal has higher energy (internal energy and enthalpy), but also higher Entropy. So the melting is driven by an increase in Entropy of the system. The molten metal and the crystalline solid metal have the same G → hence they co-exist in equilibrium.

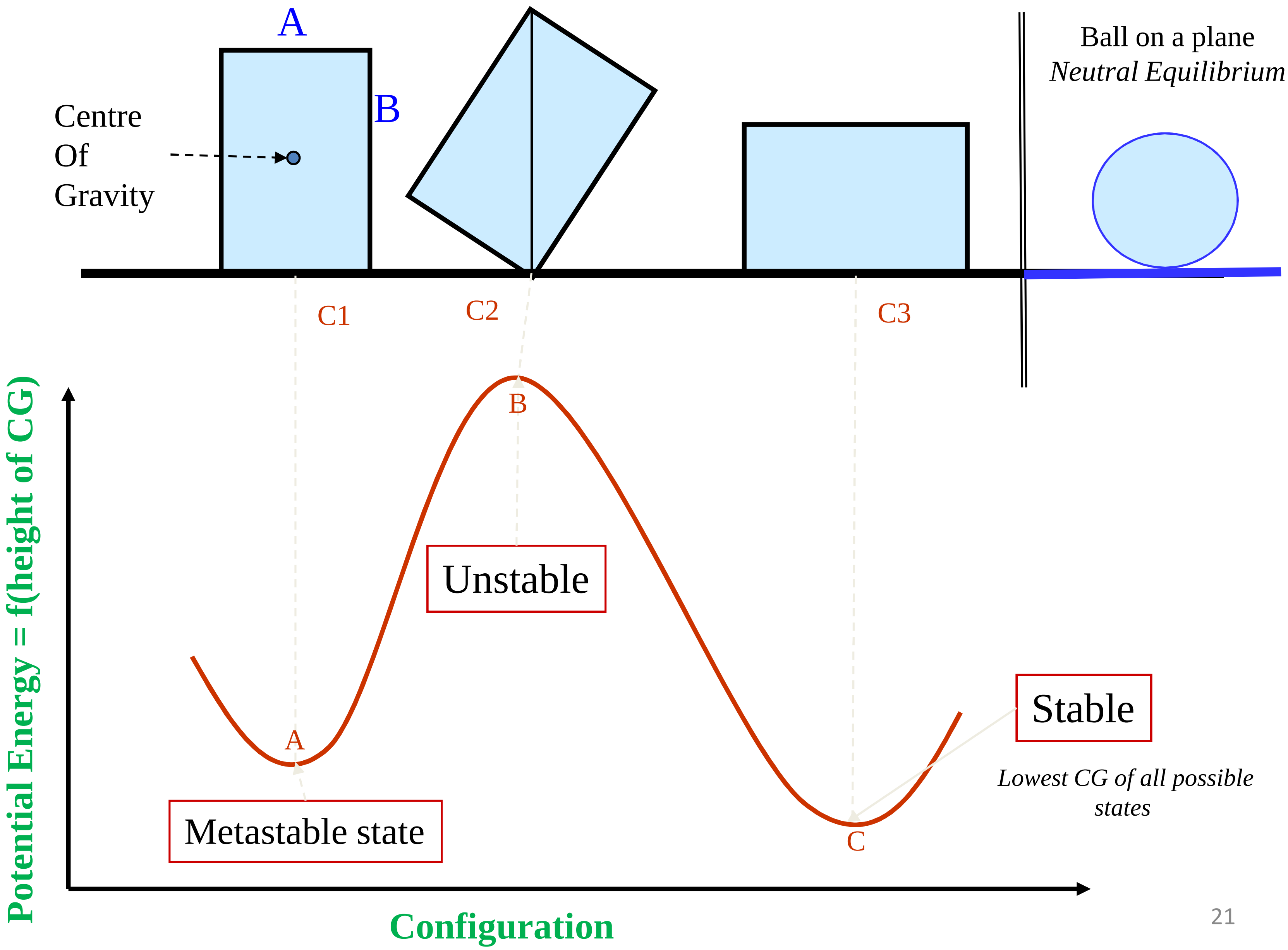
Stability and Equilibrium

- ❑ Equilibrium refers to a state → wherein there is a balance of 'forces'* (as we shall see equilibrium points have zero slope in a energy-parameter plot)
- ❑ Stability relates to perturbations (usually small perturbations** about an equilibrium state) (as we shall see stable relates to the curvature at the equilibrium points).
- ❑ Let us start with a simple mechanical system → a rectangular block *(Figure in next slide)* (under an uniform gravitational potential).
- ❑ The potential energy (PE) of the system depends on the height of the centre of gravity (CG).
- ❑ The system has higher PE when it rests on face-A, than when it rests on face-B.
- ❑ The PE of the system increases when one tilts it from C1 → C2 configuration.
- ❑ In configurations such as C1,C2 & C3 the system will be in equilibrium (i.e. will not change its configuration if there are no perturbations).
- ❑ In configuration C2 the system has the highest energy (point B) and any small perturbations to the system will take it downhill in energy → Unstable state.
- ❑ Configuration C3 has the lowest energy (point C) and the system will return to this state if there are small perturbations → the Stable state.

** Force has been used here in a generalized sense (as an agent which can cause changes)*

** Perturbation is usually a small 'force/displacement' imposed in a short span of time.

Mechanical Equilibrium of a Rectangular Block



Stability and Equilibrium

- ❑ Configuration C1 also lies in an ‘energy well’ (like point C) and small perturbations will tend to bring back the system to state C1. However this state is not the ‘global energy minimum and hence is called a Metastable state.
- ❑ Additionally, one can visualize a state of neutral equilibrium, like a ball on a plane (wherein the system is in a constant energy state with respect to configurations).
- ❑ Points to be noted:
  - ➢ A system can exist in many states *(as seen even for a simple mechanical system: block on a plane)*
  - ➢ These states could be stable, metastable or unstable
  - ➢ Using the relevant (thermodynamic) potential the stability of the system can be characterized (In the case of the block it is the *potential energy*, measured by the height of the CG for the case of the block on the plane)
  - ➢ System will ‘evolve’ towards the stable state provided ‘sufficient activation’ is provided (in the current example the system will go from C1 to C3 by ‘sufficient jolting/shaking’ of the plane)

Three kinds of equilibrium (with respect to energy)

- ❑ Global minimum → STABLE STATE
- ❑ Local minimum → METASTABLE STATE
- ❑ Maximum → UNSTABLE STATE
- ❑ Constant energy → Neutral State/Equilibrium

Law’s of Thermodynamics

❑ Zeroth law of Thermodynamics

If two systems are each in thermal equilibrium with a third, then all three are in thermal equilibrium with each other. (Similar to the transitive property of equality in mathematics; i.e. If a = b and b = c, then a = c)

If & Then

No heat flows **(A is in equilibrium with B)**

No heat flows **(B is in equilibrium with C)**

No heat flows **(A is in equilibrium with C)**

❑ First law of Thermodynamics

This is a statement of the conservation of energy i.e. When heat (Q) is added to a system, it increases the internal energy (ΔU) of the system and the system does some work (W) on the external world.

$$\Delta U = Q - W$$

For infinitesimal change of the state,

$$dU = \delta Q - \delta W$$

Signs of Q and W	
Q Positive	System gains heat
Q Positive	System loses heat
W Positive	Work done by system
W Positive	Work done on system

Law's of Thermodynamics

- ## Second law of Thermodynamics:

In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy i.e. The entropy of a system in an adiabatic enclosure always increases for spontaneous/irreversible processes and remains constant during a reversible process but it never decreases.

Entropy S is defined by the equation

$$dS = \frac{\delta Q_{rev}}{T}$$ and is a function of state.

- ## Third law of Thermodynamics:

The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

$$\lim_{T \to 0} \Delta S = 0$$

Thermodynamic parameters

- ❑ In Materials Science we are mainly interested with condensed matter systems (solids and liquids) (also sometimes with gases)
- ❑ The state of such a system is determined by 'Potentials' analogous to the potential energy of the block (which is determined by the centre of gravity (CG) of the block). These potentials are the Thermodynamic Potentials (A thermodynamic potential is a Scalar Potential to represent the thermodynamic state of the system).
- ❑ The relevant potential depends on the 'parameters' which are being held constant and the parameters which are allowed to change. More technically these are the State/Thermodynamic Variables (A state variable is a precisely measurable physical property which characterizes the state of the system- It does not matter as to how the system reached that state). Pressure (P), Volume (V), Temperature (T), Entropy (S) are examples of state variables.
- ❑ There are 4 important potentials (in some sense of equal stature). These are: Internal Energy, Enthalpy, Gibbs Free Energy, Helmholtz Free Energy.
- ❑ Intensive properties are those which are independent of the size of the system
  - ➢ P, T
- ❑ Extensive Properties are dependent on the quantity of material
  - ➢ V, E, H, S, G

Heat capacity

- Heat capacity is the amount of heat (measured in Joules or Calories) needed to raise an unit amount of substance (measured in grams or moles) by an unit in temperature (measured in °C or K).
- This 'heating' (addition of energy) can be carried out at *constant volume* or *constant pressure*. At constant pressure, some of the heat supplied goes into doing work of expansion and less is available with the system (to raise it temperature).
- Heat capacity at constant Volume (C_V): It is the slope of the plot of internal energy with temperature.
- Heat capacity at constant Pressure (C_P): It is the slope of the plot of enthalpy with temperature.
- Units: Joules/Kelvin/mole, J/K/mole, J/°C/mole, J/°C/g.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

- Heat capacity is an extensive property (depends on 'amount of matter')
- If a substance has higher heat capacity, then more heat has to be added to raise its temperature. Water with a high heat capacity (of *****) heats up slowly as compared to air (with a heat capacity, C_P = 29.07J/K/mole) ⇒ this implies that oceans will heat up slowly as compared to the atomosphere.
- As $T \to 0K$, the heat capacity tends to zero. I.e near 0 Kelvin very little heat is required to raise the temperature of a sample. (This automatically implies that very little heat has to added to raise the temperature of a material close to 0K.

Internal energy

- ❑ Internal Energy (U or E) = Kinetic Energy (KE) + Potential Energy (PE)
- ❑ The origin of Kinetic Energy → Translations, Rotations, Vibrations
- ❑ The origin of Potential Energy → Bonding between atoms (interactions in the solid)
- ❑ The increase in internal energy on heating from 0 to T Kelvin is given by the equation below; where C_V is the specific heat at constant volume and E_0 is the internal energy of the system at 0K.
- ❑ For a cyclic process, change in internal energy (**Δ**U or **Δ**E) becomes zero.

At constant temperature

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial P}\right)_V dP = f(V,P)_T$$

At constant volume

$$\Delta U = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT = f(P,T)_V$$

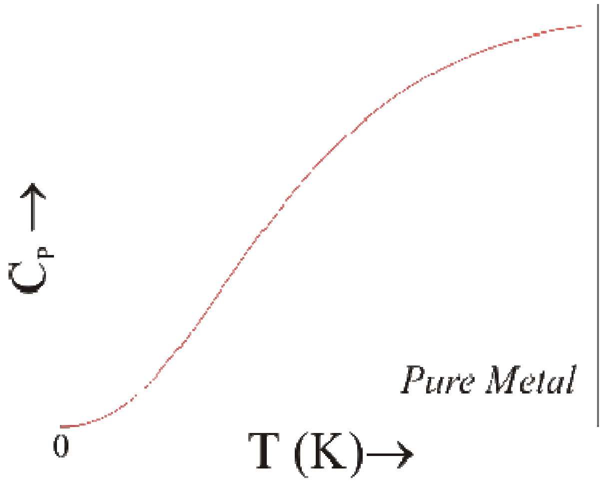
$$U = U_0 + \int_0^T C_V \, dT$$

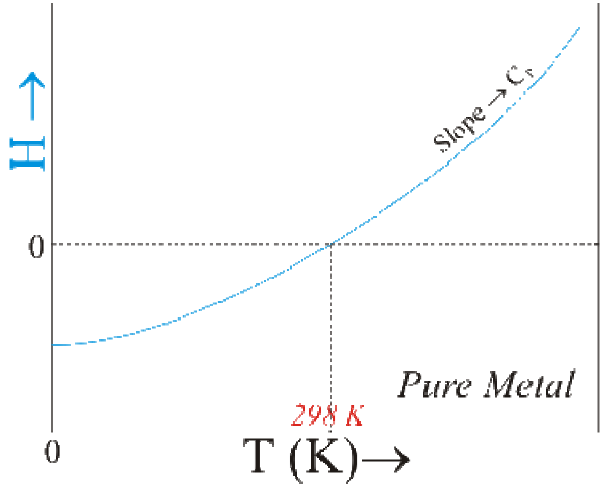
At constant pressure

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = f(V,T)_P$$

Enthalpy

- ❑ Enthalpy (H) = Internal Energy + PV (work done by the system)
- ❑ Measure of the heat content of the system
- ❑ At constant pressure the heat absorbed or evolved is given by ΔH
- ❑ Transformation / reaction will lead to change of enthalpy of system
- ❑ Gaseous state is considered as the reference state with no interactions
- ❑ For condensed phases PV << E $\Rightarrow$ H ~ E
- ❑ The increase in enthalpy on heating from 0 to T Kelvin is given by the equation below; where C_P is the specific heat at constant pressure and H_0 is the internal energy of the system at 0K (H_0 represents energy released when atoms are brought together from the gaseous state to form a solid at zero Kelvin)
- ❑ Enthalpy is usually measured by setting H = 0 for a pure element in its stable state at 298 K (RT).





$$H = H_0 + \int_0^T C_P dT$$

$$H = \int_{298}^T C_P dT$$

Relation between enthalpy and specific heat

- Let us first consider a single component system.
- If we keep the system isolated and do not allow it to interact with the surroundings, the internal energy of the system will not change. This is actually a closed system.
- However, if the system is allowed to interact with the surroundings (that is if it acts as a open system) internal energy might change.
- Suppose the system does work δW in the surroundings and takes heat δQ from the system, then according to the *first law of thermodynamics*, the change in internal energy of the system is

$$\boxed{dE = \delta Q - \delta W}$$

- So after spending some energy for work, rest of the energy is added to the system to increase the internal energy.
- Here exact differential is used for energy because it does not depend on the path and function of the state only. On the other hand heat and work depend on the path.
- If a system changes its volume by dV at a constant pressure P, the work can be expressed as $dW = PdV$
- **So,** $dE = \delta Q - PdV$, **we know** $H = E + PV$

$$dH = dE + PdV + VdP$$

$$dH = dQ + VdP$$

Relation between enthalpy and specific heat

- If we divide by dT on both sides we get

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V\frac{dP}{dT}$$

- Specific heat capacity, C_p *at a constant pressure is defined as the heat required* to increase the temperature of the system by one degree. So it can be expressed as

$$C_P = \left(\frac{\delta Q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$$

- After integration, we can write

$$\int_{H_0}^{H} dH = \int_{0}^{T} C_p dT$$

$$H_T = H_0 + \int_{0}^{T} C_p dT$$

$$H_T = \Delta H_{298} + \int_{298}^{T} C_p dT$$

- H_T , H_0 , and ΔH_{298} are the enthalpies at temperature, T, 0, and 298K respectively
- Note that we can not measure absolute thermodynamic values. We rather measure a relative value, H_{298} is considered as reference value.
- For pure metals it considered as zero.

Helmholtz Free Energy

- Helmholtz Free Energy (A or F) = E – T.S
- S is the entropy of the system
- At constant V & T, for a process/reaction* to take place spontaneously the system has to reduce its Helmholtz Free Energy. For a system to go from 'state' 1 → 2 the change in **F** would be:

  $F_2 - F_1 = \Delta F = (E_2 - E_1) - T\,(S_2 - S_1) = \Delta E - T\Delta S$

  $$\boxed{\Delta A = \Delta E - T\,\Delta S}$$

  This change of 'state' would take place spontaneously if ΔF is Negative
- This implies that reactions which lead to an increase in the internal energy (E) are allowed (at a 'sufficiently high' temperature) if there is a Entropic benefit for the process to occur *(the concept of entropy will be dealt with in the context of Gibbs Free Energy)*

Gibbs Free Energy (G)

CONCEPT OF ENTROPY

- Gibbs Free Energy (G) = H – T.S
  - S is the entropy of the system

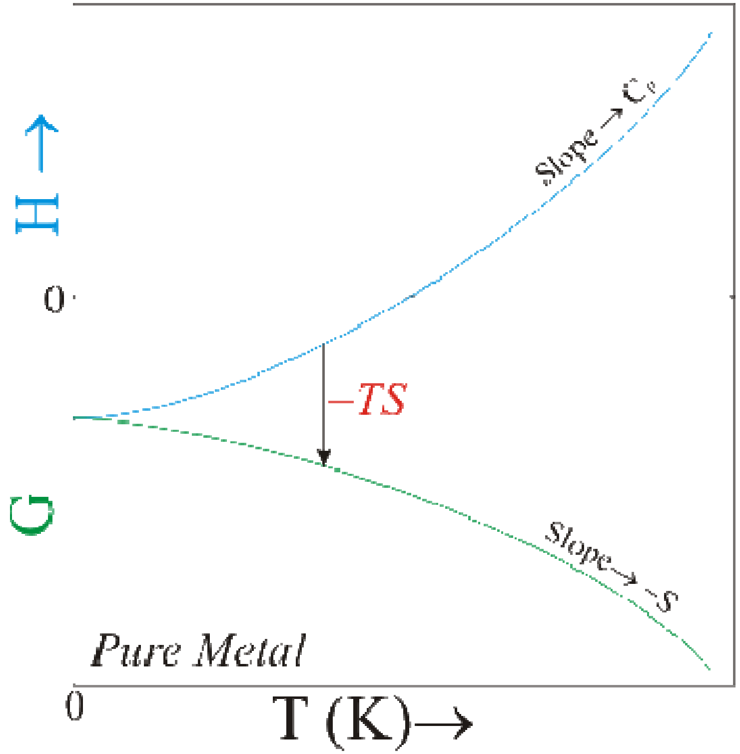
$\boxed{G = H - T.S}$

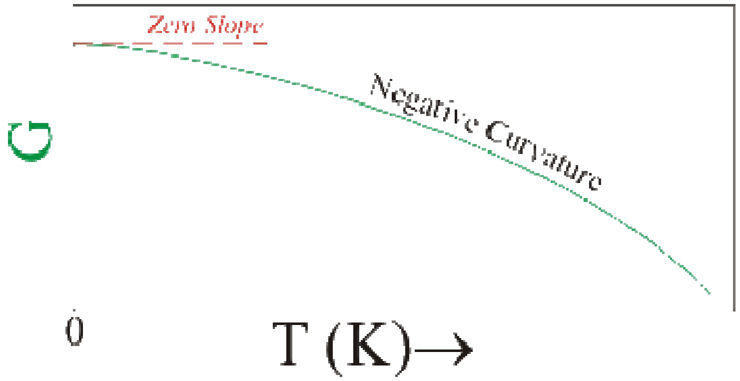
- For a process/reaction* to take place spontaneously the system has to reduce its Gibbs Free Energy (at constant P & T). For a system to go from 'state' 1 → 2 the change in G would be:

  $G_2 - G_1 = \Delta G = (H_2 - H_1) - T(S_2 - S_1) = \Delta H - T\Delta S$ $\boxed{\Delta G = \Delta H - T\,\Delta S}$

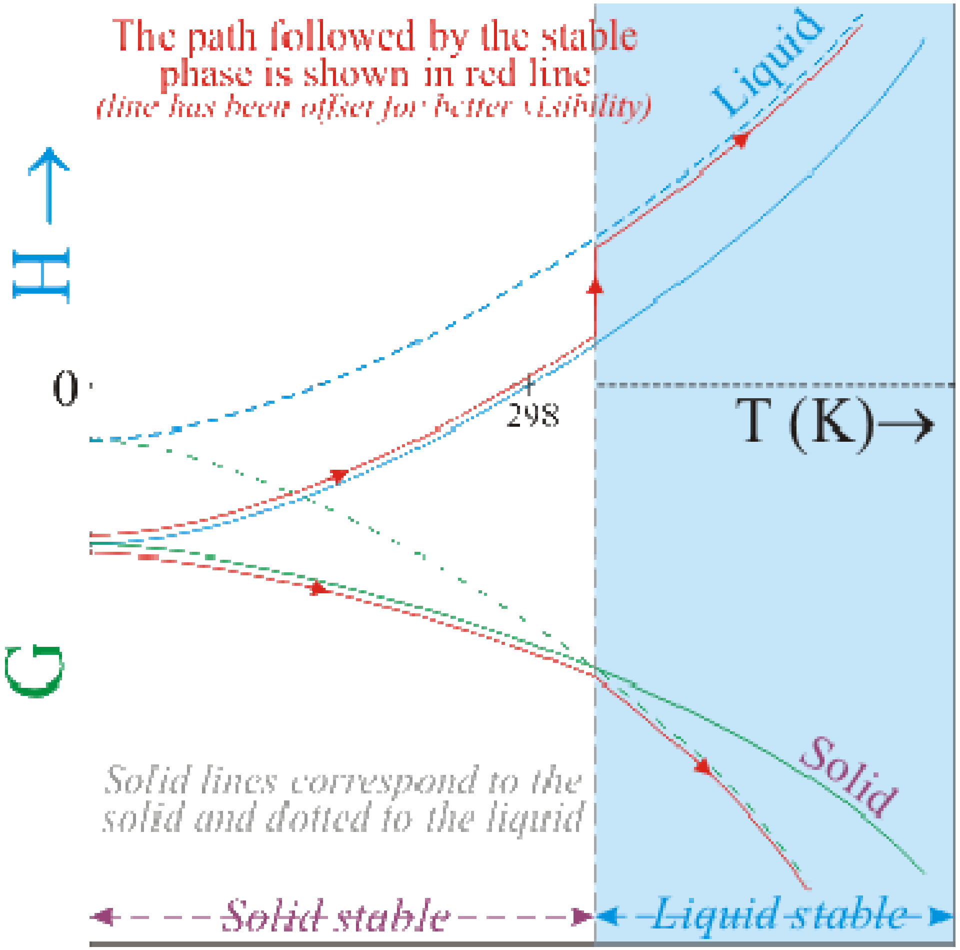
  This change of 'state' would take place spontaneously if ΔG is Negative
- This implies that *even* Endothermic reactions are allowed (at a 'sufficiently high' temperature) if there is a Entropic benefit for the process to occur
- An example of the above is the presence of ('equilibrium concentration' of) vacancies in a crystal
- Many a times we are concerned with the relative stability of two phases at a given T and P. We asks questions such as→ at 1 atm. pressure & 50°C, which of the phases is stable: ice, water or steam?

Gibbs Free Energy (G)





Melting transition

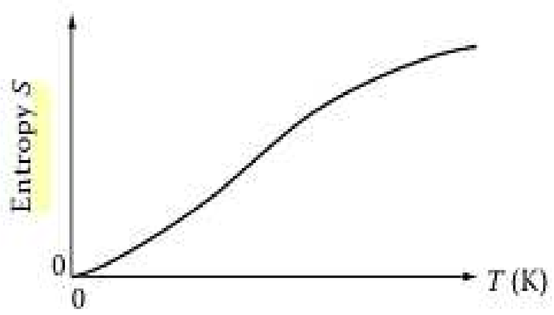

The path followed by the stable phase is shown in red line *(line has been offset for better visibility)*

Solid lines correspond to the solid and dotted to the liquid

Entropy (S)

- Entropy is perhaps one of the most profound and subtle concepts of nature.
- It is a measure of uncertainty about the system.
- Entropy can be understood looking at a Macroscopic picture (interpretation) or a Microscopic picture (interpretation) (next slide).
- Though these are different approaches to understand entropy– the result is the 'same' entropy.
- In the Macroscopic view we work at the system level and worry about *observable average quantities*. In the Microscopic view we go into all the *'details'* about the system.
- The entropy of an isolated system will increase *(cannot spontaneously decrease).*
- The microscopic interpretation (view) is the Statistical Physics/Mechanics picture, which is valid for large systems (i.e. systems with a large collections of atoms, molecules etc.).

- "Entropy is time's arrow" → time increases in the direction of increasing entropy. *The universe is in a expanding phase now. If it were to stop expanding and start contracting → entropy of the universe would decrease in the contracting phase.*



Relation between entropy and specific heat

- the knowledge on entropy (which cannot be spent to do a work) is required to determine how much energy is available (free energy) in a system to do useful work from the total heat content or enthalpy.
- Second law of thermodynamics states that the entropy of a system will either remain the same or try to increase.
- When system moves from one equilibrium state 1 to another equilibrium state 2 by changing heat of δQ, the entropy S in a reversible process can be defined as

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}}$$

- The value at zero Kelvin is zero and considered as the reference state for entropy, so that the entropy at any temperature T can be expressed as

$$\boxed{S_T = \int_0^T \frac{\delta Q}{T}}$$

- Previously we have seen from the relation $H = E + PV$ and using the first law of thermodynamics

$$\delta Q = dH$$

- We know dH = C_p dT, So the entropy at T can be expressed as

$$\boxed{S_T = \int_0^T \frac{C_P}{T} dT}$$

Relation between entropy and specific heat

- Sometimes value of the entropy at the standard state (298 K) is available and can written as

$$\boxed{S_T = \Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT}$$

- So the free energy at temperature, T can be determined

$$G_T = H_T - TS_T$$

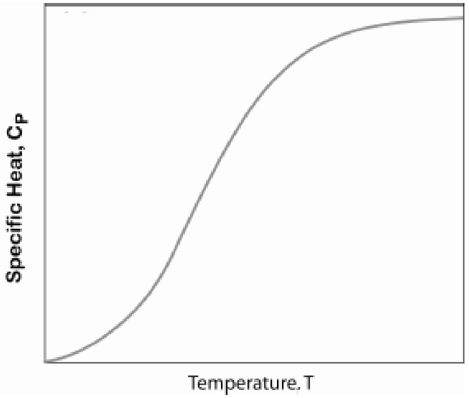
$$G_T = \Delta H_{298} + \int_{298}^{T} C_P dT - T\left(\Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT \right)$$

$$G_T = \int_{298}^{T} C_P dT - T\left(\Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} dT \right) \quad \textit{In pure elements}$$

- Specific heat is expressed as

$$C_P = A + BT - \frac{C}{T^2} \qquad \textit{A, B and C are constants.}$$

- Specific heat is expressed in terms of empirical formula as expressed above.



Specific heat changes with temperature as shown in the figure

Entropy (S)

Thermal

Two views and *not* two types

Configurational + other*

- Due to **Rudolf Clausius**
- **Macroscopic view**
- **'Classical Thermodynamic' definition**

The entropy change of a system at temperature T absorbing an infinitesimal amount of heat ΔQ in a reversible way, is:

$$S_{thermal} = \frac{\Delta Q}{T}$$

$$S_{config} = k \ln \omega$$

Zero or +ve

Boltzmann constant (1.38 × 10^{-23} J/K)

No. of different configurations the system

- Due to **Ludwig Boltzmann**
- **Microscopic view**
- **Statistical Physics Definition**

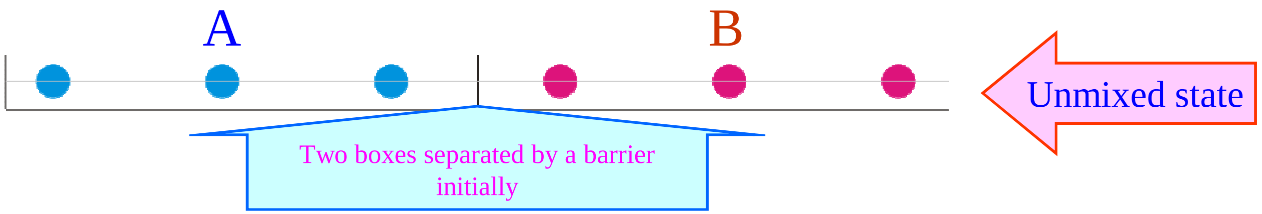
* For a system at Constant Energy, many microscopic states can give a macroscopic state of identical energy. These microscopic states could originate from various sources like Configurational, Electronic, Vibrational and Rotational states.

- In many cases the configurational term may be the predominant one considered.

$$\Delta S = \Delta S_{Configurational} + \Delta S_{Vibrational} + \Delta S_{Rotational} + \Delta S_{Electronic} + \Delta S_{Nuclear}$$

Entropy (S)

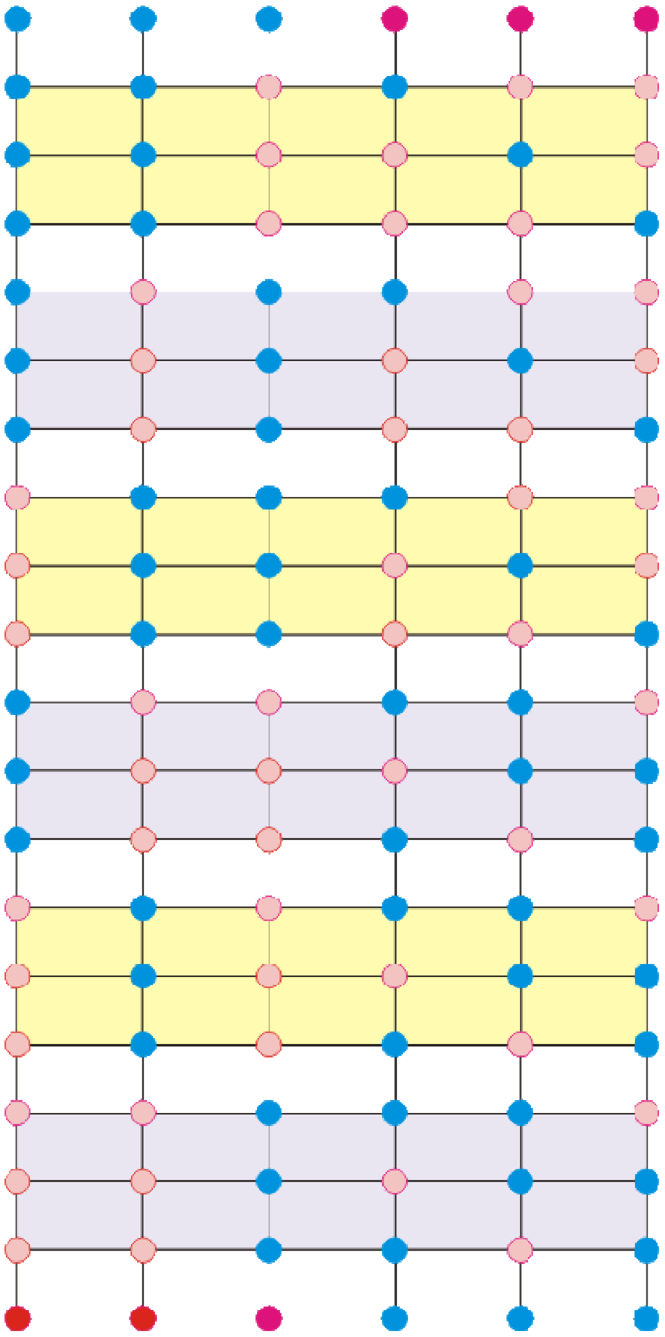
- One way of simply stating the ‘concept behind entropy’ is
  → A system will, more often than not, be found in ‘states; with *higher probability*.
  (This is nothing but the statement of the obvious!)
- However, the implications of the above are ‘profound’. This can be best understood by considering the mixing of two ideal gases (or in the ‘toy model’ below as the mixing of 6 circles- 3 red and 3 blue, on 6 fixed lattice sites).
- Assuming that red and blue circles can move about randomly on the fixed sites and also assuming that the *probability of the occurrence of each state is identical* (i.e. no state is preferred over any other state); there are 20 possible configurations as shown in the next slide.
- As seen (from the figure in the next slide) the majority of the states (18/20) are ‘mixed states’ and only two are the ‘totally’ unmixed ones.
- Hence, purely from a probabilistic point of view, mixed states occur more often than the unmixed ones.
- This implies, if we start with a unmixed configuration as in the figure below and the system can access all possible states with equal probability → the system will go from a unmixed state (of low entropy) to a mixed state (of higher entropy).



Two boxes separated by a barrier initially

Unmixed state

$$ {}^{6}C_3 = \frac{\lfloor\underline{6}}{\lfloor\underline{3}\,\lfloor\underline{3}} = \frac{6.5.4}{3.2.1} = 20 $$



Unmixed state

- In the case of two gases initially separated by a barrier, which is allowed to mix on the removal of the barrier: the number of mixed states are very large compared to the unmixed states. Hence, if all configurational states are accessible, the system will more likely found in the mixed state. I.e. the system will go from a unmixed state to a mixed state (worded differently the system will go from ‘order’ to ‘disorder).
- On the other hand it is *unlikely (improbable)* that the system will go from mixed state to a unmixed state. *(Though this is not impossible → i.e. a mixed system can spontaneously get ‘unmix’ itself!!)*

Mixed states with ‘various’ degrees of mixing

Note: the profoundness of the concept of entropy comes from its connection to energy (via T)

18 mixed states
2 unmixed states

Unmixed state

** We assume that all states have equal probability of occurring and are all accessible*

Entropy change due to mixing of two pure elements

- Let us consider the entropy change due to mixing of two pure crystalline elements **A** & **B** (a simple case for illustration of the concept of entropy).
- The unmixed state is two pure elements held separately. The mixed state (for now assuming that the enthalpy of mixing is negative- i.e. the elements want to mix) represents an atomic level mixing of the two elements.
- Let the total number of lattice sites (all equivalent) be **N**.
- The Entropy of the unmixed state is zero (as in pure crystalline elements atoms are indistinguishable and hence represent one state). $S_{\text{pure A}} = S_{\text{pure B}} = k\ln(1) = 0$
- In the mixed state the entropy of the system increases ($S_{\text{mixed state}}$)
- The number of permutations possible in the mixed system is ω

$$\omega = {}^{N}C_{n_A} = \frac{N!}{(N-n_A)!\,(n_A)!}$$

$$\Delta S = S_{mixed\ \ state} - \cancelto{Zero}{S_{pure\ elements(A\&B)}}$$

$$\Delta S = k\ln\omega = k\ \ln\frac{N!}{(n_A)!\,(n_B)!}$$

$$\Delta S = k\ln\omega = k\ \ln\frac{N!}{(N-n_A)!\,n_A!}$$

An useful formula for evaluating ln(factorials) is the Stirling's approximation: $n! \sim \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$

$$Ln(r!) = r\ln(r) - r$$

$$r! = \underline{|r}$$

~ ⇒ asymptotically equal, e = 2.718…

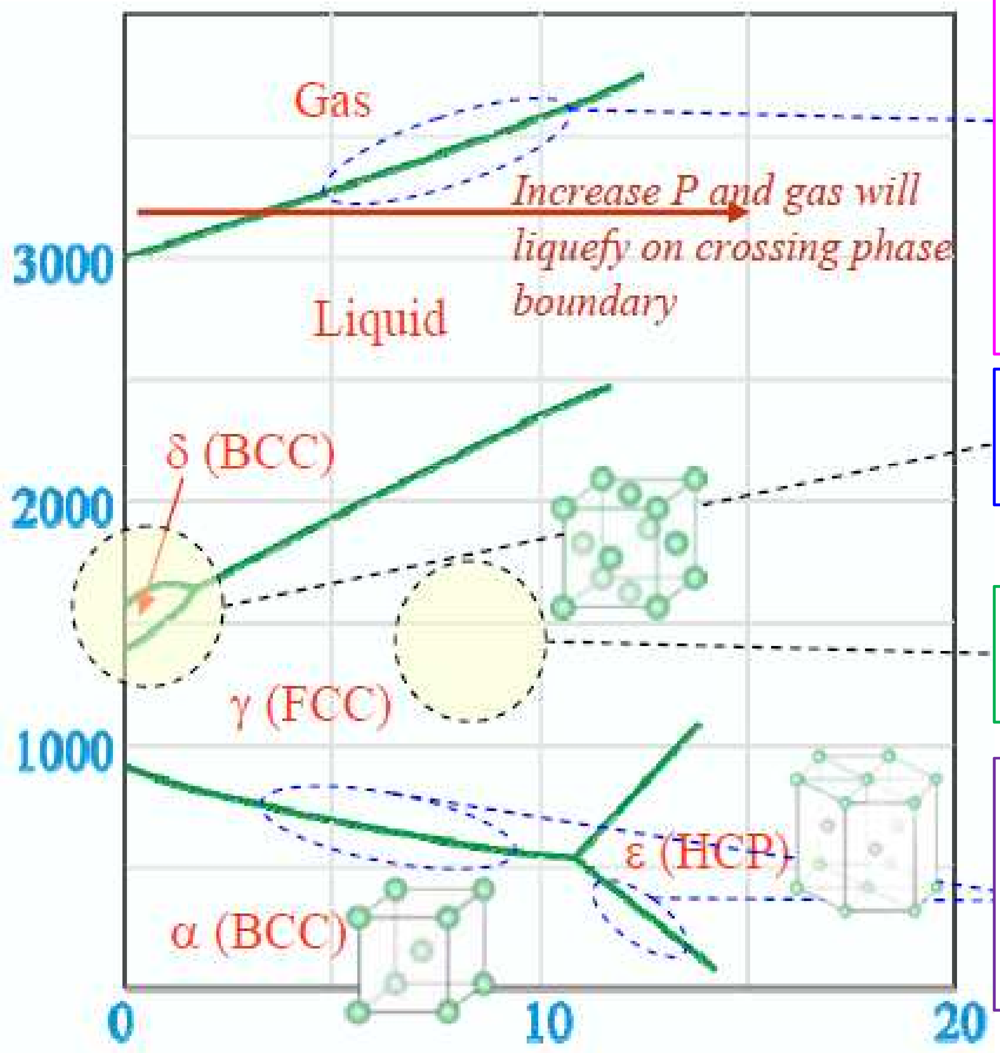
Entropy change during melting

- ❑ At the melting point of a material when heat is supplied (ΔQ) to the material it does not lead to an increase in the temperature. Instead, the absorbed heat leads to melting- i.e. the energy goes into breaking of bonds in the solid and consequently a transformation in the state of the material (solid → liquid). The entire process of melting takes place at a constant temperature (T_m). The heat absorbed is called the Latent Heat of Fusion (ΔH_{fusion}).
- ❑ Suppose we take a mole of Al atoms melt then the change in entropy can be calculated as below.
- ❑ In the solid state the atoms are fixed on a lattice (of course with vibrations!) and this represents a 'low entropy' state. On melting the entropy of the system increases as the atoms are free to move around and may configurations are possible. From this point of view often Entropy is considered as a measure of disorder (however, it must be clear that the phrase 'measure of disorder' is used with the understanding of the context)

Data: Enthalpy of fusion (ΔH_f) = 10.67 kJ/mole, Melting Point (T_m) = 933.4 K (660.25°C)

$$\Delta S_{melting\ Al} = \frac{\Delta Q}{T} = \frac{\Delta H_f}{T_m} = \frac{10.67\times 10^3}{933.4} = 11.43\ J/K/mole$$

Single component system



This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

Gibb’s free energy change with temperature in a single component system

- An isolated system always tries to maximize the entropy. That means the system is stable when it has maximum possible entropy.
- Instead of considering isolated system, we need to consider the system which interacts with the surroundings because heat transfer is always with respect to the surroundings only.
- Any transformation is possible only when $dS+dS_{Surrou} \geq 0$ where dS is the change in entropy of the system.
- In a reversible process, when system can transform back to its previous state it is equal to zero and in an irreversible process when the system cannot come back to its previous state is greater than zero.
- We need to find the stability with respect to another term, for the sake of convenience, which can be used without referring to the surroundings. We shall show now that free energy is rather a suitable property to define stability of the phases.
- Let us consider that the system absorbs some amount of heat δQ from the system. Since the surrounding is giving away the heat, we can write

$$dS_{surrou} = -\frac{\delta Q}{T}$$

Gibb’s free energy change with temperature in a single component system

- ❑ We have seen before that in an isobaric system $\delta Q = dH$. So we can write

$$dS - \frac{dH}{T} \geq 0$$

$$dH - TdS \leq 0$$

- ❑ We are considering isobaric system. If we consider the transformation at a particular temperature (*T constant*, $dT = 0$) then

$$dH - TdS - SdT \leq 0$$

$$d(H - TS) \leq 0$$

$$dG \leq 0$$

- ❑ So we have derived a more reasonable relation, which can be used without referring to the surroundings.
- ❑ In an reversible process, such as allotropic transformation or the transformation from solid to liquid or liquid to solid the free energy change is zero. There will be many irreversible transformations (later we shall see these kinds of diffusion controlled transformations), where dG is less than zero.
- ❑ This also indicates that a system will be stable when it has *minimum free energy, so* that it is not possible to get anymore dG less than zero by any further transformation.

Stability of the phases in a single component system

- One component can have different stable phases at different temperature and pressure ranges, for example, solid, liquid and the gas phase.
- One phase is said to be stable, when it has lower free energy compared to other phases in a particular range of temperature and pressure.
- Let us consider constant pressure.
- To compare the stability of different phases in a particular range of temperatures, we need to calculate the free energy of the phases with respect to temperature.
- To determine Gibb’s free energy at a particular temperature, we need to determine H and S. Similarly it can be calculated at every temperature to gain knowledge on the change in free energy with temperature.
- As mentioned previously the data on specific heat are available in literature and these parameters can be calculated.

Stability of the phases in a single component system

- ☐ From the definition, we know that the slope of the enthalpy at any temperature is equal to the specific heat at that temperature.

$$G = H - TS$$

$$dG = dH - TdS - SdT \qquad (H = E + PV)$$

$$dG = dE + PdV + Vdp - TdS - SdT \qquad (dE = \delta Q - PdV)$$

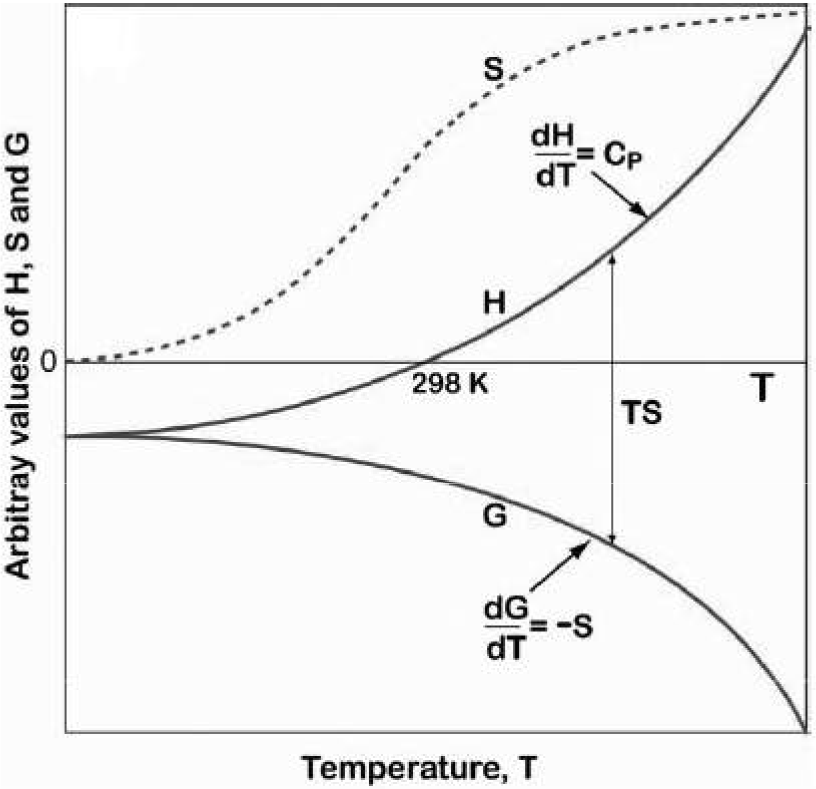
$$dG = \delta Q - PdV + PdV + VdP - TdS - SdT$$

$$dG = TdS + VdP - TdS - SdT \qquad \frac{\delta Q}{T} = dS$$

$$dG = VdP - SdT$$

- ☐ So at a constant pressure the slope of the free energy curve

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

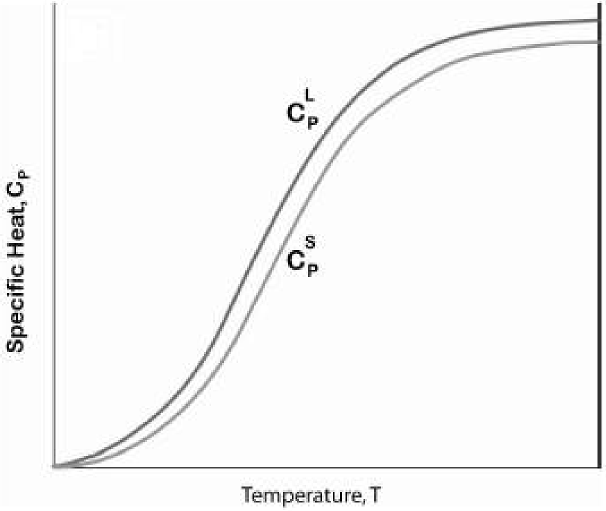


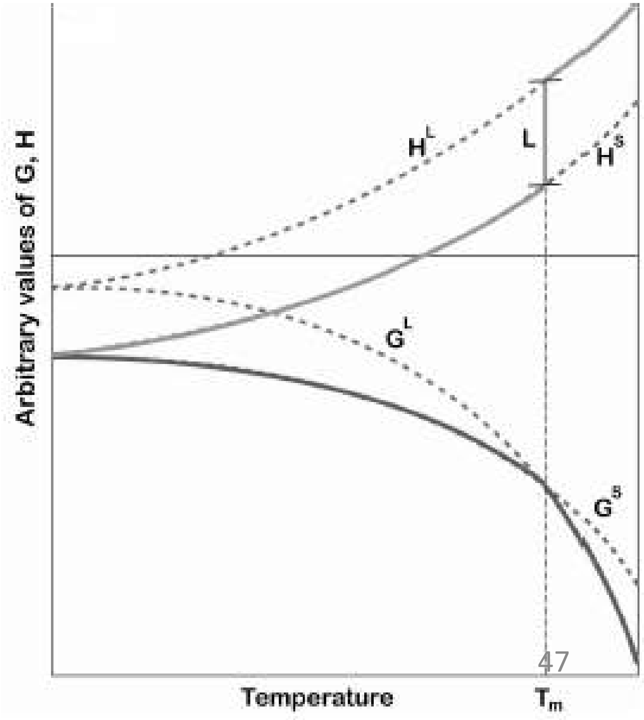
Typical variation of thermodynamic parameters are shown in the figure.

- ☐ *If we want to know whether a solid or liquid phase will be stable at a particular temperature or in a temperature range, we need to find free energy for both the phases.*

Stability of the phases in a single component system

- For that we need to know the variation of specific heat with temperature for both the phases as shown in the figure.
- Specific heat for a liquid phase is always higher than the solid phase. That means energy required to increase the temperature by one degree for liquid phase is higher than the solid phase.
- Superscript, S and L denote the solid and liquid phases.
- Free energy for liquid phase changes more drastically compared to the free energy of the liquid phase because entropy of the liquid phase is always higher, which is the slope of the free energy.
- At melting point, free energy for both the phases are the same and the difference between the enthalpy of these two phases is equal to the latent heat of fusion L.





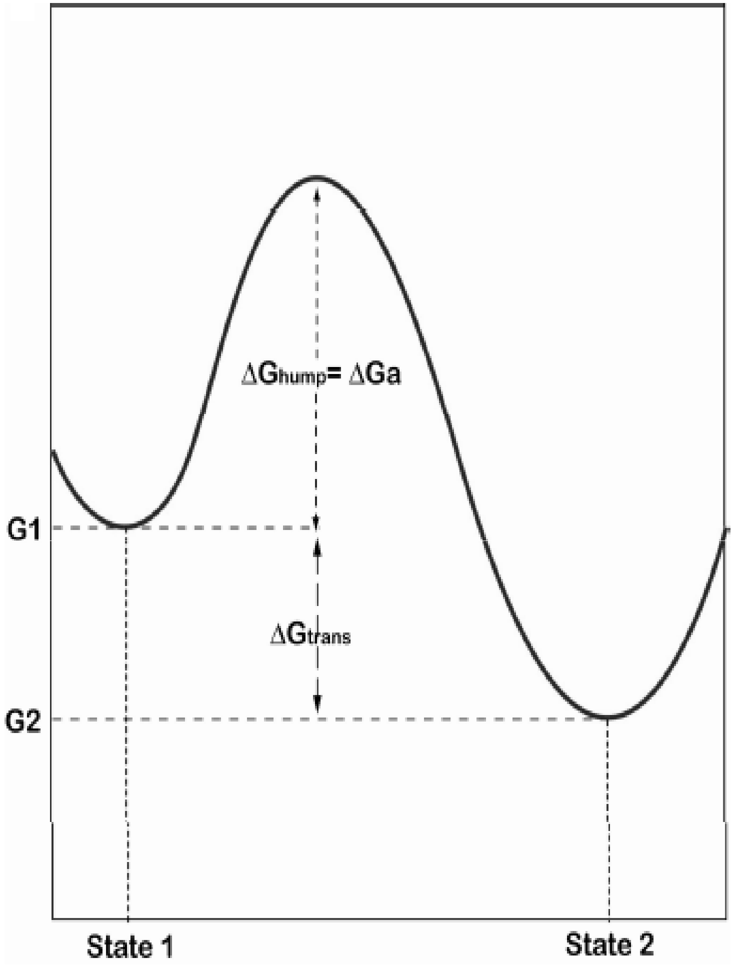
Stability of the phases in a single component system

- It must be apparent that one particular phase at certain temperature range will be stable, if the free energy, G is lower of that phase than the other phase.
- At low temperature range, one particular phase will be stable, which has low enthalpy, since "TS" term will not dominate. That is why solid phase is stable at low temperature range.
- On the other hand, at higher temperature range, phase having higher entropy will be stable since in this range "TS" term will dominate. That is why liquid phase is stable at high temperature range.
- This is the reason that α-Ti with close packed HCP structure is stable at low temperature range, whereas, at high temperature range β-Ti with relatively more open BCC structure is stable.
- If we fix a temperature, we have seen that one material/element will be stable as one type of phase with a particular state compared to other.
- It can stay in equilibrium if it has minimum free energy and dG=0, it indicates that for small fluctuation it does not move to another state.
- Only dG = 0 is not sufficient condition, since we have seen that at the melting point both the liquid any solid phases can stay together.

Stability of the phases in a single component system

- Let us consider two different states (different atomic arrangements) of a material, as shown in the figure.
- State 1 fulfills the condition dG=0, but G is not minimum.
- State 2 is in the most stable condition, since G is minimum and also dG= 0
- Material at state 1 is called metastable state, for example, diamond, metallic glass.
- Material at state 2 is the equilibrium state or most stable state, for example, graphite. Given chance, material will transform from the state 1 to state 2.
- Transformation is possible only when driving force for transformation, ΔG_{Trans} is negative

$$\Delta G = \Delta G_d = G_{final} - G_{initial} = G_2 - G_1$$



- However, straightforward transformation is not possible. It should cross a barrier.
- The barrier is $\Delta G_{Hump} = \Delta G_a$ = activation energy that is the barrier for the phase transformation. The barrier comes from the need for nucleation and diffusion.

Clausius - Clapeyron Equation

From previous studies

$$dG = VdP - SdT$$

$$G^l = G^s \rightarrow \Delta G = 0$$

$$consider : S \rightarrow L$$

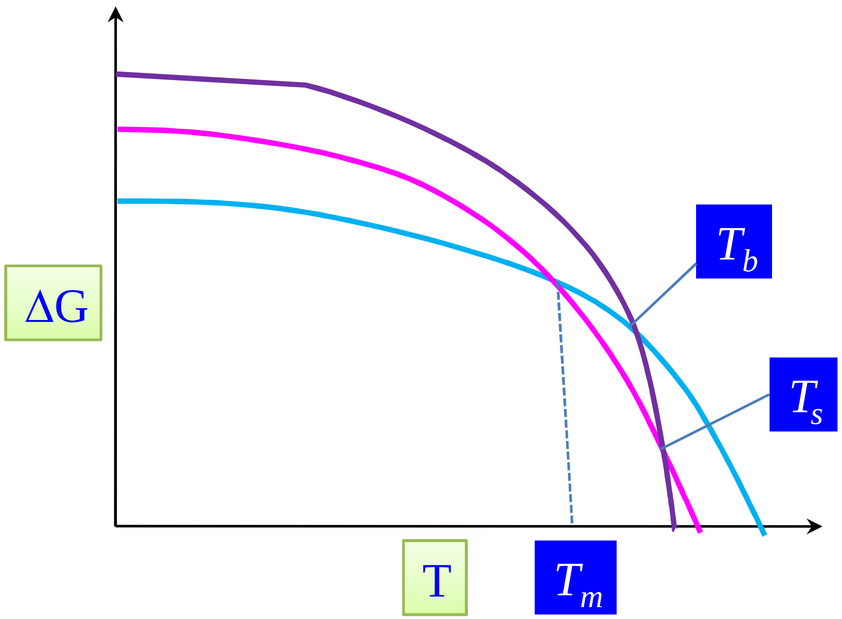
$$dG^S = V^S dT - S^S dT$$

$$dG^L = V^L dT - S^L dT$$

$$(V^S - V^L)dP = (S^S - S^L)dT$$

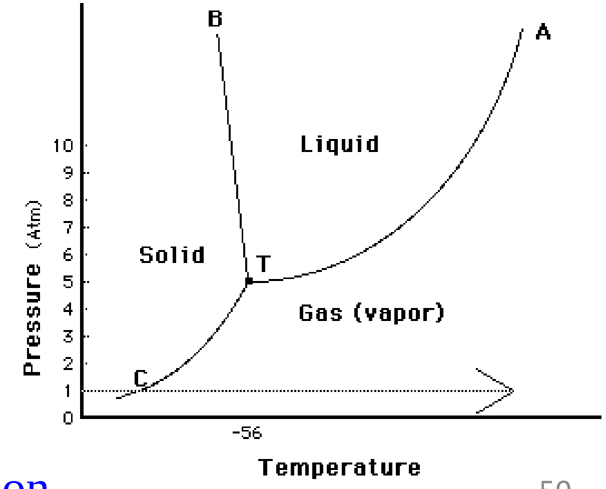
$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{V^S - V^L}{S^S - S^L}$$

$\dfrac{dT}{dP} =$ *The rate of change of transformation temperature as a function of pressure*



$$\boxed{\frac{dT}{dP} = \frac{\Delta V}{\Delta S}}$$

Is known as Clausius-Clapeyron equation

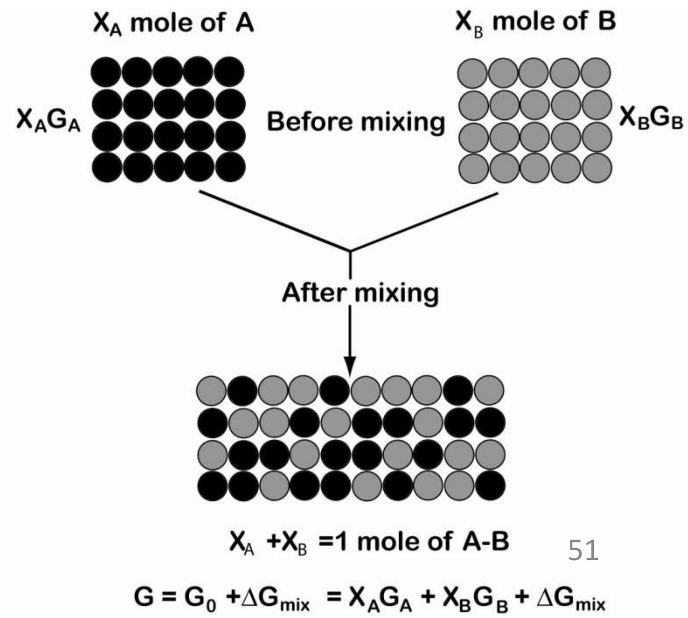


Thermodynamic parameters in a binary system

- Previously we are considered one element only. Now we consider interaction between two elements. This is not straightforward since elements can interact differently and thermodynamic parameters may change accordingly.
- Let us consider a Binary system with elements A and B. For our analysis, we consider X_A mole of A and X_B mole of B so that $\boldsymbol{X_A + X_B = 1}$
- That means we consider total one mole of the system That further means we consider total number of atoms equal to the Avogadro number, N_0 $(= 6.023 \times 10^{23})$,

Where $X_i = \frac{N_i}{N_0}$ *is the number of atoms of element i.*

- Unlike single component system, where we determine the change in free energy with temperature, in the binary case we shall find the change in free energy with the change in composition at different constant temperature at a time.
- Let us consider the free energy for one mole of element A is G_A and one mole of B is G_B.



$$G = G_0 + \Delta G_{mix} = X_AG_A + X_BG_B + \Delta G_{mix}$$

Thermodynamic parameters in a binary system

- ❑ So before mixing when kept separately, X_A mole of A and X_B mole of B will have the free energy of $X_A G_A$ *and* $X_B G_B$ respectively

Total free energy before mixing $G_0 = X_A G_A + X_B G_B$

- ❑ After mixing there will be change in free energy
- ❑ Total free energy after mixing $G = G_0 + \Delta G_{mix}$

- ❑ ΔG_{mix} is the free energy change of the alloy because of mixing

$$\Delta G_{mix} = G - G_0 = H - TS - (H_0 - TS_0) = (H - H_0) - T(S - S_0)$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

- ❑ So, once we determine the change in free energy because of mixing, we can determine the total free energy after mixing.
- ❑ Let us first determine, the enthalpy change because of mixing (ΔH_{mix}) and the change in entropy because of mixing (ΔS_{mix})
- ❑ Note that system always tries to decrease enthalpy and increase entropy for stability.

The change in enthalpy because of mixing, ΔH_{mix}

- ❑ We take the following assumptions:
  - ✓ The molar volume does not change because of mixing
  - ✓ Bond energies between the pure elements do not change with the change in composition
  - ✓ We neglect the role of other energies.
- ❑ After mixing, the system can have three different types of bonding, A-A, B-B and A-B
- ❑ Enthalpy of mixing can be expressed as $\Delta H_{mix} = N_0 Z X_A X_B \Delta\varepsilon$

  N_0 - *Avogrado number, Z = coordination number*

- ❑ The change in internal energy

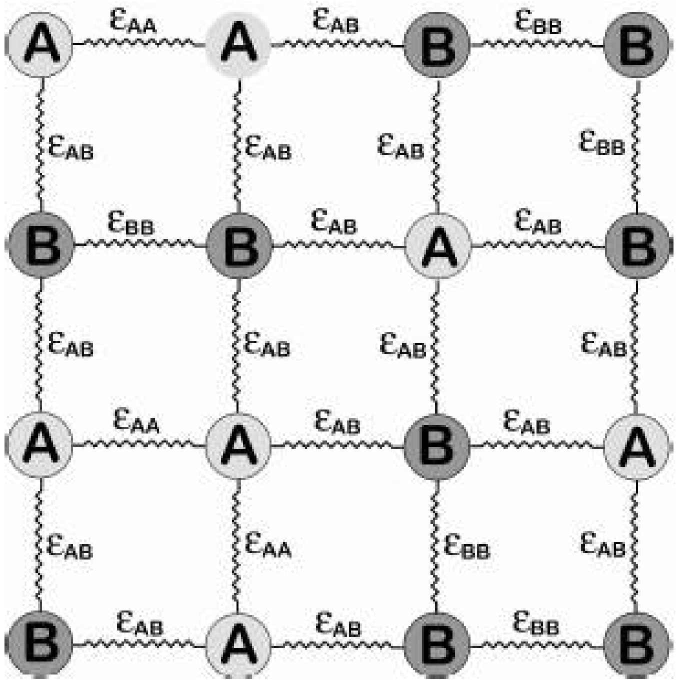
$$\Delta\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

ε_{AB} is the bond energy between A and B
ε_{AA} *is the bond energy between A and A*
ε_{BB} *is the bond energy between B and B*

- ❑ It can be written as

$$\Delta H_{mix} = \Omega X_A X_B$$

Where $\Omega = N_0 Z \Delta\varepsilon$



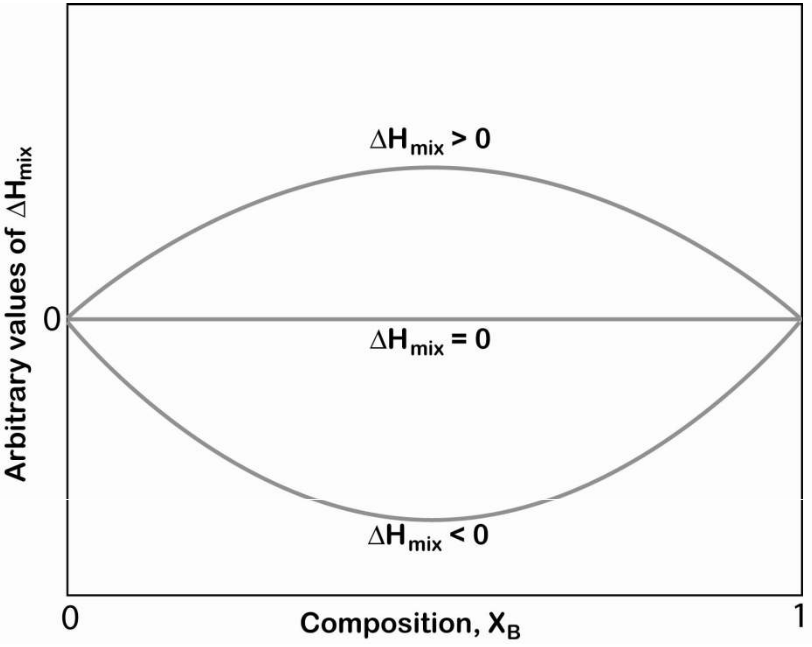
The change in enthalpy because of mixing, ΔH_{mix}

Situation 1: Enthalpy of mixing is zero

$$\Delta H_{mix} = \Omega X_A X_B = 0$$

That means $\varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.

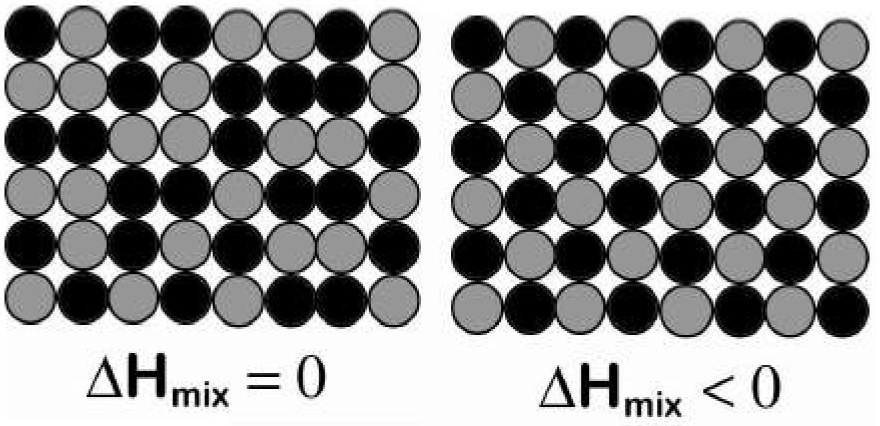


Situation 2: Enthalpy of mixing is less than zero

$$\Delta H_{mix} = \Omega X_A X_B < 0$$

That means $\varepsilon_{AB} < \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will decrease. That means transformation is exothermic. Atoms will try to maximize A-B bonds.



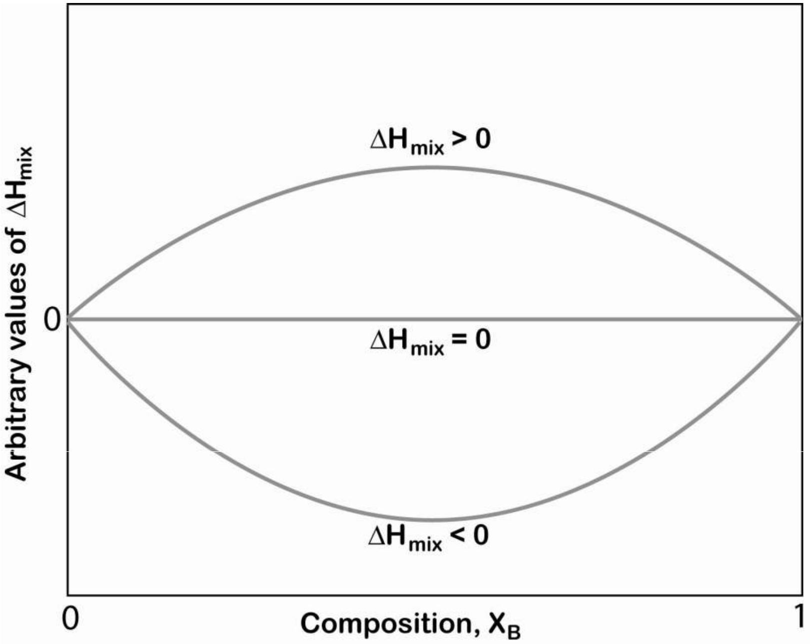
The change in enthalpy because of mixing, ΔH_{mix}

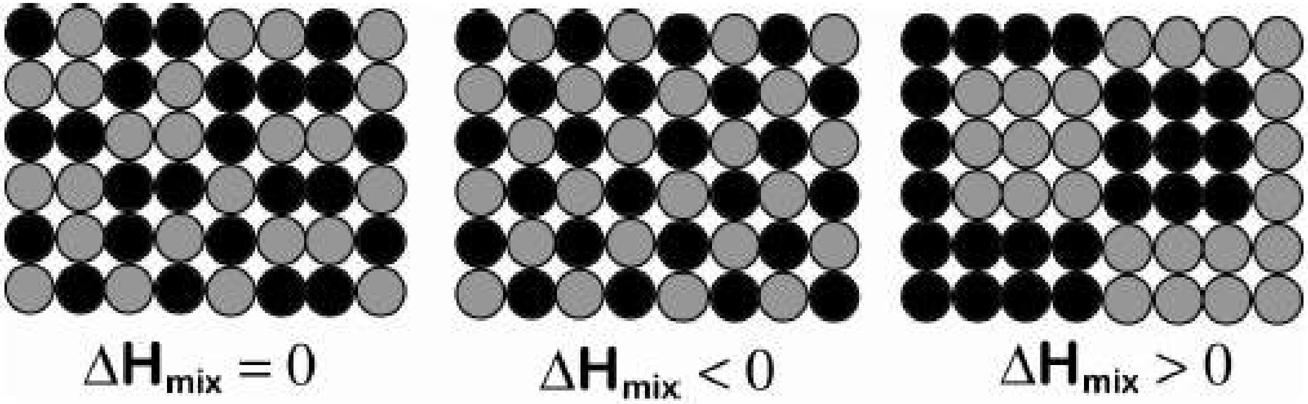
Situation 3: Enthalpy of mixing is greater than zero

$$\Delta H_{mix} = \Omega X_A X_B > 0$$

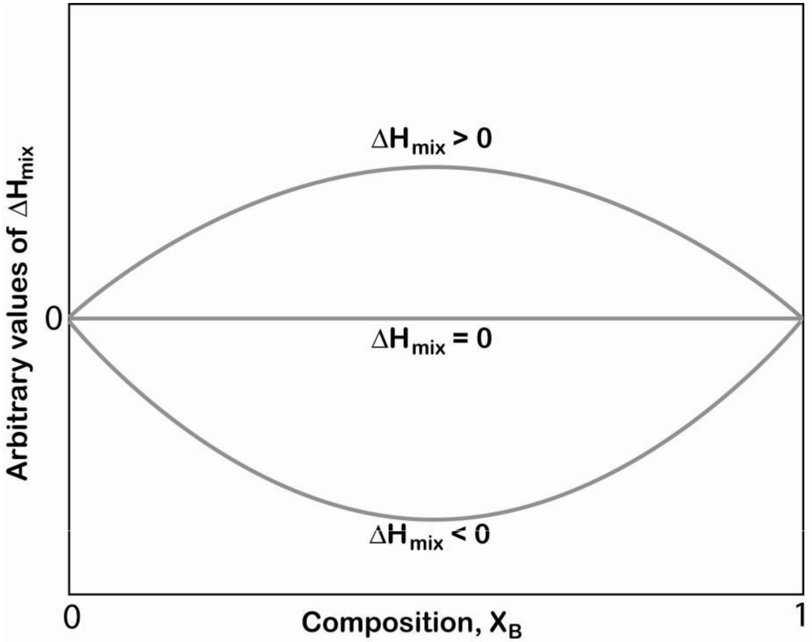
That means $\varepsilon_{AB} > \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Because of transformation internal energy will increase. That means transformation is to be endothermic. Atoms will try to maximize A-A and B-B bonds.





Slope/maximum/minimum of the enthalpy of mixing curve



$$\Delta H_{mix} = \Omega X_A X_B = \Omega(X_B - X_B^2)$$

$$\frac{d(\Delta H_{mix})}{dX_B} = \Omega(1 - 2X_B)$$

At maximum/minimum $$\frac{d(\Delta H_{mix})}{dX_B} = 0$$

This implies X_B = 0.5. That means maximum or minimum will be at X_B =0.5

Further $$\frac{d(\Delta H_{mix})}{dX_B} at X_B \xrightarrow{\lim} 0 = \Omega$$

That means the slope at the beginning has a finite value of x

The change in entropy because of mixing, ΔS_{mix}

- ❑ Since we are considering transformation at a particular temperature, the change in entropy because of the change in temperature can be neglected.
- ❑ We need to consider only the configurational entropy change. Configurational entropy change comes from the possibilities of different ways of arrangement of atoms.
- ❑ Following statistical thermodynamics the configurational entropy can be expressed as

$$S = l \ln \omega$$

k is the Boltzmann constant
w is the measure of randomness

$$\Delta S_{mix} = S - S_0 = k \ln \omega - k \ln 1 = k \ln \omega$$

since atoms at their pure state before mixing can be arranged in only one way

- ❑ If we consider the random solid solution, then

$$\omega = \frac{(n_A + n_B)!}{n_A! n_B!}$$

n_A and n_B are the number of atoms of A and B

- ❑ *Following Stirling's approximation* $\ln N! = N \ln N - N$

The change in entropy because of mixing, ΔS_{mix}

- ❑ ***So, ΔS_{mix} can be written as***

$$\Delta S_{mix} = k\ln\omega = k\{[(n_A+n_B)\ln(n_A+n_B)-(n_A+n_B)]-[n_A\ln n_A - n_A]-[n_B\ln n_B - n_B]\}$$

$$\Delta S_{mix} = -k\left[n_A \ln\frac{n_A}{n_A+n_B} + n_B \ln\frac{n_A}{n_A+n_B}\right]$$

Number of atoms can be related to the mole fraction, X and the Avogadro number N_0 following

$$n_A = X_A N_0 \qquad n_B = X_B N_0$$

$$X_A + X_B = 1 \qquad n_A + n_B = N_0$$

$$\Delta S_{mix} = -kN_0[X_A \ln X_A + X_B \ln X_B]$$

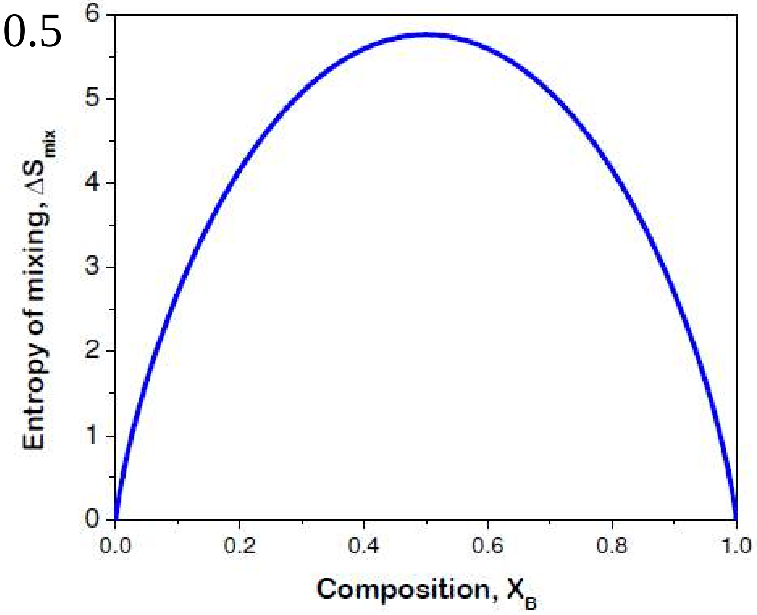
$$= R[X_A \ln X_A + X_B \ln X_B]$$

where, R is the gas constant

Slope/maximum of the entropy of mixing curve

$$\frac{d(\Delta S_{mix})}{dX_B} = -R\left[-\ln(1-X_B) - (1-X_B)\frac{1}{(1-X_B)} + \ln X_B + X_B\frac{1}{X_B}\right] = -R\ln\frac{X_B}{1-X_B}$$

$$\frac{d(\Delta S_{mix})}{dX_B} = 0$$ at maximum, this corresponds to $X_B = 0.5$



Further, the slope at $X_B \rightarrow 0$ is infinite. That means the entropy change is very high in a dilute solution

As mentioned earlier the total free energy after mixing can be written as $G = G_0 + \Delta G_{mix}$

where

$$G_0 = X_A G_A + X_B G_B$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = \Omega X_A X_B$$

$$\Delta S_{mix} = -R[X_A \ln X_A + X_B \ln X_B]$$

So ΔG_{mix} can be written as $\Delta G_{mix} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$

Following, total free energy of the system after mixing can be written as

$$\boxed{G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]}$$

Free energy of mixing

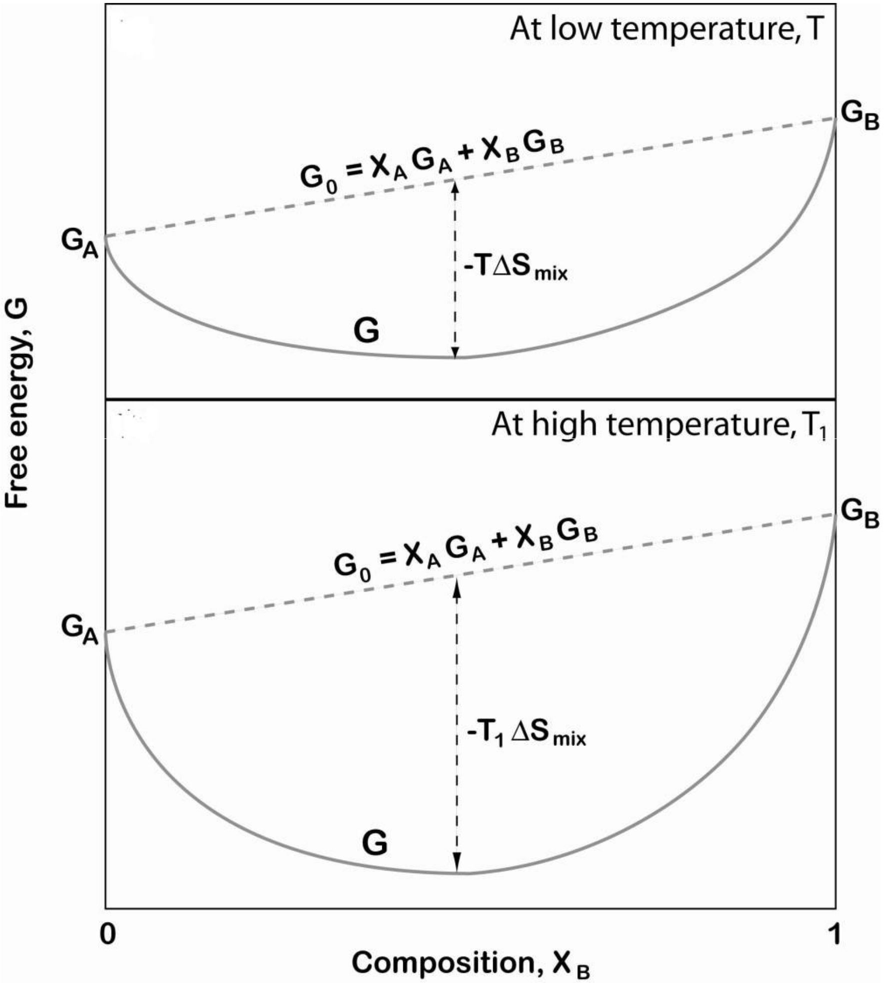
We need to consider three situations for different kinds of enthalpy of mixing

Situation 1: Enthalpy of mixing is zero

$$G = G_0 + \Delta G_{mix}$$

$$= G_0 - T\Delta S_{mix}$$

$$= \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$



- ☐ With the increase in temperature, $-T\Delta S_{mix}$ will become even more negative.
- ☐ The values of G_A and G_B also will decrease.
- ☐ Following the slope G_o *might change since* G_A *and* G_B will change differently with temperature.

Free energy of mixing

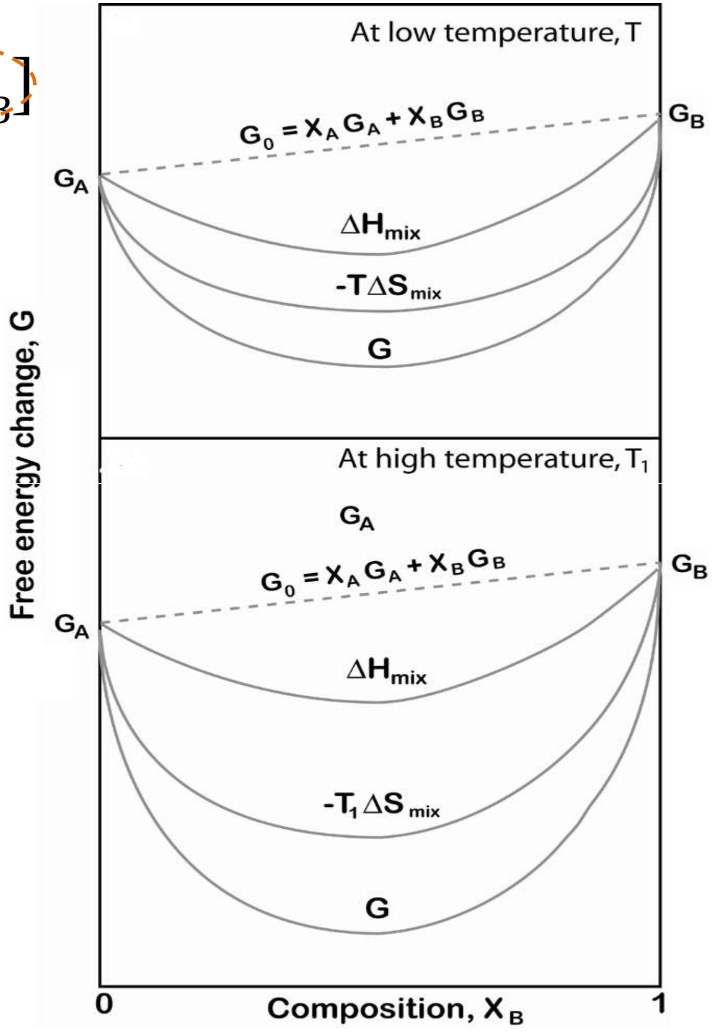
Situation 2: Enthalpy of mixing is negative

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Negative } \Delta H_{mix}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$

- ❑ Here both ΔH_{mix} and $-T\Delta S_{mix}$ are negative

- ❑ With increasing temperature G will become even more negative.

- ❑ Note that here also G_0 may change the slope because of change of G_A and G_B differently with temperature.

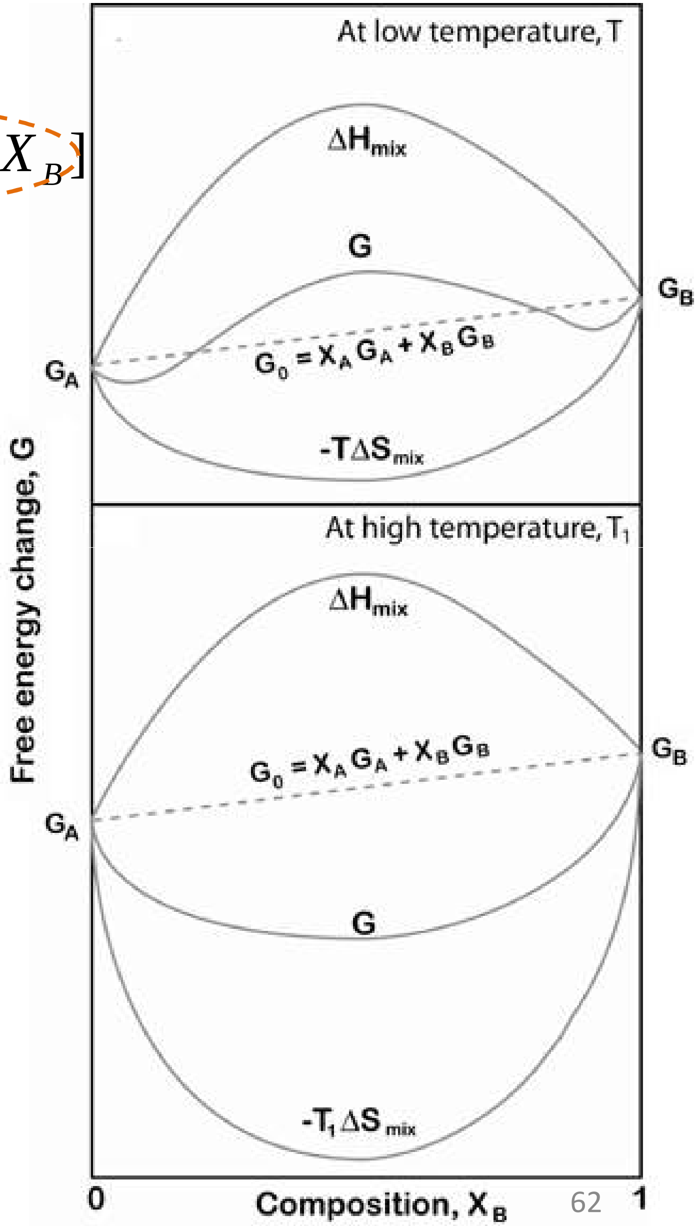


Free energy of mixing

Situation 3: Enthalpy of mixing is positive

$$G = \underbrace{X_A G_A + X_B G_B}_{G_0} + \underbrace{\Omega X_A X_B}_{\text{Positive } \Delta H_{mix}} + \underbrace{RT[X_A \ln X_A + X_B \ln X_B]}_{-T\Delta S_{mix}}$$

- ❑ ΔH_{mix} is positive but $-T\Delta S_{mix}$ is negative. At lower temperature, in a certain mole fraction range the absolute value of ΔH_{mix} could be higher than $T\Delta S_{mix}$ so that G goes above the G_0 line.
- ❑ However to G_A and G_B, G will always be lower than G_0, since ΔH_{mix} has a finite slope, where as ΔS_{mix} has infinite slope. The composition range, where G is higher than G_0 will depend on the temperature i.e., $-T\Delta S_{mix}$
- ❑ Because of this shape of the G, we see miscibility gap in certain phase diagrams.
- ❑ At higher temperature, when the absolute value of $-T\Delta S_{mix}$ will be higher than ΔH_{mix} at all compositions, G will be always lower than G_0



Concept of the chemical potential and the activity of elements

- ☐ Gibb's free energy, G is function of temperature, T, pressure, P and amount of elements, n_A, $n_{B.}$

  $$\boldsymbol{G = G\,(T, P, n_A, n_B \ldots\ldots)}$$

- ☐ At particular temperature and pressure, partial derivative gives

$$dG = \frac{\partial G}{\partial n_A} dn_A + \frac{\partial G}{\partial n_B} dn_B$$

$$= \mu_A dn_A + \mu_B dn_B$$

$\frac{\partial G}{\partial n_A} = \mu_A$ is the chemical potential of element A. It measures the change in free energy because of very minute change of element A.

$\frac{\partial G}{\partial n_B} = \mu_B$ is the chemical potential of element B. It measures the change in free energy because of very minute change of element B.

- ☐ It should be noted here that the change should be so minute that there should not be any change in concentration because the chemical potential is a concentration dependent parameter.

Concept of the chemical potential and the activity of elements

- Let us consider an alloy of total X moles where it has X_A mole of A and X_B mole of B. Note that x is much higher than 1 mole.
- Now suppose we add small amounts of A and B in the system, keeping the ratio of $X_A : X_B$ the same, so that there is no change in overall composition.
- So if we add four atoms of A, then we need to add six atoms of B to keep the overall composition fixed. Following this manner, we can keep on adding A and B and will reach to the situation when X_A mole of A and X_B mole of B are added and total added amount is $X_A + X_B = 1$
- Since previously we have considered that the total free energy of 1 mole of alloy after mixing is G, then we can write

$$G = \mu_A X_A + \mu_A X_B$$

- ***Previously, we derived***

$$G = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

- ***Further, we can write*** $X_A X_B = X_A^2 X_B + X_A X_B^2$

$$G = X_A(G_A + \Omega X_B^2 + RT \ln X_B) + X_B(G_B + \Omega X_A^2 + RT \ln X_B)$$

Concept of the chemical potential and the activity of elements

Further, comparing the expressions for free energy, we can write

$$\mu_A = G_A + \Omega X_B^2 + RT\ln X_A$$

$$\mu_A = G_A + \Omega(1 - X_A)^2 + RT\ln X_A$$

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT\ln X_B$$

In terms of activity

$$\mu_A = G_A + RT\ln a_A$$

$$\mu_B = G_B + RT\ln a_B$$

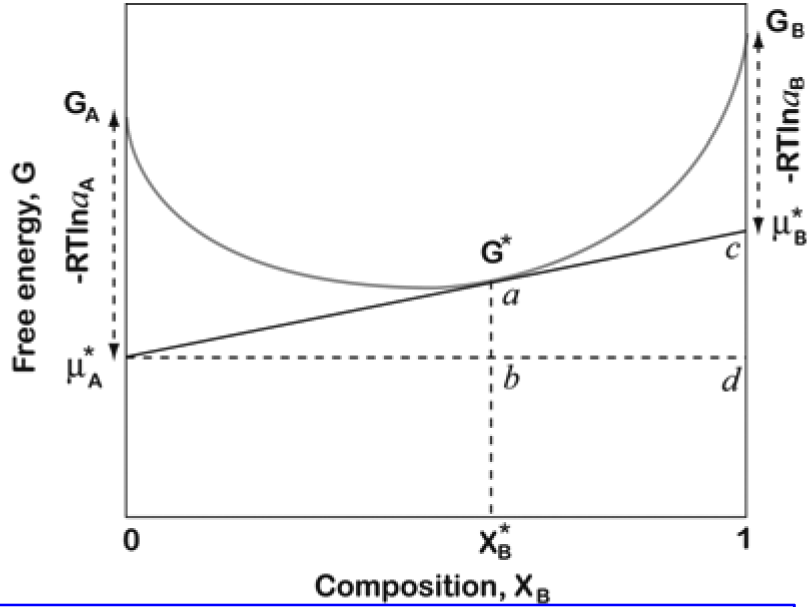
So the relations between the chemical potential and activity are

$$RT\ln a_A = \Omega(1 - X_A)^2 + RT\ln X_A$$

$$RT\ln a_B = \Omega(1 - X_B)^2 + RT\ln X_B$$

Concept of the chemical potential and the activity of elements

- Activities and chemical potentials are determined from a free energy curve after taking a slope, as explained in the figure.
- If we are interested to determine the activities or chemical potentials in a binary system A-B, let say at X_B^*, we need to take a slope on the free energy curve at the free energy, G^* and extended it to pure element, A ($X_B = 0$) and pure element B ($X_B = 1$).



- The point at which it hits $N_B = 0$, the value corresponds to the chemical potential of element A (μ_A^*).
- From previous slide, we can write $-RT\ln a_A = G_A - \mu_A^*$
- So, once the chemical potential is known, the activity of the element can be calculated using the above equation, as explained in the graph.
- It can be proved that, by taking slope and then extending to $X_B = 0$ and $X_B = 1$, we can find the chemical potentials. We can write $G^* = \mu_A^* + ab$
- Further we can write $\dfrac{ab}{X_B^*} = \dfrac{cd}{1}$ $\Rightarrow ab = X_B^* cd = X_B^*(\mu_B^* - \mu_A^*)$ $\boxed{\Rightarrow G^* = \mu_A^* X_A^* + \mu_B^* X_B^*}$

Concept of the chemical potential and the activity of elements

Further, we can write

$$\ln\left(\frac{a_A}{X_A}\right) = \frac{\Omega}{RT}(1-X_A)^2$$

$$a_A = X_A \exp\left[\frac{\Omega}{RT}(1-X_A)^2\right] = \gamma_A X_A$$

$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1-X_A)^2\right]$$

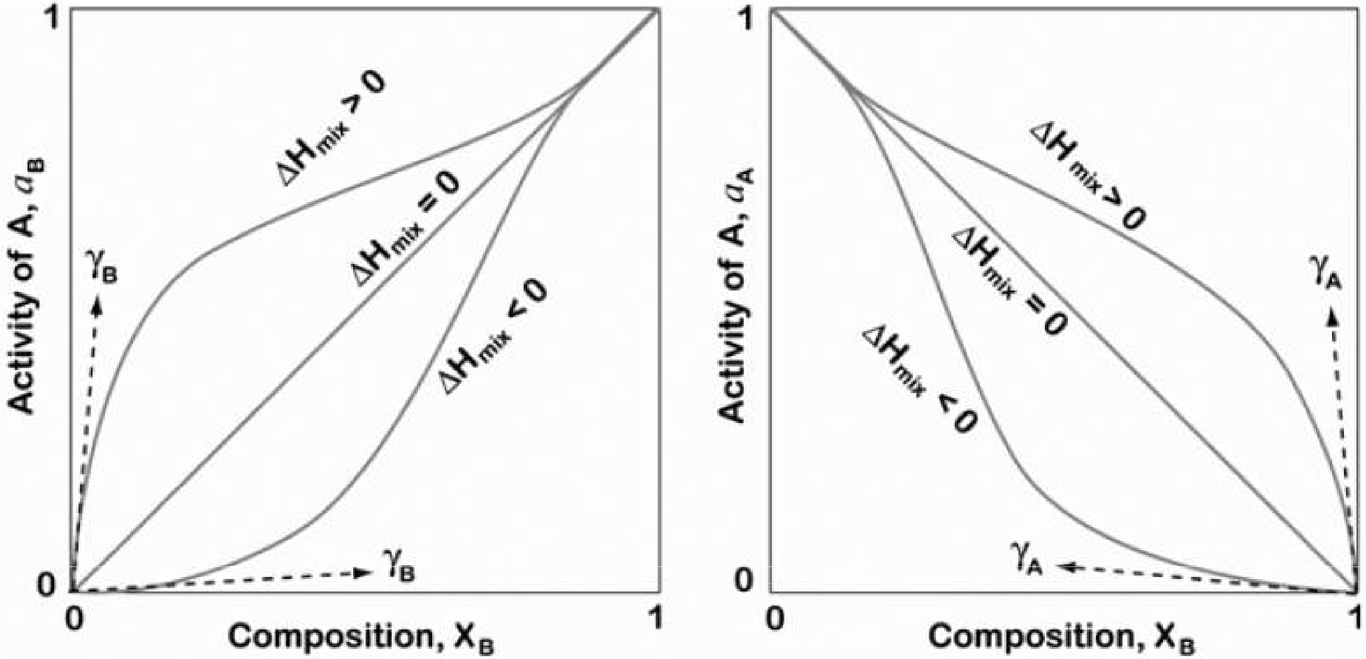
$$\ln\left(\frac{a_B}{X_B}\right) = \frac{\Omega}{RT}(1-X_B)^2$$

$$a_B = X_B \exp\left[\frac{\Omega}{RT}(1-X_B)^2\right] = \gamma_B X_B$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1-X_B)^2\right]$$

- γ_i are the activity coefficient of element i.
- In an ideal solution, $\Omega = 0$, and $A_i = X_i$.
- In a non ideal solution, activity coefficient indicates the deviation from the ideal line.

Concept of the chemical potential and the activity of elements



$$\gamma_A = \exp\left[\frac{\Omega}{RT}(1 - X_A)^2\right]$$

$$\gamma_B = \exp\left[\frac{\Omega}{RT}(1 - X_B)^2\right]$$

In the case of positive enthalpy of mixing, activity deviates positively and in the case of negative enthalpy of mixing activity deviates negatively from the ideal mixing line.

$$X_A \to 0, \gamma_A \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_B \to 0, \gamma_B \to \exp\left(\frac{\Omega}{RT}\right)$$

$$X_A \to 1, \gamma_A \to 1$$

$$X_B \to 1, \gamma_B \to 1$$

Henry’s law: activity of elements is more or less the constant in a very dilute solution.

Rault’s law: activity is equal to the mole fraction near the mole fraction of 1.

Equilibrium conditions between different phases

- ☐ As explained previously, while discussing the phase diagrams, we have shown that at certain conditions two phases, such as solid and liquid or two solid phases α and β can stay together.
- ☐ This can be explained with respect to chemical potential of elements. For the sake of explanation let us consider that there are two phases α and β which are staying together.
- ☐ If you remove dn_B of element B from the β phase and add them to α phase, then the change in free energy of the α and β phases will be

$$dG^{\alpha} = \mu_B^{\alpha} dn_B$$

$$dG^{\beta} = -\mu_B^{\beta} dn_B$$

- ☐ So the total free energy change of the system will be

$$dG = \mu_B^{\alpha} dn_B - \mu_B^{\beta} dn_B = (\mu_B^{\alpha} - \mu_B^{\beta}) dn_B$$

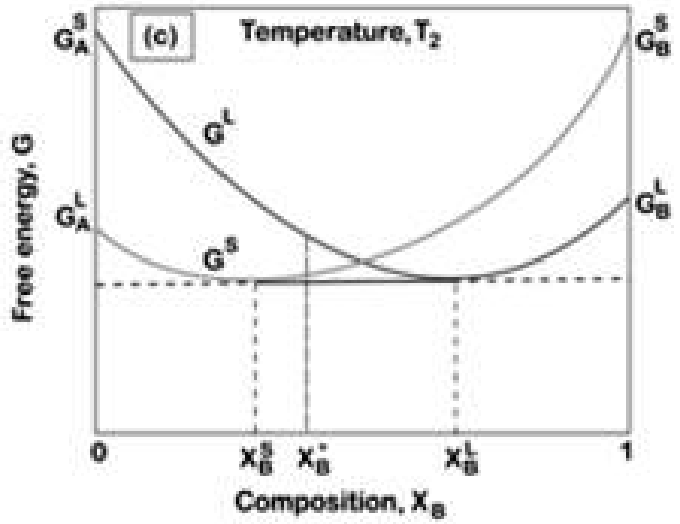
- ☐ However we know that in equilibrium condition dG = 0. That means the chemical potential of element B in both the phases should be the same.
- ☐ That further means that even if a small amount of material is transferred from the β to the α phase, there will be no difference in equilibrium as long as the chemical potential of elements are the same in both the phases.

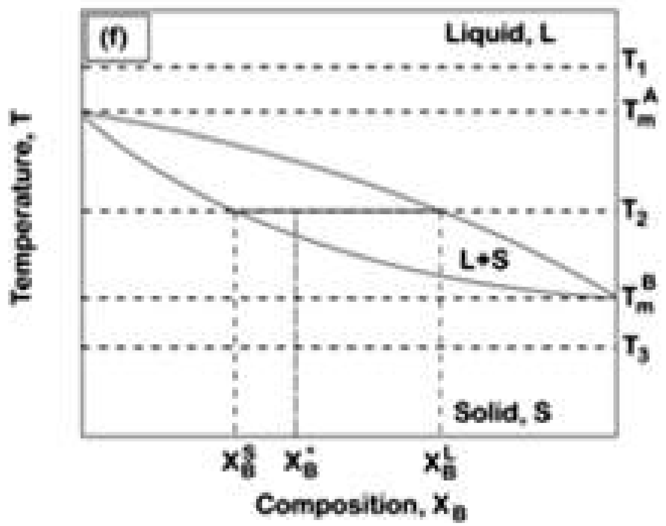
Equilibrium conditions between different phases

- Previously, we have shown that the system will not be in equilibrium that is it will go through irreversible transformation if *dG < 0. That means*

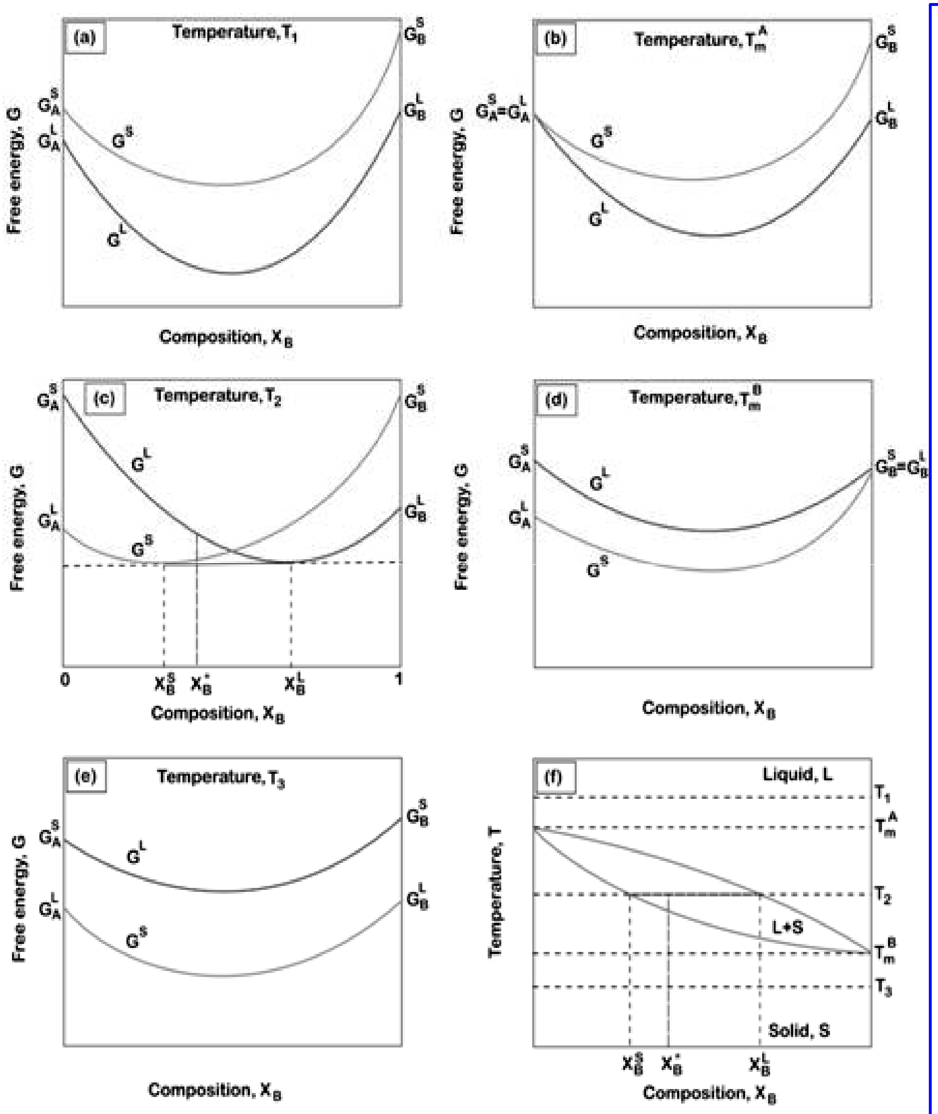
$$(\mu_B^{\alpha} - \mu_B^{\beta})dn_B < 0$$

- This indicates that the chemical potential of B in the α phase is less then the chemical potential of the same element in the β phase.
- So to reach to the equilibrium system will transfer B from the β phase to the α phase.
- Now we understand, why both solid and liquid phases can stay together in certain composition range. It can be understood from the common tangent between X_B^S and X_B^L chemical potential of any of the elements are the same in both the phases .





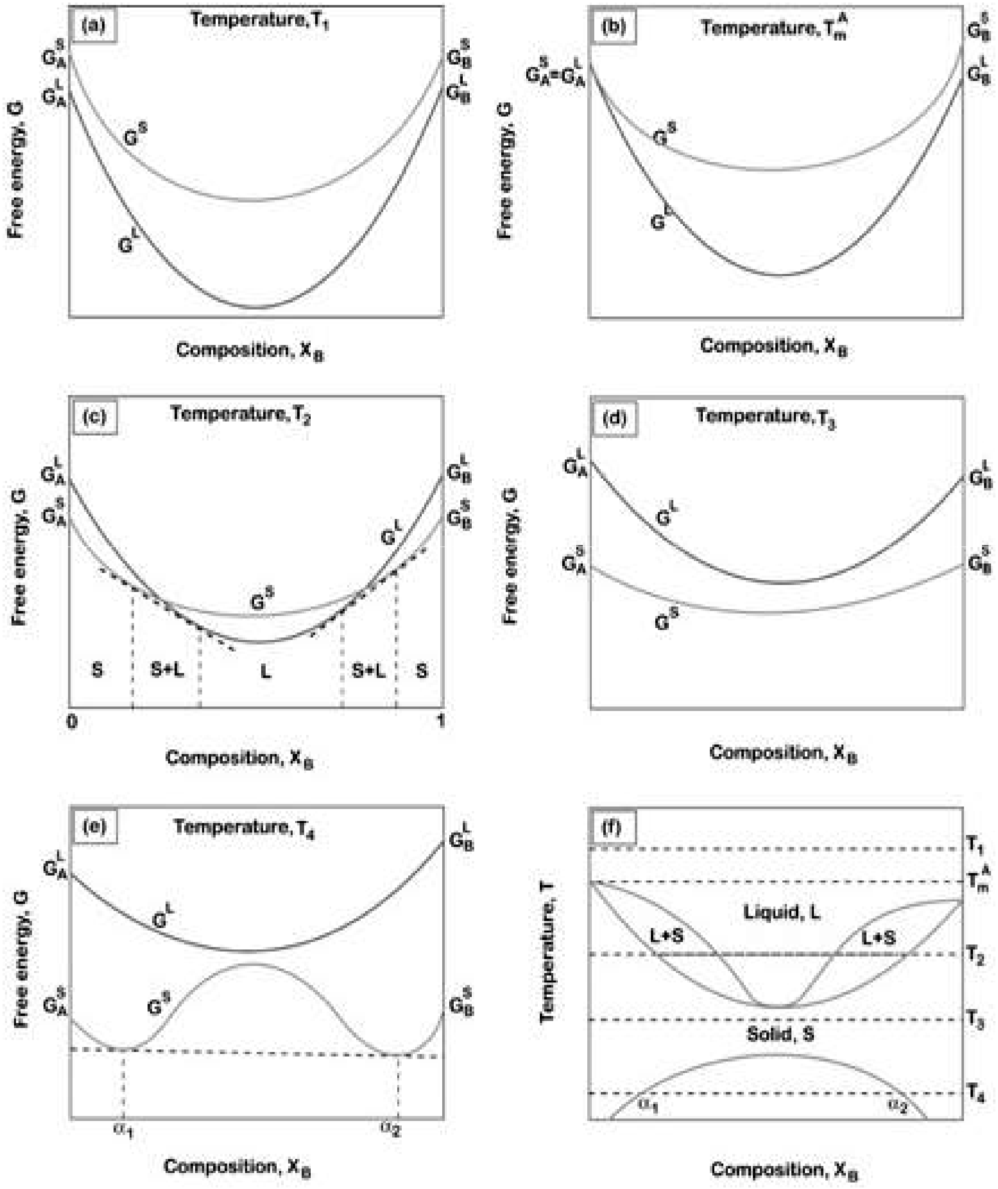
Free energy Vs Composition Phase Diagrams



Both the liquid and solid phases can stay together because overall free energy will be less than the free energy when considered separately.

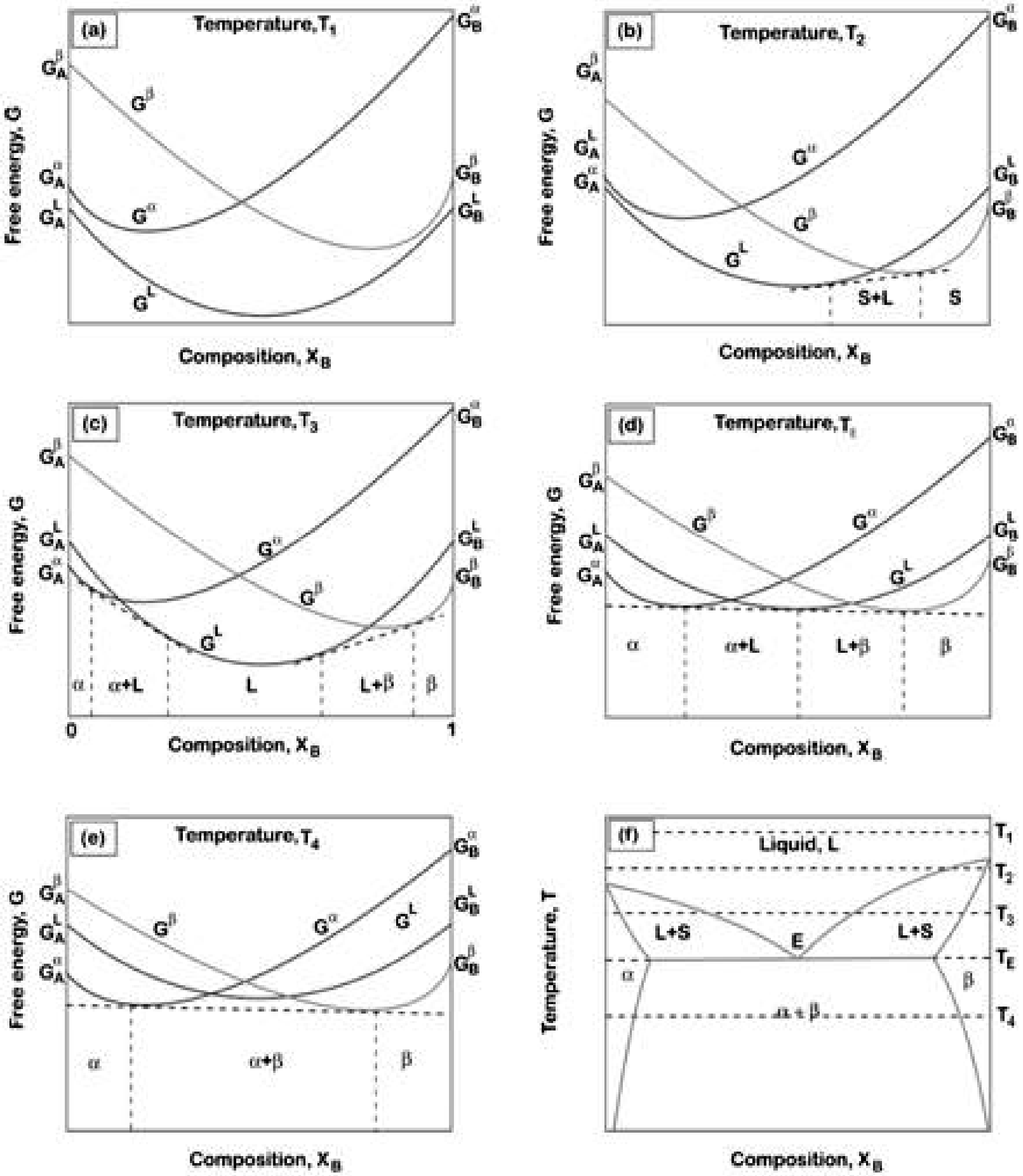
- With decreasing temperature, free energy for the solid, G_S and liquid phase G_L will change differently with different rates of change of G_A and G_B.
- At higher temperature, $G_L < G_S$ (fig a), so that the liquid phase is stable. At lower temperature $G_S < G_L$ (fig e) so that the solid phase is stable.
- In between, G_S and G_L intersects to find the situation as explained in Fig. c.
- Common tangent drawn gives the composition range where both solid and liquid phases can be found together.
- That means, if average composition is X_B* as shown in the phase diagram, it will have the solid phase with composition of X_B^S and the liquid phase with composition of X_B^L Phase fractions can be found with the help of lever rule.

Free energy Vs Composition Phase Diagrams



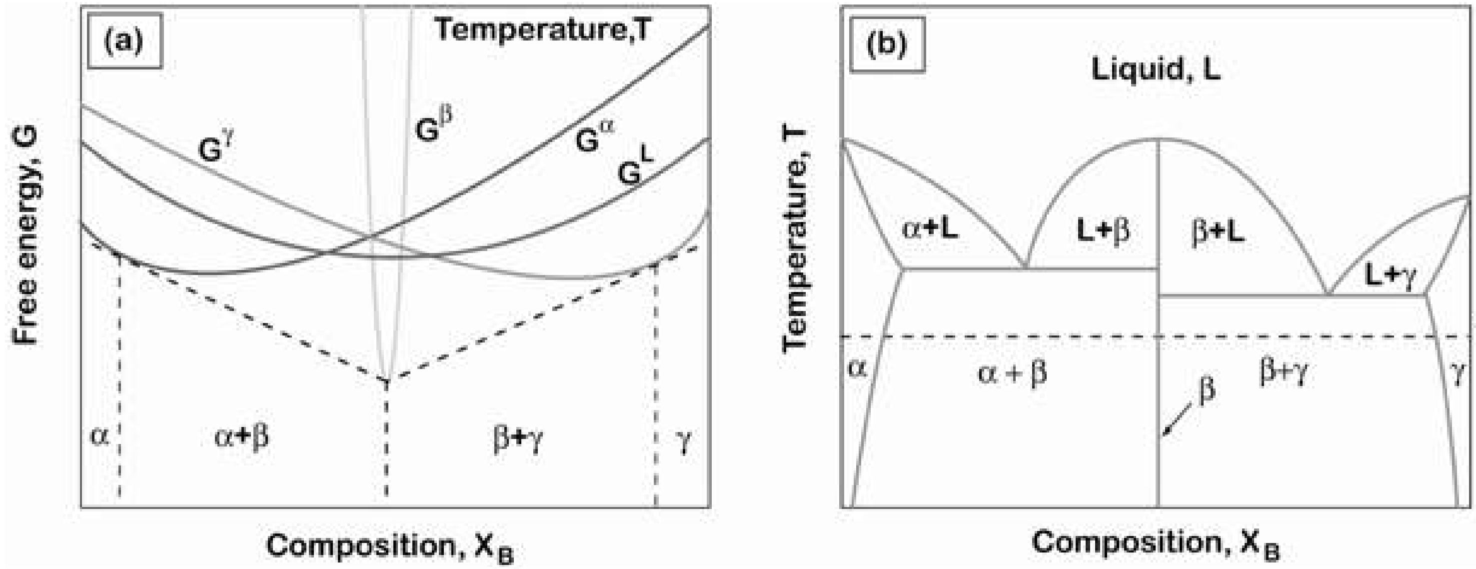
- This kind of phase diagram is found when the system has positive enthalpy of mixing, especially for the solid phase.
- Because of the shape of the G_S at low temperature as as shown in Fig. e, it is possible to draw a common tangent, which indicates that the solid phase with the average composition between α_1 and α_2 will have a phase separation . This corresponds to the miscibility gap in the phase diagram.
- It may also come to the situation, as it is shown in Fig. c, G_L and G_S intersects twice. In that case these will be two separate regions where both the solid and liquid phases coexist.

Free energy Vs Composition Phase Diagrams

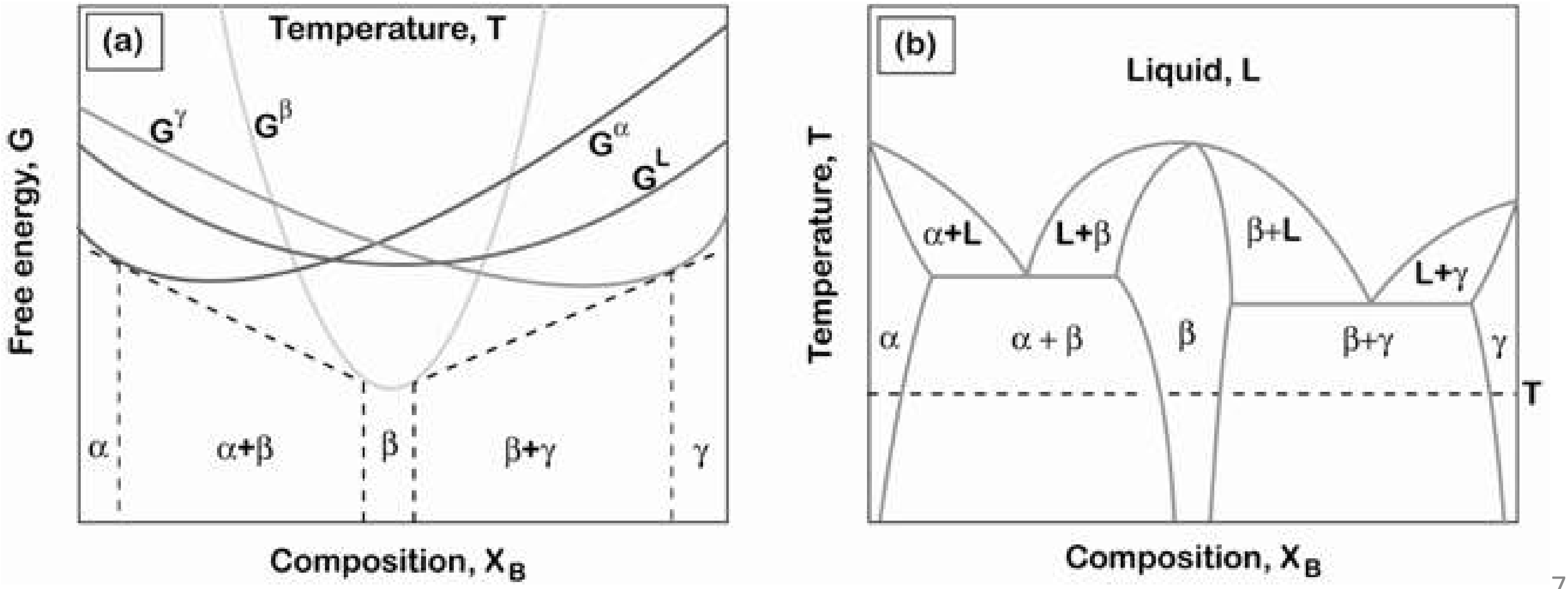


- In this system, there are two solid state phases and one liquid phase. So three free energy curves should be considered.
- At certain temperature, T_E, one common tangent can be drawn, which will touch all the free energy curves.
- This indicates that all the three phases at a particular composition E, as shown in Fig. d and f can coexist. This is called eutectic point.

Free energy Vs Composition Phase Diagrams



β phase is an intermetallic compound that is an ordered phase with very narrow homogeneity range.



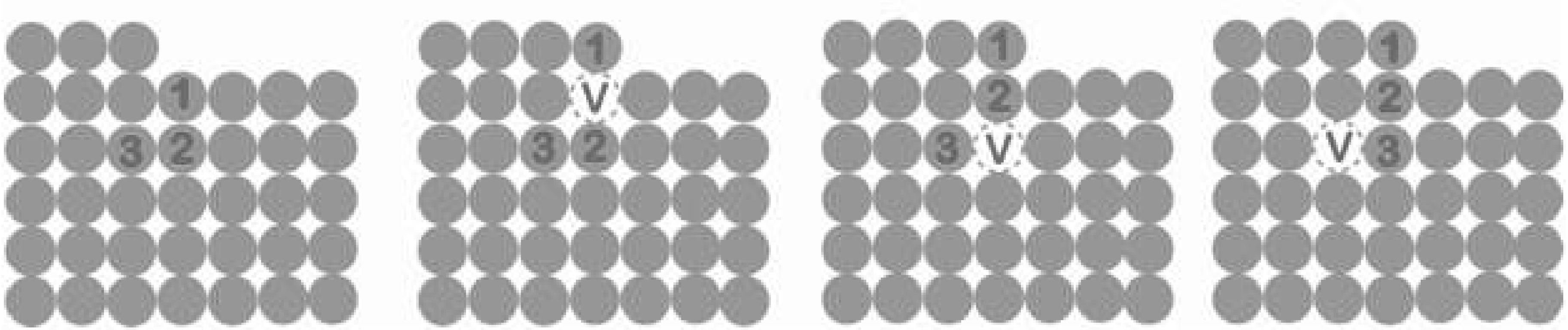
Sometimes β phase can be found with wider homogeneity range.

Equilibrium vacancy concentration

- Diffusion of elements is possible because of the presence of defects. For example, substitutional diffusion occurs because of exchange of an atom with vacancies. Further, impurities are present at the interstitial positions, which could diffuse to any neighboring vacant interstitial sites. This is called interstitial diffusion.
- Certain concentration of these impurities are always present in the pure elements in equilibrium condition, which will be discussed here.
- Further in the intermetallic compounds (ordered phases), antisites defects also could be present along with vacancies. Moreover, different sublattices could have different concentration of defects, which makes the diffusion process complicated.
- Let us not get confused with the structural defects present in pure elements.
- To understand simple atomic mechanism of diffusion at this point, we shall calculate the equilibrium concentration of point defects that is the equilibrium concentration of vacancies and interstitial atoms in pure elements
- Interesting point to be mentioned here that unlike dislocations, grain boundary or interfaces, point defects are equilibrium defects. It means that the system will try to have certain concentration of defects to decrease the free energy.

Let us first calculate the equilibrium concentration of vacancies, because of which lattice substitutional diffusion is possible

Equilibrium vacancy concentration in a pure element



- Pure elements A and vacancies (V) can be considered as a mixture of two entities and follow the similar treatment as we did to calculate the total free energy after mixing of elements A and B.
- It can be easily visualized how the movement of atoms can create vacancies in the material in few steps.
- Equilibrium number of vacancies is so small that we can neglect the interaction between them.
- This means that we are neglecting V-V interactions. This also means that we are, at this point, neglecting the presence of divacancies, which are actually present in the material.

Equilibrium vacancy concentration in a pure element

- ☐ If we consider that the number of vacancies is very small then the increase of enthalpy because of formation of vacancies can be written as

$$\Delta H \approx X_V \Delta H_V$$

ΔX_V ***is the mole fraction of vacancy and***

ΔH_V ***is the increase in enthalpy because of one mole of vacancies***

- ☐ There will be the change in the pattern of vibration of atoms next to vacancies because of extra free space. The increase in (thermal) entropy because of the extra freedom of vibration can be written as

$$\Delta S_{thermal} = X_V \Delta S_V$$

ΔS_V ***is the increase in entropy for one mole of vacancies***

- ☐ In both the cases, we are actually assuming linear relationship because of very small concentration of vacancies.
- ☐ NOTE: In the case of entropy change of A-B mixture, we did not consider the thermal entropy change, since we are considering the change at a particular temperature. However, in this case, although we are considering again at a particular temperature, we still need to consider the contribution because of the change in vibration pattern of atoms next to vacancies.

Equilibrium vacancy concentration in a pure element

- ☐ Further there will be change in configurational entropy considering the mixing of A and V and can be expressed as (Note that we are considering $X_A + X_V = 1$

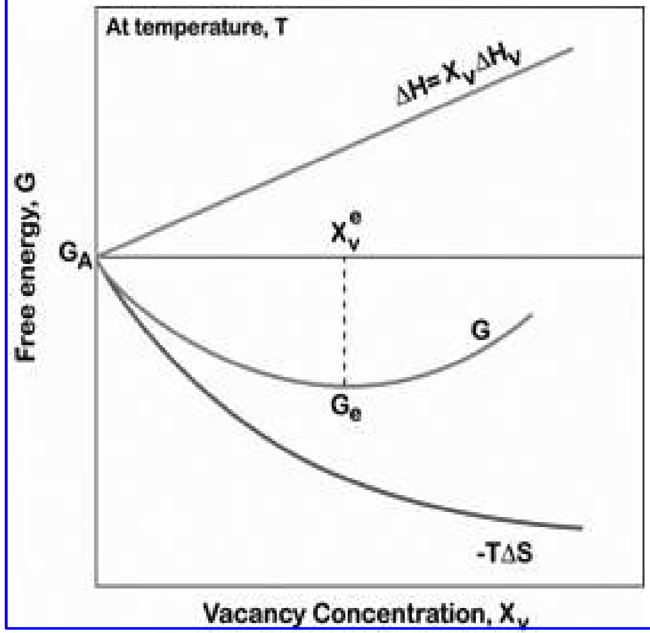
$$\Delta S_{config} = -R[X_V \ln X_V + X_A \ln X_A] = -R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]$$

- ☐ Total entropy of mixing $\Delta S_{mix} = \Delta S_V X_V - R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]$

(Total contribution from thermal and configurational entropy)

- ☐ Total free energy in the presence of vacancies

$$\begin{aligned} G &= G_A + \Delta G \\ &= G_A + \Delta H - T\Delta S \\ &= G_A + X_V \Delta H_V - T\{\Delta S_V - R[X_V \ln X_V + (1-X_V)\ln(1-X_V)]\} \end{aligned}$$



Note here that G of element A when vacancies are present decreases. So always there will be vacancies present in materials. Further G decreases to a minimum value and then increases with the further increase in vacancy concentration. So, in equilibrium condition, certain concentration of vacancies will be present, which corresponds to G_e.

Equilibrium vacancy concentration in a pure element

- Since the slope is zero at the minima, we can find the equilibrium vacancy concentration from

$$\frac{dG}{dX_V}=0$$

$$\Delta H_V - T\Delta S_V + RT\left[\ln X_V + X_V.\frac{1}{X_V} - \ln(1-X_V) - (1-X).\frac{1}{(1-X_V)}\right]=0$$

- Since the number of vacancies that can be present in the system is very small

$$1-X_V \approx 1$$

$$\Delta H_V - T\Delta S_V + RT\ln X_V = 0$$

- The relation for equilibrium concentration of vacancies can be written as

$$X_V^e = X_V = \exp\left(-\frac{\Delta H_V - T\Delta S_V}{RT}\right)=\exp\left(-\frac{\Delta G_V}{RT}\right)$$

- Although there is increase in configurational entropy because of the presence of vacancies, it is not included in the activation energy barrier, $\Delta G_{V.}$
- Although there is activation energy barrier present because of formation, vacancies will still be present because of overall decrease in free energy of the materials.

Equilibrium vacancy concentration in a pure element

- From the equation in previous slide, we can also write

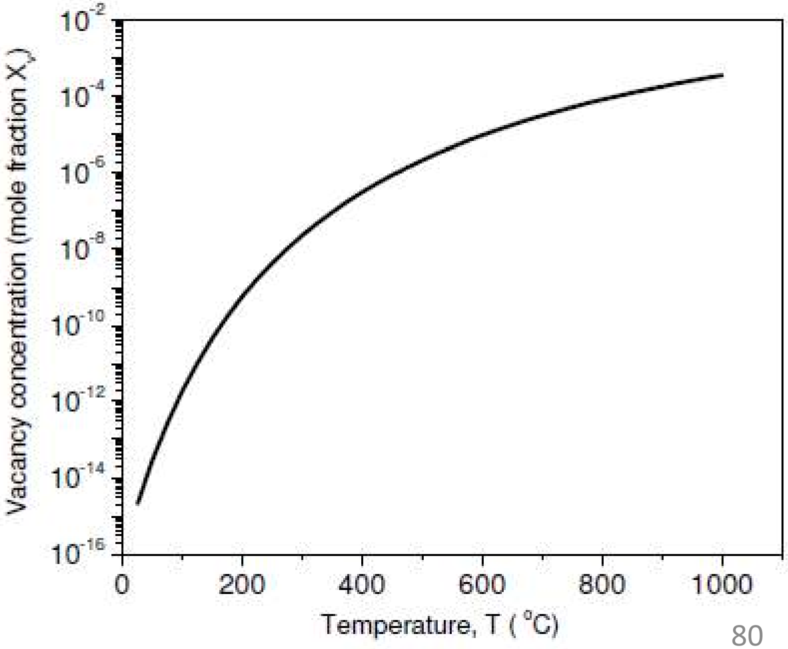
$$X_V^e = X_V^0 \exp\left(-\frac{\Delta H_V}{RT}\right)$$

- ΔH_V is the activation enthalpy for the formation of vacancies and

$$X_V^0 = \exp\left(\frac{\Delta S_V}{R}\right)$$ Is the pre-exponential factor.

- The change in concentration of vacancies in pure Cu is shown in below graph, considering activation energy for vacancy formation to be 83.7 kJ/mole.

The concentration of vacancies in mole fraction at 1000°C is 3.68×10^{-4}. *That means in a cube of 14 atoms in each direction, only one vacancy will be present in Cu at this temperature!!!*



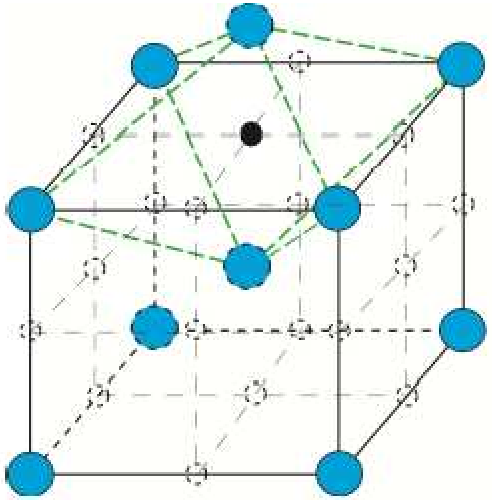
Equilibrium concentration of interstitial atoms

- ☐ In many metals, especially in transition metals, interstitial atoms such as carbon, nitrogen, oxygen, hydrogen can be present up to a certain extent depending on the metal.
- ☐ There are mainly two types of interstitial voids present in the structure, where these atoms can sit: tetrahedral (surrounded by four solvent atoms) and octahedral (surrounded by six solvent atoms).
- ☐ However, since impurities prefer to occupy octahedral interstices, we shall mainly consider this type of voids only.

LET US FIRST CONSIDER A BCC CRYSTAL

- ☐ In general the size of the interstitial atoms is much larger than the interstitial void and lattice surrounding the interstitial will be strained. That means enthalpy of the system will be increased.
- ☐ Consider the increase in enthalpy because of addition of one mole of interstitial atoms is , ΔH_I.
- ☐ The enthalpy increment of the system because of addition of X_I is expressed by $\Delta H = X_I \Delta H_I$

$$where X_I = \frac{n_I}{N_o} \quad Number\ of\ interstitial\ atom\ is\ n_I$$



Equilibrium concentration of interstitial atoms

- Further, there will be two different types of contribution on entropy
- Vibration of atoms A, next to interstitial atoms will change from normal mode of vibration and will be more random and irregular because of distortion of the lattice

$$\Delta S_{thermal} = X_I \Delta S_I$$

- ΔS_I is the change of the entropy of one mole of atoms because of change in vibration pattern
- From the crystal structure, we can say that for 2 solvent atoms there are 6 sites for interstitial atoms. So if we consider that there are N_0 numbers of A atoms then there will be $3N_0$ numbers of sites available for interstitial atoms.
- In other sense, we can say that n_I atoms will randomly occupy in $3N_0$ sites available. So the configurational entropy can be written as

$$\Delta S_{config} = k \ln w = k \ln \frac{3N_0!}{n_I!(3N_0 - n_I)} \quad \textit{Following Stirling's approximation} \quad \ln N! = N \ln N - N$$

$$\Delta S_{config} = k[3N_0 \ln 3N_0 - n_I \ln n_I - (3N_0 - n_I)\ln(3N_0 - n_I)]$$

$$\Delta S_{config} = R\left[3 \ln 3N_0 - \frac{n_I}{N_0}\ln n_I - \frac{3N_0 - n_I}{N_0}\ln(3N_0 - n_I)\right]$$

Equilibrium concentration of interstitial atoms

$$\Delta S_{config} = R\left[3\ln\frac{3N_0}{3N_0 - n_I} - \frac{n_I}{N_0}\ln\frac{n_I}{3N_0 - n_I}\right]$$

$$\Delta S_{Config} = R\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

- ☐ So the total entropy change

$$\Delta S = X_I \Delta S_I + R\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

- ☐ Free energy in presence of interstitial impurities

$$G = G_A + \Delta G = G_A + \Delta H - T\Delta S_I$$

$$G = G_A + X_I\Delta H_I - TX_I\Delta S_I - RT\left[3\ln\frac{3}{3 - X_I} - X_I\ln\frac{X_I}{3 - X_I}\right]$$

Equilibrium concentration of interstitial atoms

- To find the equilibrium concentration, we need to take

$$\frac{dG}{dX_I}=0$$

$$\Delta H_I - T\Delta S_I - RT\left[-\frac{3}{3-X_I}-\frac{X_I}{X_I}-\ln X_I+\ln(3-X_I)-\frac{X_I}{3-X_I}\right]=0$$

$$\Delta H_I - T\Delta S_I + RT\ln\frac{X_I}{3-X_I}=0 \qquad \textbf{since} \quad X_I \approx 0$$

$$X_I = 3\exp\left(-\frac{\Delta H_I - T\Delta S_I}{RT}\right)=3\exp\left(-\frac{\Delta G_I}{RT}\right)$$

- G_I is the activation barrier.

Equilibrium concentration of interstitial atoms

LET US NOW CONSIDER A FCC CRYSTAL

- ☐ If we consider FCC crystal, then the number of sites available for interstitial atoms are 4. Further in a FCC unit cell, total 4 solvent atoms are accommodated. So we can say that for N_0 solvent atoms there will be N_0 sites available for interstitial atoms. Like previous example, we consider n_I interstitial atoms which will occupy randomly.
- ☐ Then following similar procedure, we can show the equilibrium concentration of interstitial atoms present in a metal with FCC crystal as

$$X_I = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

- ☐ So in general, we can write that the equilibrium concentration of interstitial impurities present is

$$X_I = B\exp\left(-\frac{\Delta G_I}{RT}\right) \quad B \text{ depends on the crystal structure}$$

$$X_I = X_I^0 \exp\left(-\frac{\Delta H_I}{RT}\right)$$

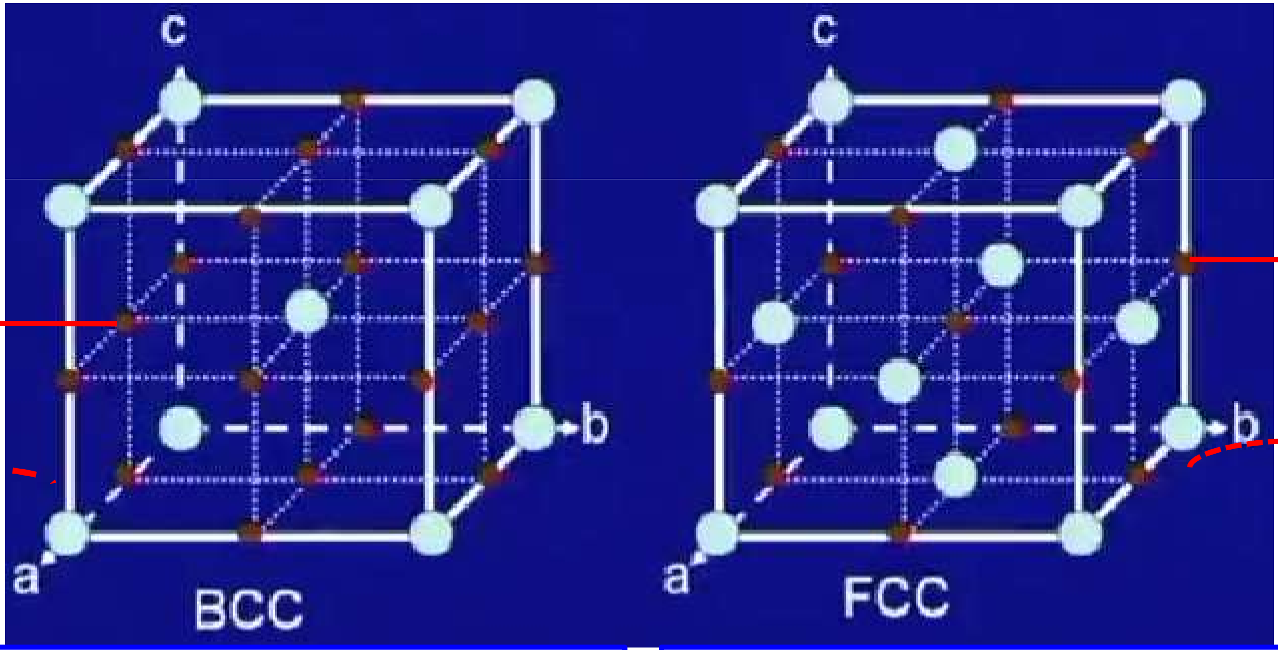
ΔH_I *is the activation enthalpy for interstitial impurities*

$$X_I^0 = B\exp\left(\frac{\Delta S}{R}\right) \text{ is the pre-exponential factor}$$

Carbon Solubility in Iron

Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice ?



Octahedral sites

Octahedral sites

6 faces sharing with two sides (6/2)=3
12 edges sharing with four sides (12/4)=3
Total sites is (3+3), 6 per unit cell
Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
12 edges sharing with four sides (12/4)=3
Total sites is (1+3), 4 per unit cell
Every one Fe atom we have 1 interstitial site

Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- FIRST LET US CONSIDER FCC STRUCTURE (γ-Fe)
- Packing factor of FCC lattice 0.74
- This indicates the presence of voids. Let us discuss it more elaborately.
- In a FCC crystal there are mainly two types of voids:
- Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.
- Octahedral: CN is 6. That means the void is surrounded by 6 atoms.
- There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- However, impurities prefer to occupy octahedral voids.
- Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- Distortion will be less if it occupies the octahedral voids.
- Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.

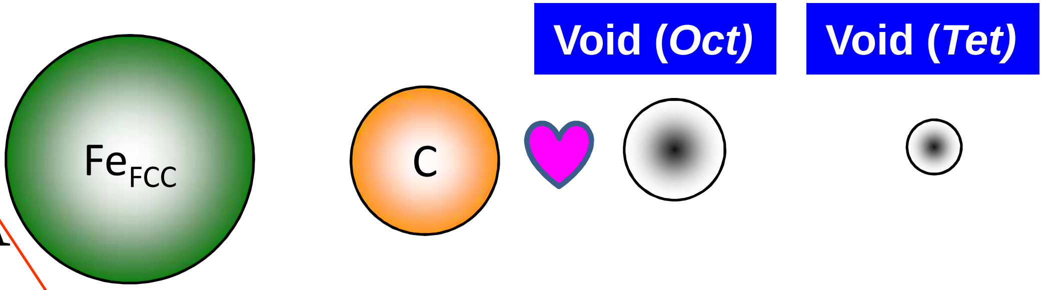
Carbon Solubility in Iron

FCC

Size of Fe atom CCP crystal $r_{FCC}^{Fe} = 1.292\ \mathring{A}$

Size of the OV $x_{FCC}^{Fe}(oct) = 0.534\ \mathring{A}$

Size of Carbon atom $r^{C} = 0.77\ \mathring{A}$



Relative sizes of voids w.r.t atoms

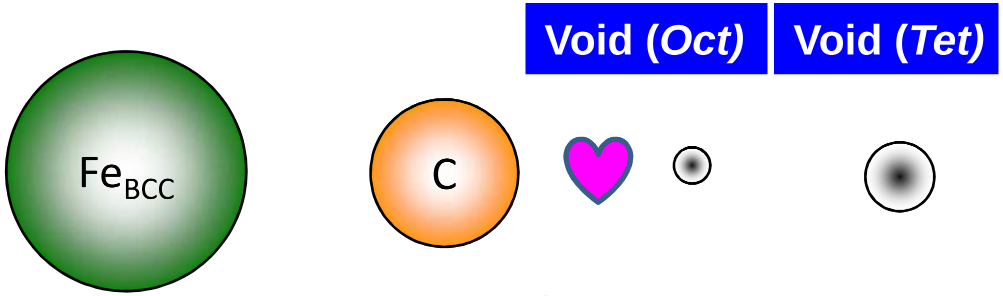
Note the difference in size of the atoms

BCC

Size of Fe atom BCC crystal $r_{BCC}^{Fe} = 1.258\ \mathring{A}$

Size of the TV $x_{BCC}^{Fe}(d.tet) = 0.364\ \mathring{A}$

Size of the OV $x_{BCC}^{Fe}(d.oct) = 0.195\ \mathring{A}$



Relative sizes of voids w.r.t atoms

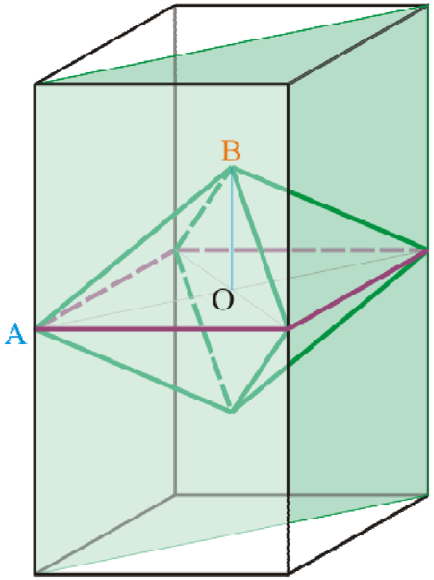
Remember

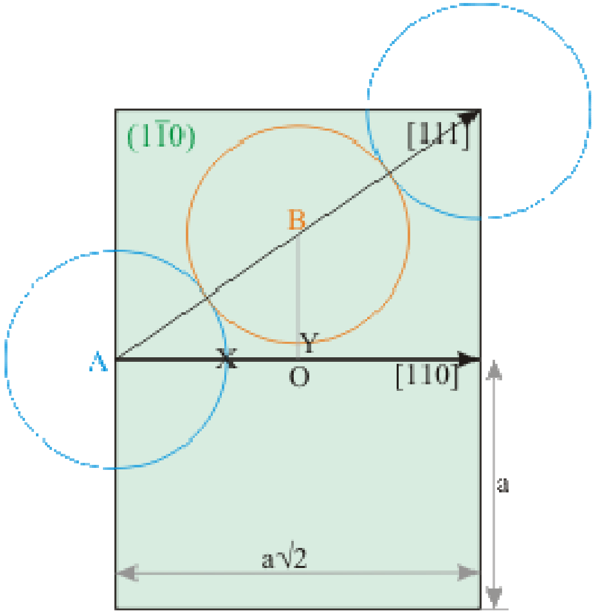
- ❑ **FCC** Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414
- ❑ **BCC** Size of the largest atom which can fit into the *d.tetrahedral* is 0.29 and *d.octahedral* void is 0.154

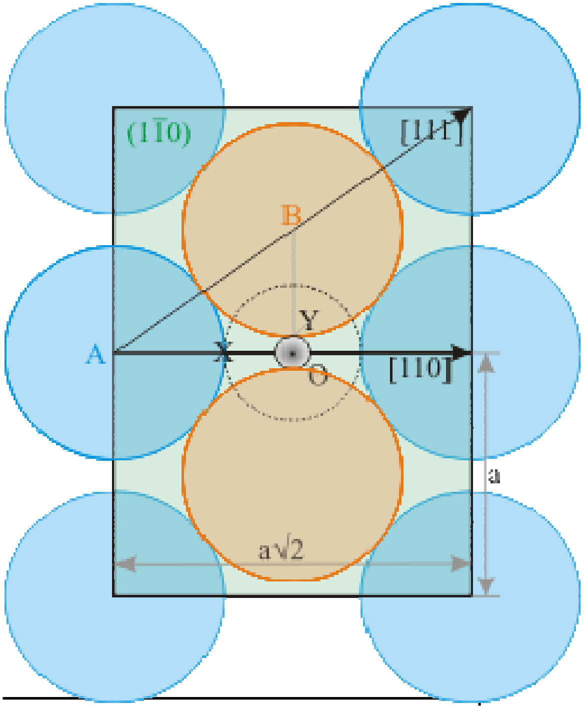
Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- ❑ NOW LET US CONSIDER THE BCC UNIT CELL (α - Fe)
- ❑ Packing factor of BCC lattice 0.68. So total void in a BCC unit cell is higher than FCC cell.
- ❑ However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present. This number is higher than the number of voids present in a FCC unit cell.
- ❑ Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- ❑ The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- ❑ The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612. So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- ❑ However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger that the C atom size. That means it needs to distort only other two atoms.
- ❑ On the other hand if C sits in the tetrahedral void it has to distort all four atoms. So in α – Fe with BCC unit cell C occupies the octahedral voids
- ❑ Now the octahedral void size in g-Fe (FCC) is higher than a-Fe (BCC). So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- ❑ This is the reason that we find much lower solubility limit of C in a-Fe.

Why carbon preferentially sits in the apparently smaller octahedral void in BCC ?







Ignoring the atom sitting at B and assuming the interstitial atom touches the atom at A

$$OA = r + x_A = \frac{\sqrt{2}a}{2}$$

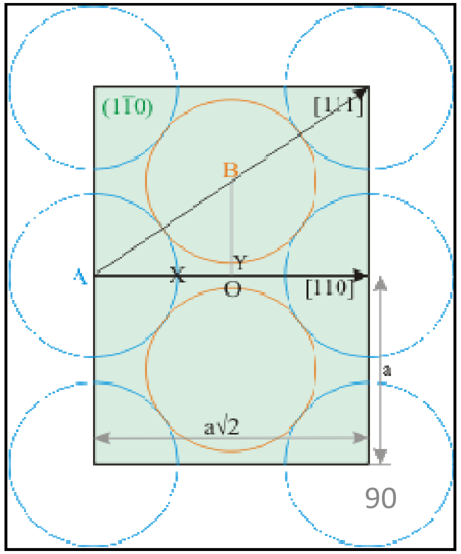
$$r_{BCC}^{Fe} = 1.258\ \overset{\circ}{A}$$

$$r + x_A = \frac{2\sqrt{6}\,r}{3}$$

$$BCC : \sqrt{3}a = 4r$$

$$\frac{x_A}{r} = \left(\frac{2\sqrt{6}}{3} - 1\right) = 0.6329$$

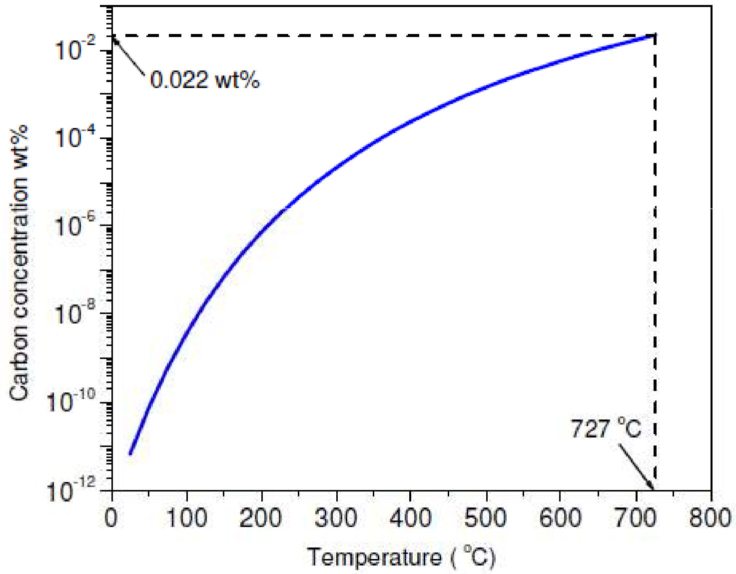
$$OX = x_A = 0.796\ \overset{\circ}{A} \qquad OY = x_B = 0.195\ \overset{\circ}{A} \qquad x_{BCC}^{Fe}(d.tet) = 0.364\ \overset{\circ}{A}$$

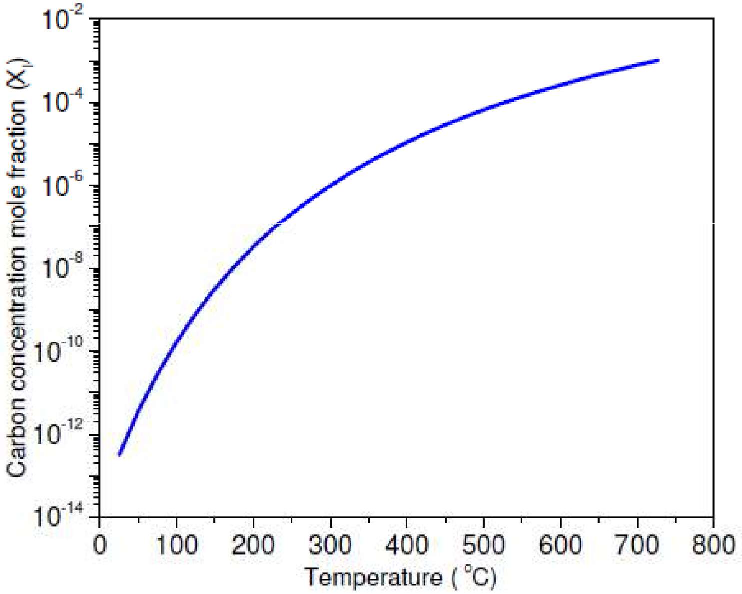


Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- ❑ Let us consider the C concentration in α-Fe (BCC)

$$Wt\% = 240\exp\left(-\frac{77300\,{}^{J}\!/\!{}_{mol}}{RT}\right) \quad \textit{In terms of mole fraction} \quad X_1 = 11.2\exp\left(-\frac{77300\,{}^{J}\!/\!{}_{mol}}{RT}\right)$$



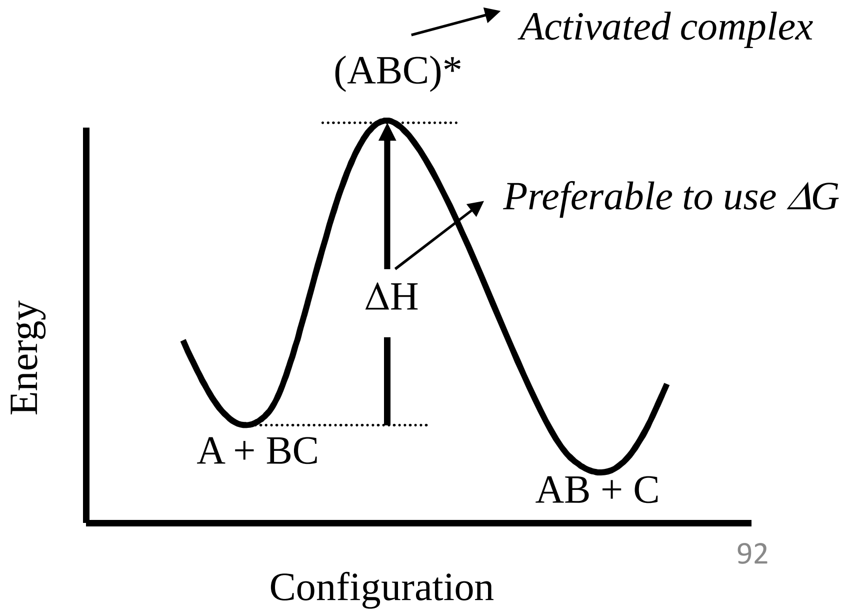


- ❑ At 727°C, carbon concentration in α-Fe is maximum (0.022 wt%), which is equivalent to mole fraction of ~10^{-3}. That means there is one C atom present in a cube of 10 atoms in each direction. That further means that only one carbon atom is present in 3000 octahedral voids

KINETICS

- In earlier we are learned about Equilibrium we had seen that the thermodynamic feasibility of processes is dictated by ‘Thermodynamic Potentials’ (e.g. Gibbs Free Energy, at constant T, P, N_i).
- If (say) the Gibbs Free Energy for a process is negative then the process CAN take place spontaneously.
- However, IF the process WILL actually take place (and if it will take place- how long will it take to occur?) → will be determined by the ‘Kinetics of the process’.
- Deeper the ‘metastable energy well’, higher will be activation energy required to pull the system out of the ‘well’ and take it to the equilibrium state (or some other metastable state).

- To give an example: Fe_3C is a metastable phase. it can decompose 3Fe + C after hundreds of years. *‘Thermodynamics warrants, Kinetics delays’*
- For a given process to occur heat and mass transfer may have to take place and this would take time → hence in ‘kinetics’ we deal with time and rates (1/t)



KINETICS

- A homogenous reaction is one which involves only one phase.
  - E.g. a reaction involving only gaseous phase
- In a heterogeneous reaction more than one phase is present.

Let us consider a homogenous balanced chemical reaction, occurring in a single step:

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

Rate of consumption of a reactant is proportional to the stoichiometric coefficient in a balanced reaction

$$\frac{dn_A}{dt} \propto a \qquad \frac{dn_B}{dt} \propto b \qquad \Rightarrow \qquad \frac{dn_A/dt}{dn_B/dt} = \frac{a}{b}$$

- $n_A \rightarrow$ number of moles of A present at time t
- $J \rightarrow$ Rate of conversion
- $r \rightarrow$ rate of reaction (= J/V)

Rate of Conversion (J) is defined as:

$$J = -\frac{1}{a}\frac{dn_A}{dt} = -\frac{1}{b}\frac{dn_B}{dt} = \frac{1}{c}\frac{dn_C}{dt} = \frac{1}{d}\frac{dn_D}{dt}$$

A, B are being consumed and hence dn/dt for these species is negative and J is positive

J depends on system size and is an extensive quantity, the conversion rate per unit volume (J/V) is the reaction rate is an intensive quantity

$$r = \frac{J}{V} = \frac{1}{V}\left(-\frac{1}{a}\frac{dn_A}{dt}\right)$$

The reaction rate (r) is a function of P, T and the concentration of species

KINETICS

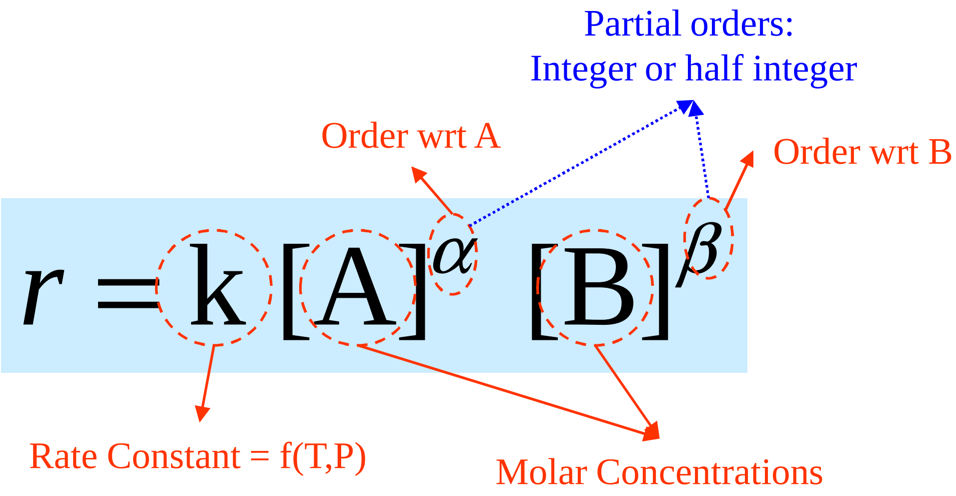
In many of the reactions the volume is constant. If the volume is constant during the reaction:

$$r = \frac{1}{V}\left(-\frac{1}{a}\frac{dn_A}{dt}\right)$$

$$r = -\frac{1}{a}\frac{d(n_A/V)}{dt} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{a}\frac{dc_A}{dt}$$

- $n_A \rightarrow$ number of moles of A present at time t
- J $\rightarrow$ Rate of conversion
- r $\rightarrow$ Rate of reaction (= J/V)
- [A] $\rightarrow$ Molar concentration of A (= c_A)

For many reactions it is seen that the rate can be related to the concentration of species by a reaction of the form:



Partial orders:
Integer or half integer

Order wrt A

Order wrt B

$$r = \mathrm{k}\,[\mathrm{A}]^{\alpha}\;[\mathrm{B}]^{\beta}$$

Rate Constant = f(T,P)

Molar Concentrations

$$r = \mathrm{k}\,[\mathrm{A}]^{\alpha}\;[\mathrm{B}]^{\beta}$$

- *The rate constant k is a function of T and P*
  - *The pressure dependence is usually small*
- *The exponents: α, β are usually integers or half integers: (1, ½, 3/2, …)*
  and are the partial orders (i.e. the reaction has got an order α wrt to A and β wrt B
- *$\alpha + \beta = n$ is the order of the reaction (overall order)*
- *Units of k $\rightarrow$ [concentration]$^{1-n}$ [t]$^{-1}$*

KINETICS

- ❑ Rate constants depend strogely on temperature (usually increasing rapidly with increasing T).
- ❑ For many reactions in solution, a thumb rule can be used that near room temperature ‘k’ doubles or triples every 10°C increase in temperature.
- ❑ In 1889 Arrhenius noted that for many reactions k = f(T) fits an exponential function.

Arrhenius equation

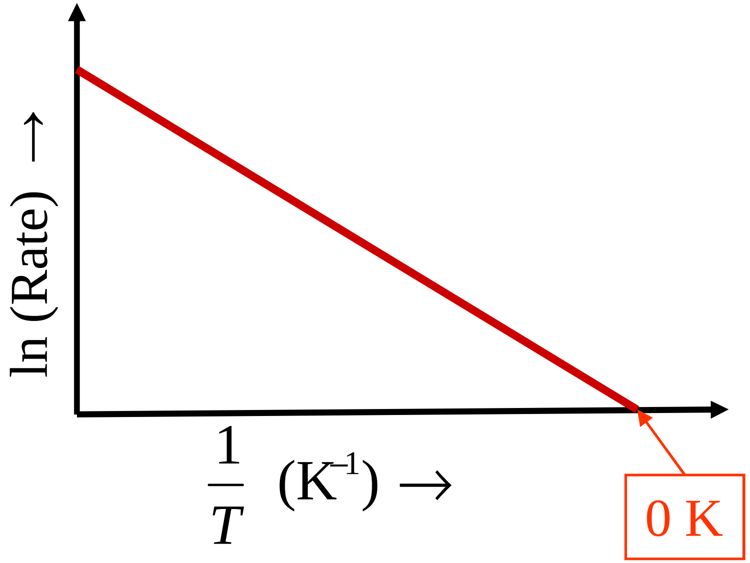
$$k = Ae^{\left[-\frac{Q}{RT}\right]}$$

Activation Energy
Affected by catalyst

T in Kelvin

Frequency factor

- A → pre-exponential factor [units of k]
- Q → activation energy [J/mole]
- R → gas constant



A is a term which includes factors like the frequency of collisions and their orientation.
It varies slightly with temperature, although not much.
It is often taken as constant across small temperature ranges.

DIFFUSION

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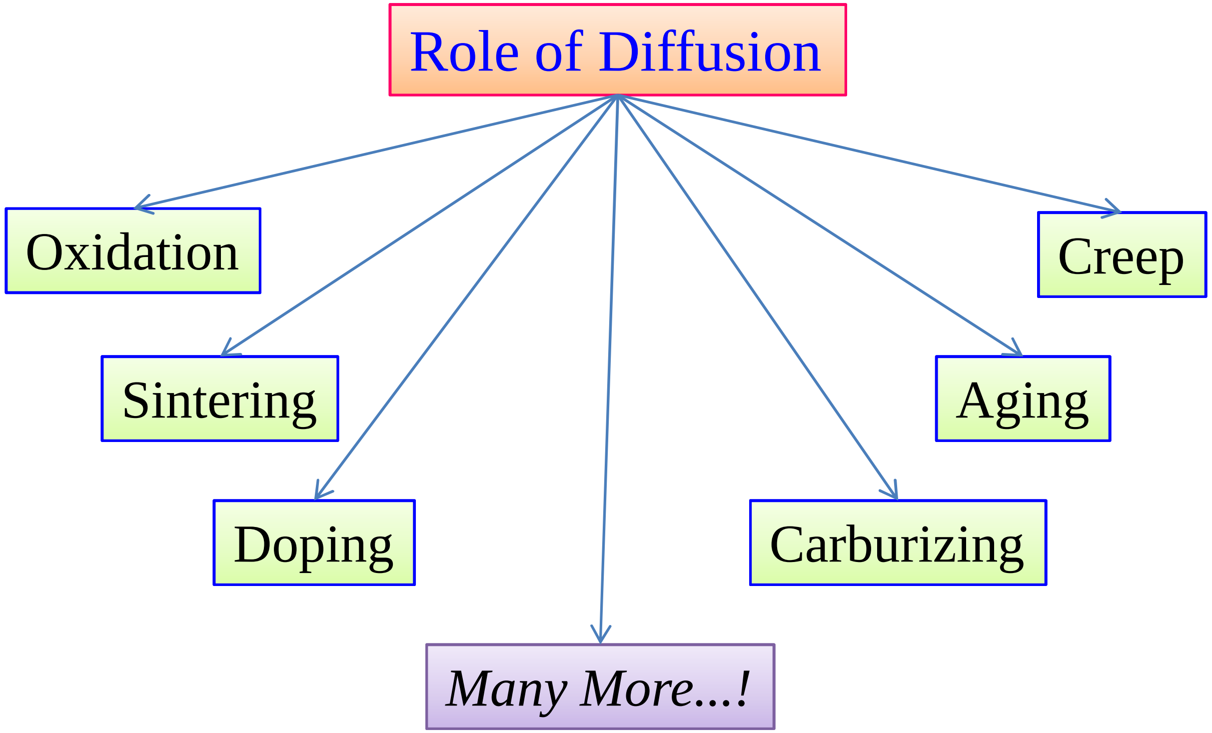
Introduction

- Diffusion is defined as, random movement of atoms/ molecules in solid, liquid and gas. For example dissolution of ink in water and smoke in air
- It can also defined as, Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- To comprehend many materials related phenomenon one must understand diffusion.



Role of Diffusion

Oxidation

Creep

Sintering

Aging

Doping

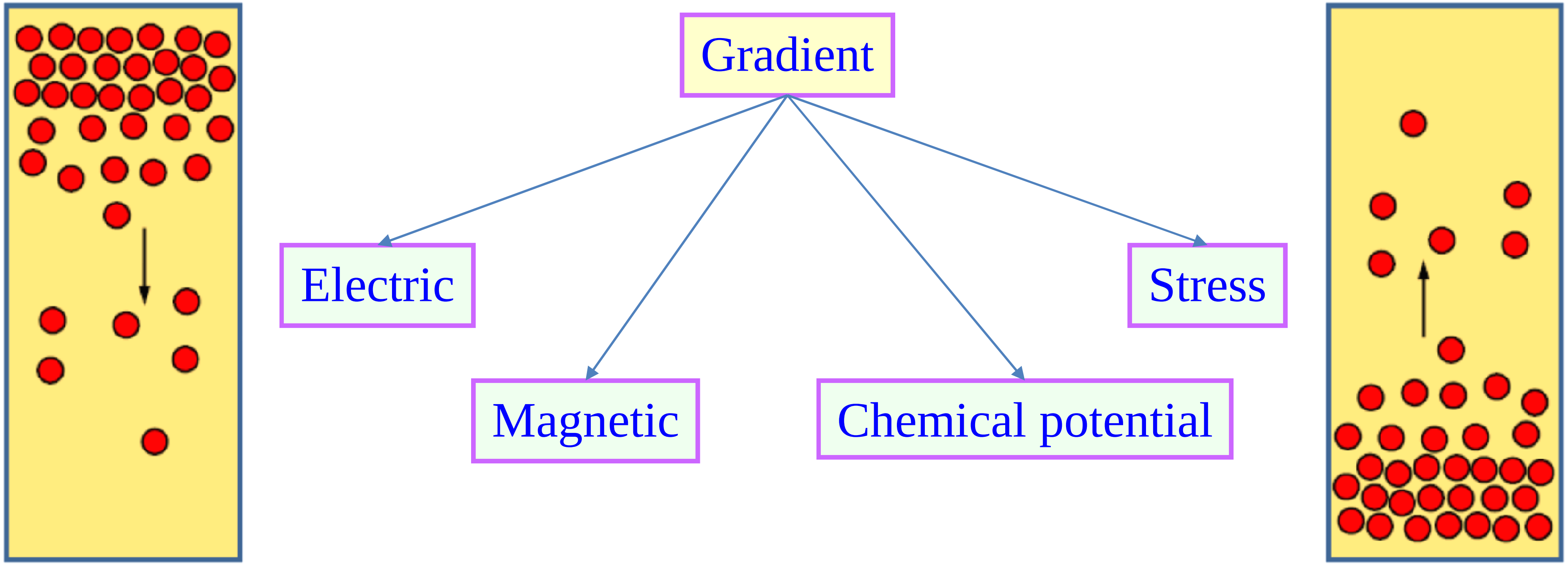
Carburizing

Many More...!

Materials Joining : Diffusion Bonding

Diffusion Phenomena

- Mass flow process by which species change their position relative to their neighbors.
- Driven by *thermal energy* and a *gradient*
- Thermal energy → thermal vibrations → Atomic jumps
- Atoms move from higher to lower concentration region. If this movement is from one element to another e.g. Cu to Ni, then it is termed as *Inter-diffusion.* If the movement is within similar atoms as in pure metals, it is termed *self-diffusion.*



Gradient

Electric

Magnetic

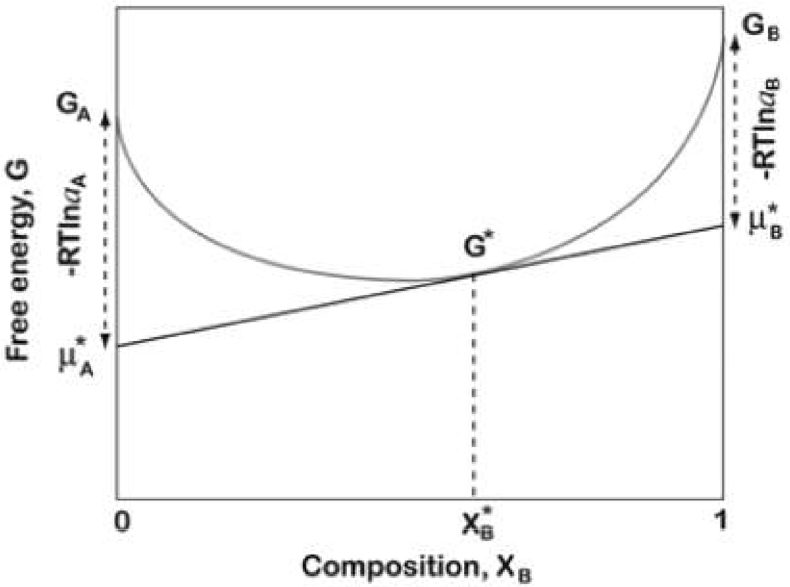
Chemical potential

Stress

Diffusion under thermodynamic driving force

- ❑ As explained before and in the figure below, the chemical potential of elements at any composition can be determined by taking a slope on the Gibb's free energy curve and then by extending it to X_B = 0 (chemical potential of element A, μ_A) and X_B = 1 (chemical potential of element B, μ_B)
- ❑ From the chemical potentials, we can determine the activities, a_A and a_B from the knowledge of free energies of pure elements.

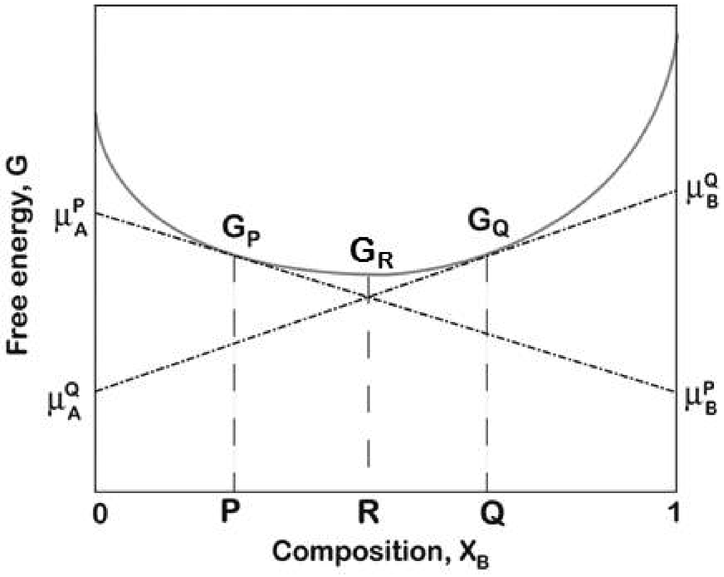
$$-RT\ln a_A = G_A - \mu_A \qquad -RT\ln a_B = G_B - \mu_B$$

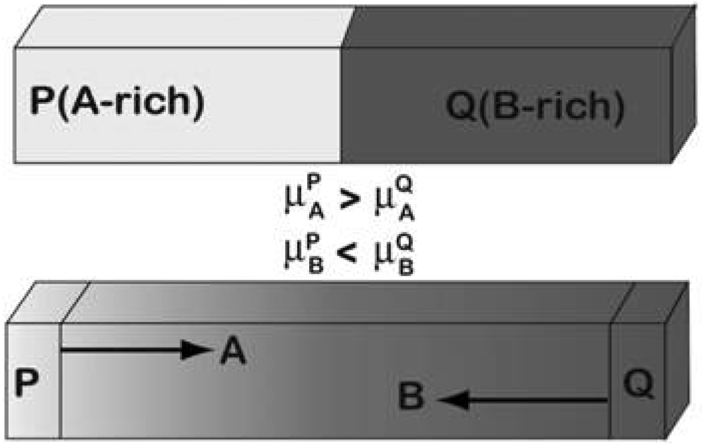


- ❑ So it must be clear that μ_B decreases from G_B at X_B = 1 to a infinitely small value close to X_B = 0.
- ❑ Following, a_B decreases from 1 at X_B = 1 to 0 at X_B = 0. It may vary ideally, that is $a_B = X_B$ or deviate positively/negatively, as explained previously.
- ❑ Similarly, μ_A decreases from G_A at X_B = 0 to a infinitely small value close to X_B = 1. a_B decreases from 1 at X_B = 0 to 0 at X_B = 1
- ❑ So, μ_A and a_A, and μ_B and a_B follow the same trend of increasing or decreasing with X_B.

Diffusion under thermodynamic driving force

- ❑ Now let us consider, two different AB alloys P (A rich) and Q (B rich).
- ❑ If these alloys are kept separately, these alloys will have free energy of G_P and G_Q, respectively.
- ❑ However, if we bond these two blocks, they will not be anymore in equilibrium condition.
- ❑ If the amount of material P and Q are taken such that overall mole fraction is R, then the equilibrium free energy will be G_R.
- ❑ So the system will try to move to its new equilibrium free energy.
- ❑ Now if we don't melt the alloy, it can only move to the equilibrium composition by solid state diffusion.

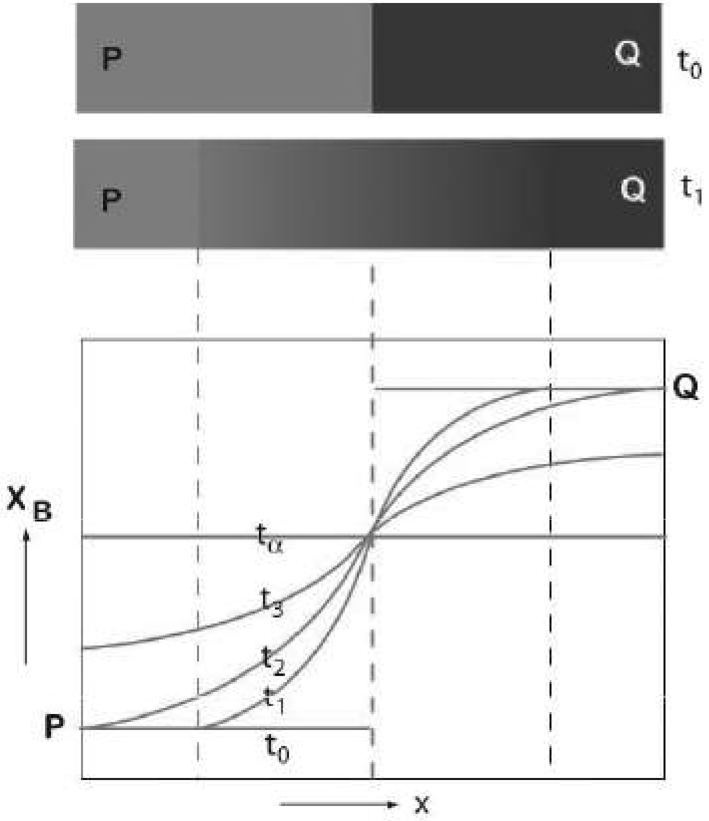




Diffusion under thermodynamic driving force

- If it is held at elevated temperature at which diffusion rate is reasonable, the system will reach to the equilibrium after certain time depending on the diffusion rate.
- It can be seen that at equilibrium alloy R, the chemical potential of A is μ_A^R , which is lower than the chemical potential of the same element, μ_A^P , in alloy P but higher than in alloy Q, that is μ_A^Q .
- On the other hand, μ_B^R is less than μ_B^Q but higher than μ_B^P .
- So to reach the equilibrium, the alloy P should decrease the chemical potential of A and increase the chemical potential of B. On the other hand, the alloy Q should increase the chemical potential of A and decrease the chemical potential of B.
- Since the chemical potential of A decreases from the A rich to the B rich alloy and the chemical potential of B decreases from B rich to A rich alloy, P should decrease the content of A and Q should decrease the content of B.
- In this condition it is possible only by the diffusion of element A out of P and diffusion of element B out of alloy Q, as shown in the figure in the previous slide.
- If we allow the system to go to equilibrium at temperature T, there will be no composition in the blocks P and Q at time zero that is t_0. Then with the increase in time in the order of $t_3 > t_2 > t_1 > t_0$, as shown in the figure (next slide), interaction zone increases. Following, after infinite time of annealing, t_α it will reach to equilibrium composition.

Diffusion under thermodynamic driving force



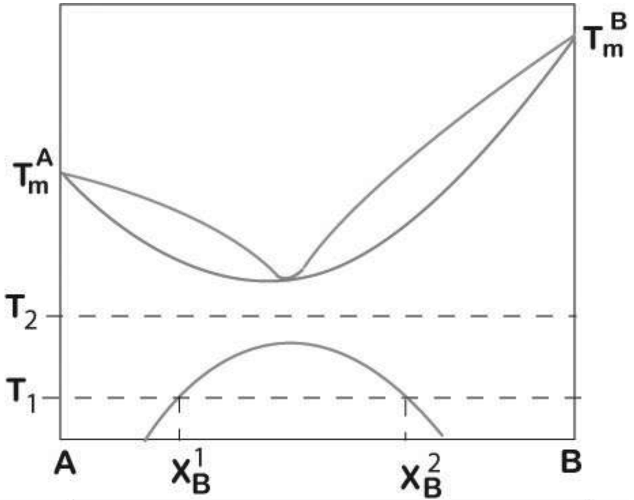
Note here that infinite time is rather notional. It means that long time enough to reach it to equilibrium. So this time will depend on the thickness of the blocks and the diffusion rate at the temperature of annealing.

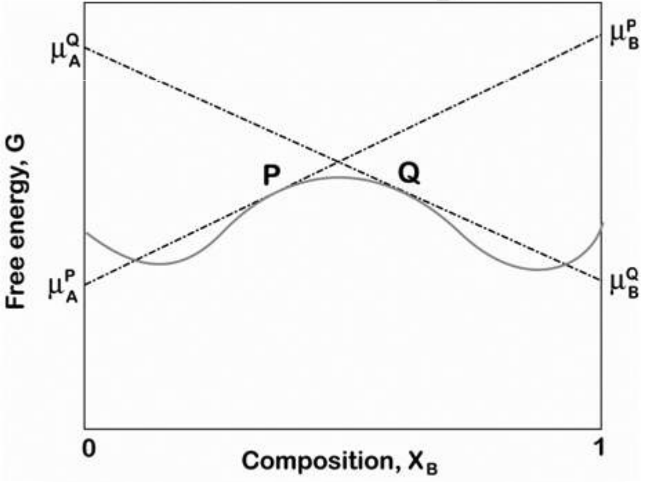
Diffusion under thermodynamic driving force

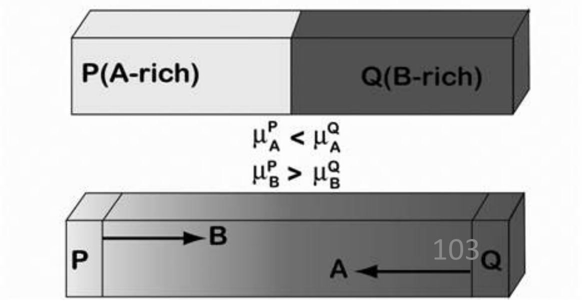
- Now let us consider a system with miscibility gap.
- If we anneal two block with any compositions at temperature, T_2, the explanation of the diffusion process will be similar as explained before.
- However, if we couple two blocks with the composition of P and Q, which are inside the miscibility gap, different situation will happen.
- From the slopes taken at P and Q, we find

$$\mu_A^P < \mu_A^Q \qquad and \qquad \mu_B^P < \mu_B^Q$$

- That means, the chemical potential of A is less in A rich alloy, P compared to the A lean alloy, Q.
- Similarly, the chemical potential of B is higher in B lean alloy, P compared to the B rich alloy, Q.
- If we couple blocks of P and Q then the average free energy of the systemis, let say, R depending on the relative amounts of P and Q.
- However, since the system always tries to decrease free energy, it will try to reach to the lowest free energy G_{α_1} and G_{α_2}







Diffusion under thermodynamic driving force

- That means A rich alloy P should increase the content of A and the B rich alloy Q should increase the content of B.
- From the chemical potential point of view also it must be clear that B will diffuse out of the B lean alloy P towards Q and A will diffuse out of the B lean alloy Q towards P.
- The direction of elements is just opposite compared to the previous example explained.
- Since elements diffuse up the concentration gradient instead of down the concentration gradient, it is called uphill diffusion.
- In terms of chemical potential gradient

$$J_A \alpha \frac{\mu_A^P - \mu_A^Q}{\Delta x} \Rightarrow J_A \alpha \frac{\mu_A^P - \mu_A^Q}{\Delta x} \Rightarrow J_A = -L_A \frac{d\mu_A}{dx}$$

Since A diffuse from Q to P and and B diffuse from P to Q

$$J_B \alpha \frac{\mu_B^Q - \mu_B^P}{\Delta x} \Rightarrow J_A \alpha \frac{\mu_B^Q - \mu_B^P}{\Delta x} \Rightarrow J_A = -L_A \frac{d\mu_B}{dx}$$

- In terms of concentration gradient

$$J_A = D_A \frac{C_A^P - C_A^Q}{dx} \Rightarrow J_A = D_A \frac{dC_A}{dx}$$

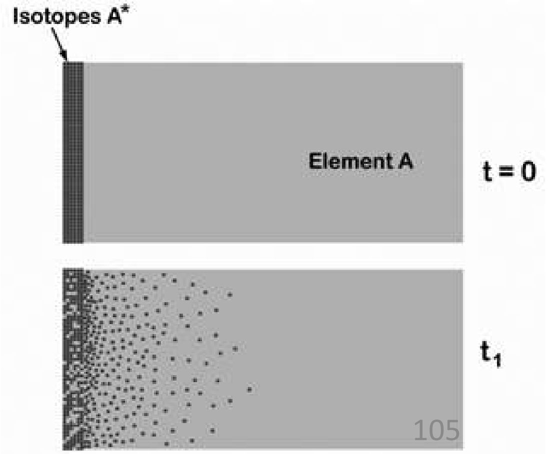
$$J_B = D_B \frac{C_B^Q - C_B^P}{dx} \Rightarrow J_B = D_B \frac{dC_B}{dx}$$

- It can be seen that negative sign is not present in the Fick's first law for this case.

Diffusion under thermodynamic driving force

- In previous slides we have shown diffusion of elements because of chemical potential driving forces. However, diffusion occurs even without the presence of thermodynamical driving force or any other driving forces.
- For example, in pure material, where there are no forces present but atoms still to jump to another position.
- In a low melting point material, like in Sn or Pb, jump of atoms possible even at room temperature. However, jump of atoms in this case is completely random. Presence of driving forces rather make net flux of atoms to a particular direction.
- To test the possibility of diffusion without any driving forces tracer diffusion experiments are conducted. Radiotracer elements which has one or two neutron mass difference are deposited on a material of the same element and then annealed at elevated temperature.
- Concentration of these tracer elements can be measured at different depths even in low concentration because of radiation of different rays

- .As shown in a schematic figure, these tracer elements diffuse inside the material. Since both are pure elements there is no chemical potential difference.
- These tracer elements are used to trace the diffusion of elements.
- There will be very small gain (increase in entropy) because of spreading of these tracer elements.
- If we do not use the tracer elements we will not be able to detect the jump of atoms.

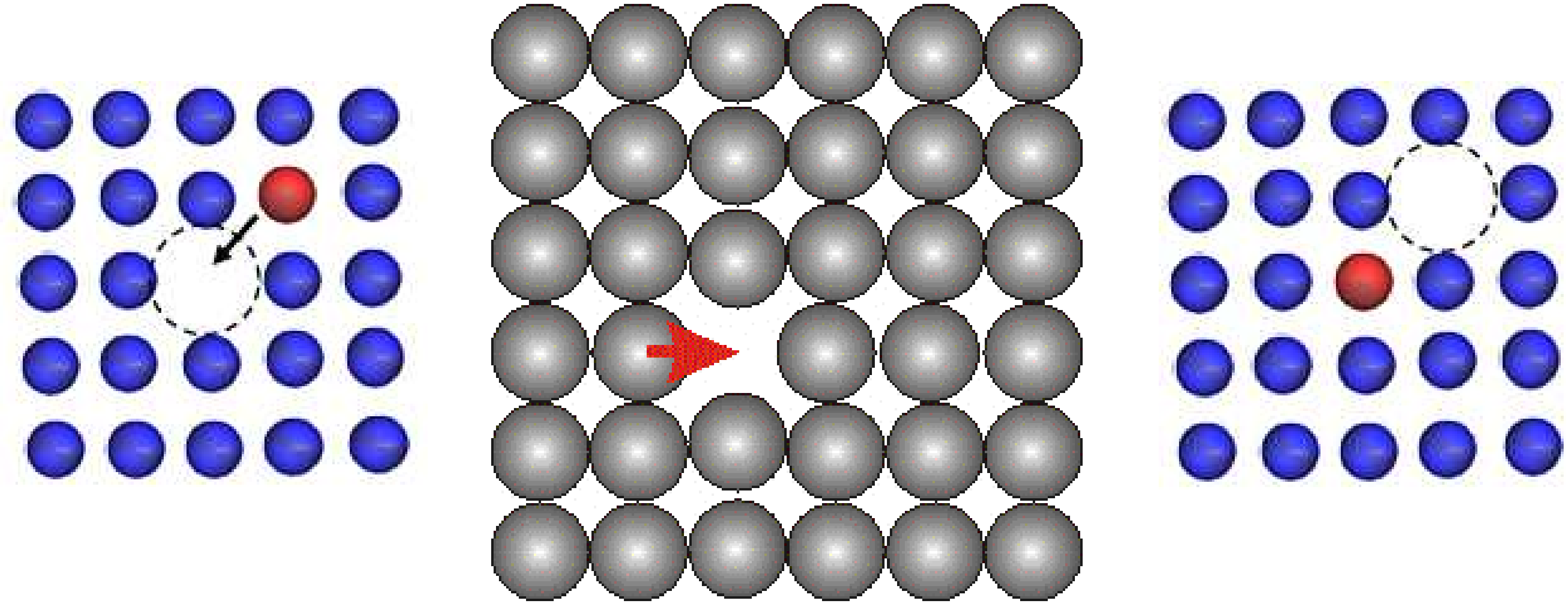


Diffusion Mechanism

- Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

Vacancy Mechanism

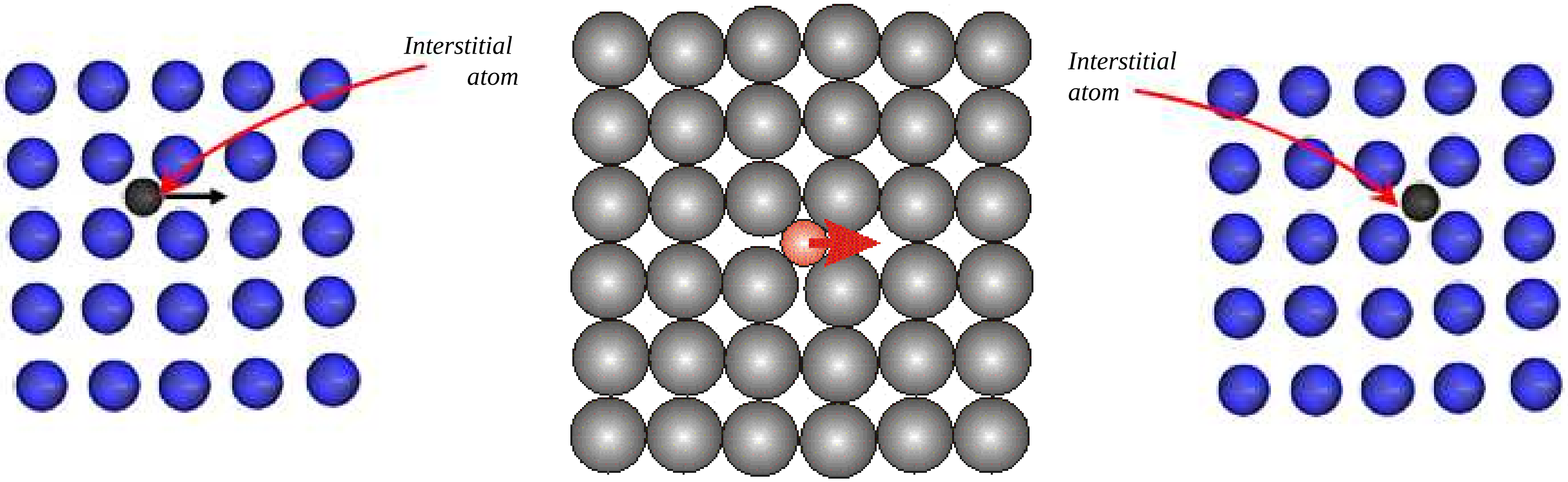
- This mechanism involves movement of atoms (we are interested in substitutional atoms) from a regular lattice site to an adjacent vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.



Diffusion Mechanism

Interstitial Mechanism

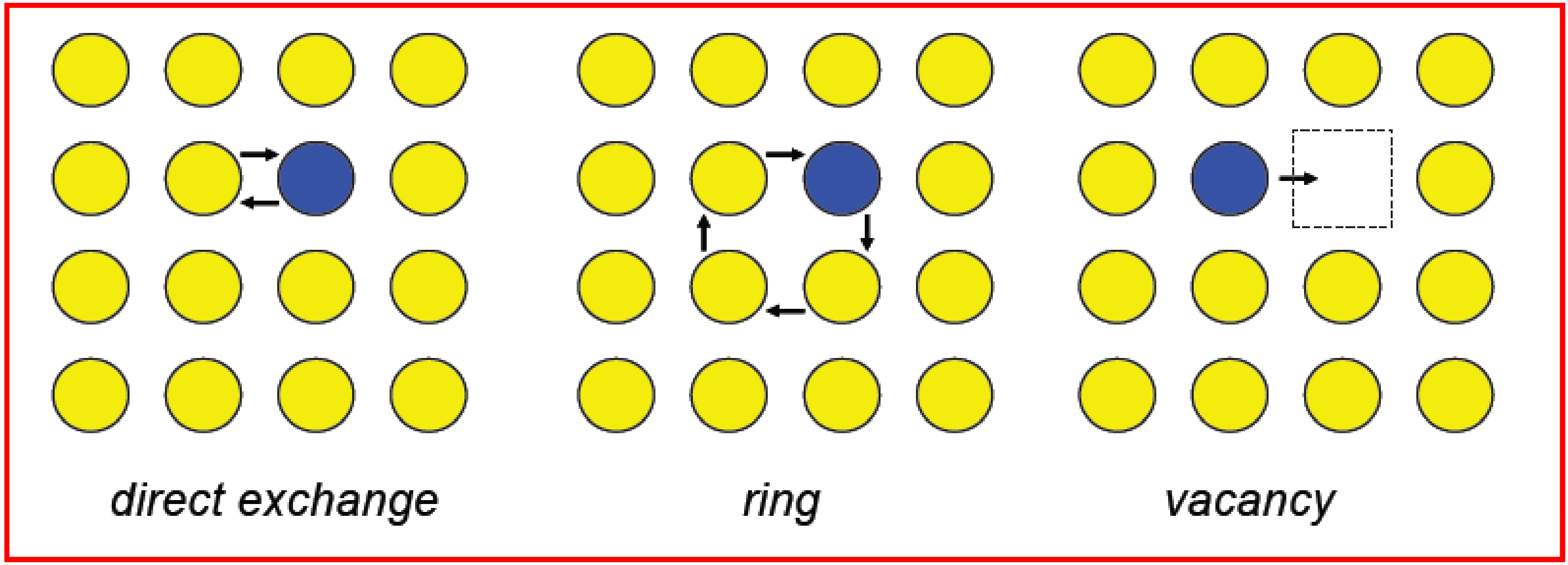
- ❑ This mechanism Involves migration of atoms from one interstitial site to a neighboring empty interstitial site.
- ❑ Usually the solubility of interstitial atoms (e.g. carbon in steel) is small. This implies that most of the interstitial sites are vacant. Hence, if an interstitial species wants to jump, ‘most likely’ the neighboring site will be vacant and jump of the atomic species can take place.
- ❑ This mechanism is more prevalent for impurity such a hydrogen, carbon, nitrogen, oxygen which are small enough to fit into an interstitial position.



Diffusion Mechanism

Atom Interchange Mechanism

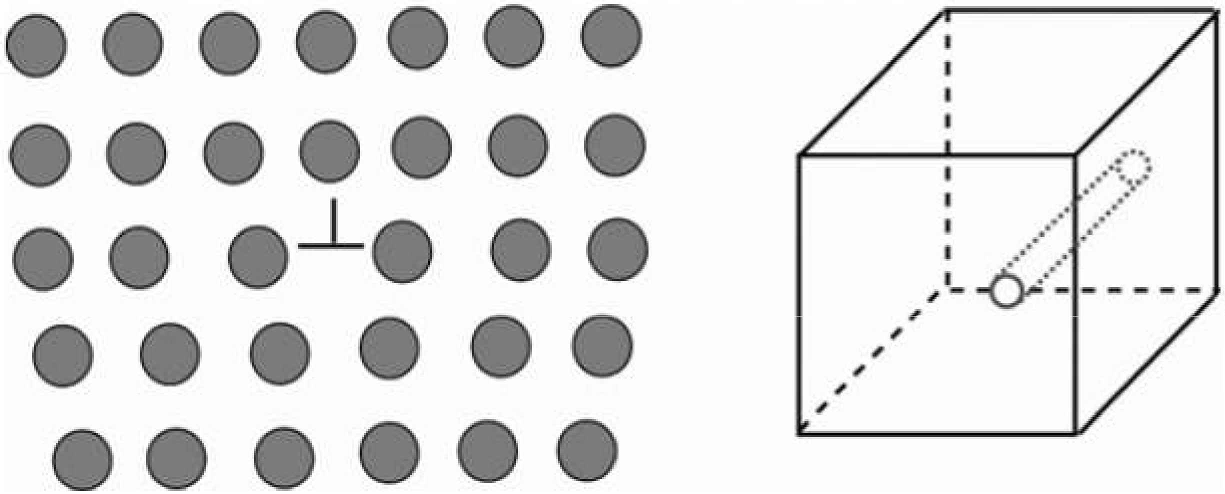
- ❑ It is possible for movement to take place by a direct interchange between two adjacent atoms or by a four –atom ring interchange.
- ❑ However, these would probably occur only under special conditions, since the physical problem of squeezing between closely packed neighboring atoms would increase the barrier for diffusion.
- ❑ Note: The rate of diffusion is much greater in a rapidly cooled alloy than in the same alloy slow cooled. The difference is due to the larger number of vacancies retained in the alloy by fast cooling.



Diffusion Mechanism

Pipe Diffusion

- ❑ When diffusion occurs via edge dislocation, it is called pipe diffusion.

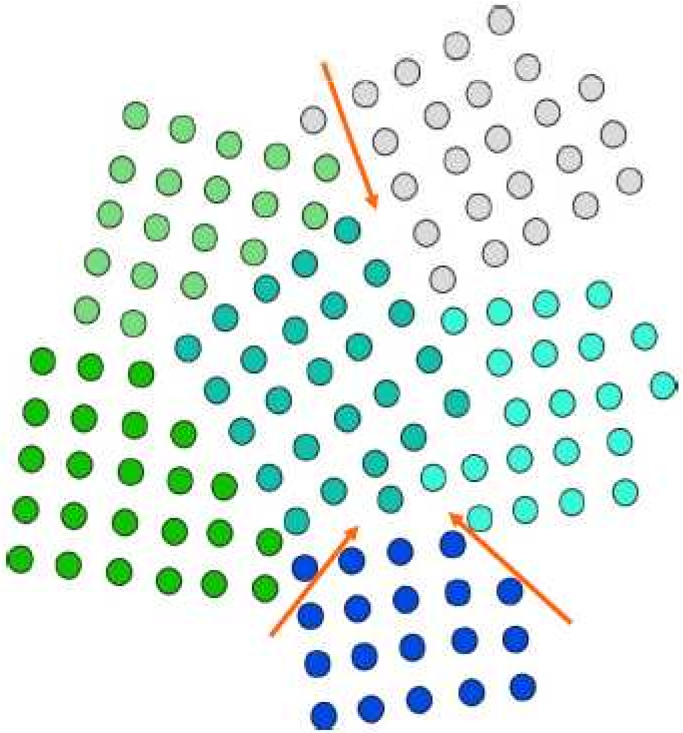


- ❑ Since it feels like movement of atoms through a pipe.
- ❑ Note that both interstitial and substitutional diffusion can occur via dislocations.
- ❑ Even impurities are attracted by the dislocations because of availability of more space and chance to release stress.
- ❑ This is also the reason (more open space) that it has lower activation barrier and diffusion rate through dislocation is higher than the diffusion through lattice.

Diffusion Mechanism

Grain boundary diffusion

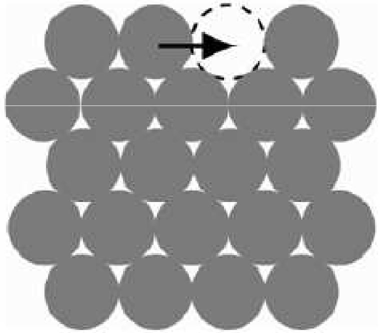
- ❑ Diffusion occurs via grain boundaries even easily and it is called grain boundary diffusion.
- ❑ Since grain boundaries are relatively more open structure compared to atomic structure inside the grains, the barrier for diffusion through grain boundary is much less and the diffusion rate is higher.
- ❑ Rate of diffusion increases with the increase in misorientations.



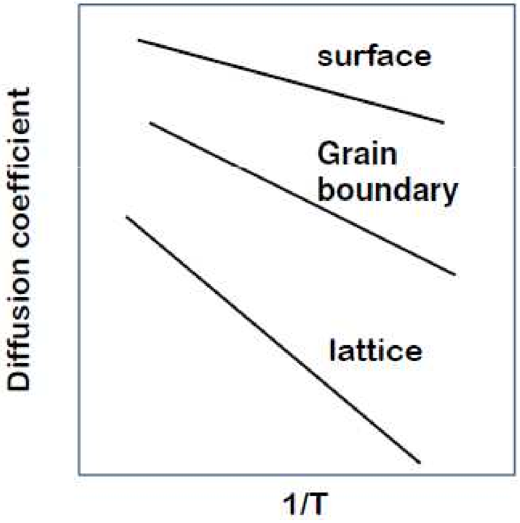
Diffusion Mechanism

Surface diffusion

- When diffusion occurs over a surface, it is called surface diffusion.
- Here activation energy for diffusion is the lowest since there are no atoms above the atom of interest, which exchanges position with the vacancy. So diffusion rate is the highest compared to other diffusion mechanisms.



Surface diffusion

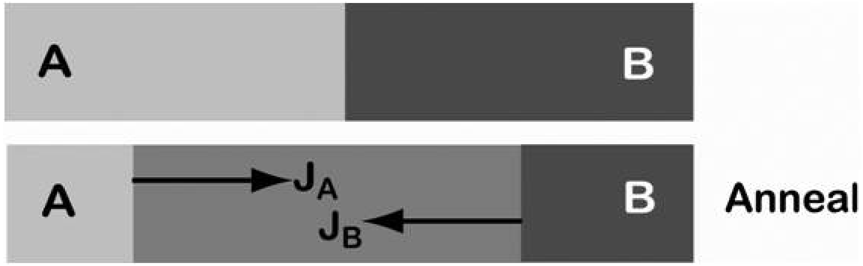


- Note that both interstitial and substitutional diffusion can happen through, lattice, dislocations, grain boundaries and surface.
- Slope of the diffusion coefficient vs. 1/T gives the activation barrier for diffusion. Activation barrier is the lowest and diffusion rate is the highest for the surface diffusion. Activation barrier is the highest and diffusion rate is the lowest for lattice diffusion.

Diffusion Mechanism

Diffusion Couple

- When two blocks with different compositions are joined (coupled) together and annealed to allow diffusion between them, it is called diffusion couple.



Interdiffusion (chemical diffusion)

- Since elements in the diffusion couple interdiffuse to each other, it is called interdiffusion.
- The diffusion coefficient is in general called as interdiffusion coefficient and if sometimes any new compound forms during the diffusion at the interface, occasionally, it is called chemical diffusion coefficient.
- Note that actually elements A and B diffuse. Diffusion of these elements are called intrinsic diffusion of elements.

Diffusion Mechanism

Self diffusion

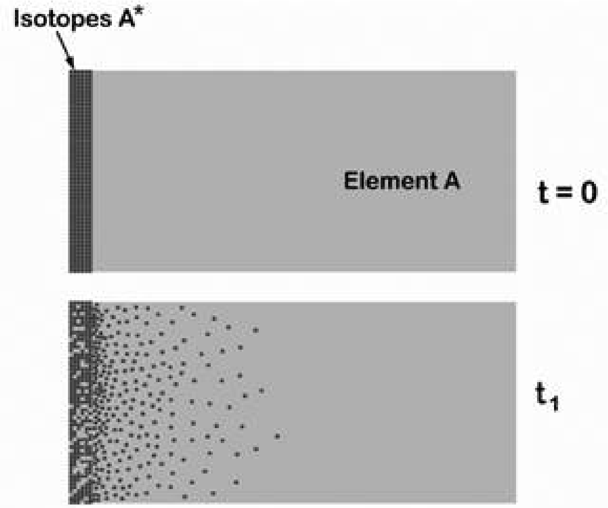
- When diffusion occurs without any presence of driving force, it is called self diffusion.
- Atoms vibrate at their positions and because of some violent jumps, it can cross the activation barrier to make the jump successful.
- Since there is no driving force to direct the jump of atoms to a particular direction, self diffusion is truly random in nature.
- This indicates that when a pure metal is kept at elevated temperature jump of atoms is always happening.
- In low melting point metals, like In or Sn, even at room temperature, atoms exchange their position.
- However, since these are very small in size, we cannot follow a particular atom jump.
- We shall see that the jump can be many orders of magnitude in one second. This makes it even difficult to follow the jump of atoms.
- To obviate this problem, concept of tracer diffusion is introduced.

Diffusion Mechanism

Tracer diffusion

- ☐ Radio isotopes are used in tracer method so that the movement of atoms can be traced and diffusion coefficient can be measured.
- ☐ It has only one or two neutron mass difference.
- ☐ Diffusion rate of these tracer atoms are called tracer diffusion coefficient.
- ☐ Note: Self diffusion coefficient (D_s) is not necessarily equal to the tracer diffusion coefficient (D^*). These two are related as

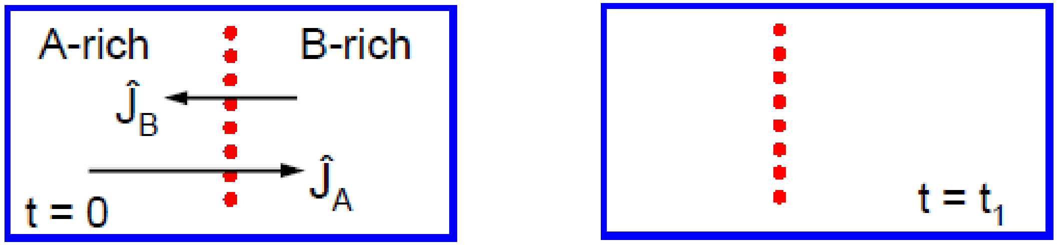
$$D^* = fD_s$$ *f is the correlation factor (f = 1 for interstitial diffusion)*



- ☐ When tracer diffusion coefficient of element B in pure material A is measured, it is called impurity diffusion coefficient.

Kirkendall Effect

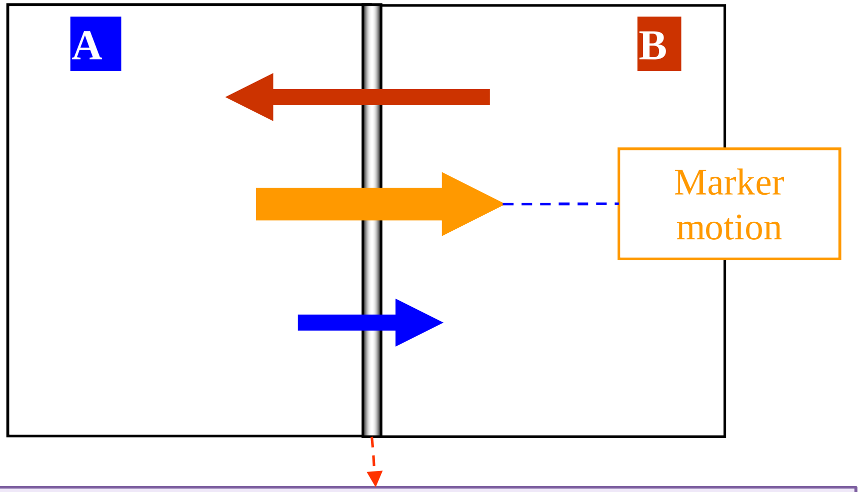
- If the diffusion rates of two metals A and B into each other are different, the boundary between them shifts and moves towards the faster diffusing metal.



Diffusion rate
$\hat{J}_A > \hat{J}_B$
t = time

- This is known as kirkendall effect. Named after the inventor Ernest Kirkendall (1914-2005). It can be demonstrated experimentally by placing an inert marker at the interface

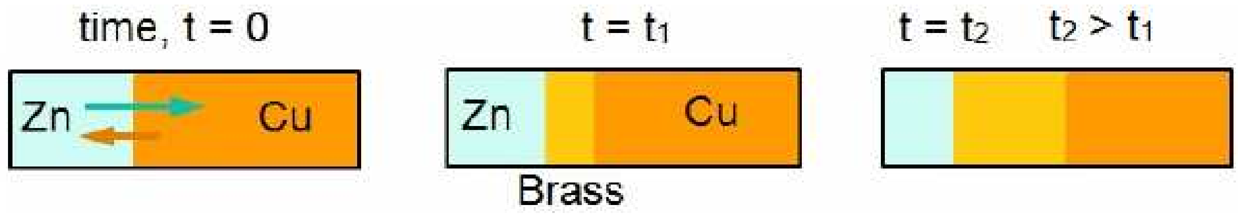
✓ Materials A and B welded together with inert marker and given a diffusion anneal
✓ Usually the lower melting component diffuses faster (say B)



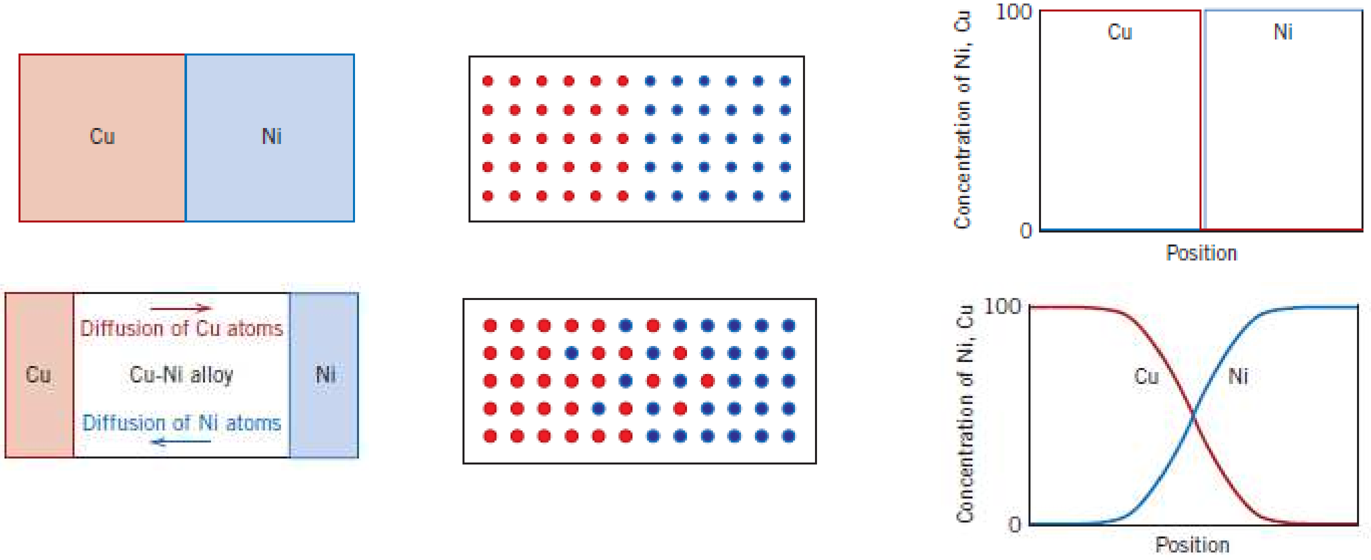
Inert Marker *– thin rod of a high melting material which is basically insoluble in A & B*

Kirkendall Effect

- ❑ Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (*Brass*).



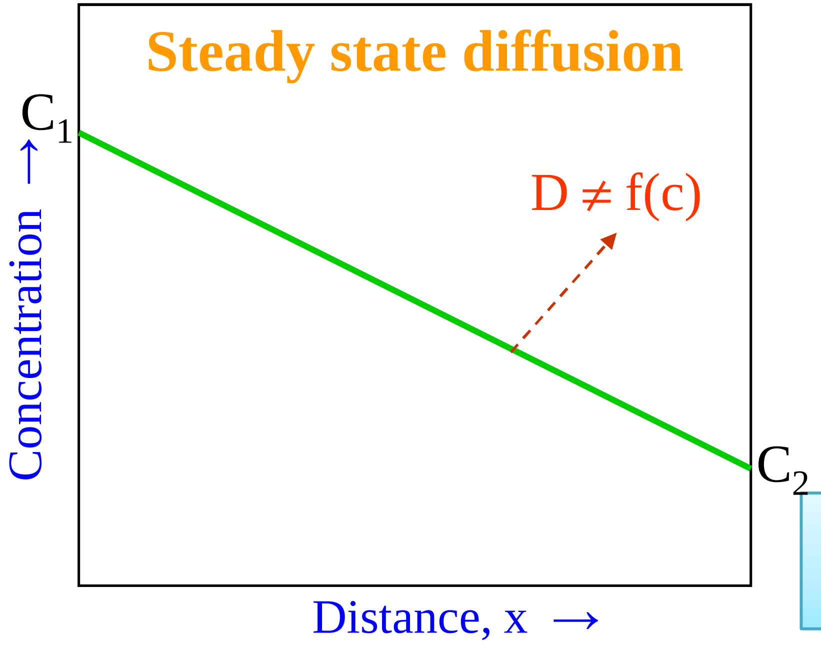
- ❑ Same will happen in a Cu-Ni couple as copper diffuses faster in nickel than nickel in copper.
- ❑ Since this takes place by vacancy mechanism, pores will form in cu (of the Cu-Ni couple as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.



steady and non-steady state diffusion

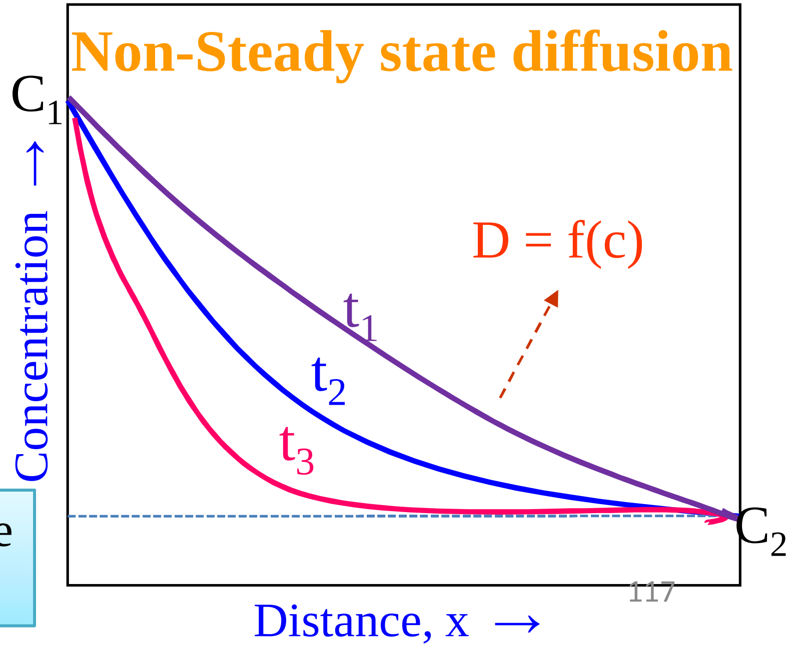
- Diffusional processes can be either steady-state or non-steady-state. These two types of diffusion processes are distinguished by use of a parameter called flux.
- It is defined as net number of atoms crossing a unit area perpendicular to a given direction per unit time. For steady-state diffusion, flux is constant with time, whereas for non-steady-state diffusion, flux varies with time.
- A schematic view of concentration gradient with distance for both steady-state and non-steady-state diffusion processes are shown below.

- Flux (J) *(restricted definition)* → Flow / area / time [Atoms / m^2 / s]



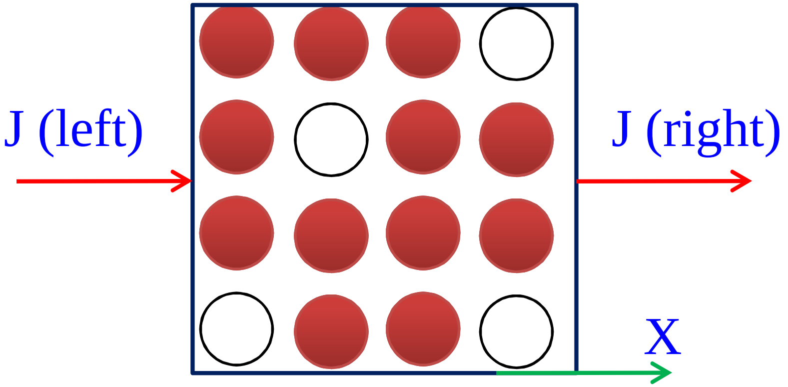
Steady state
$J \neq f(x,t)$

Non-steady state
$J = f(x,t)$



steady and non-steady state diffusion

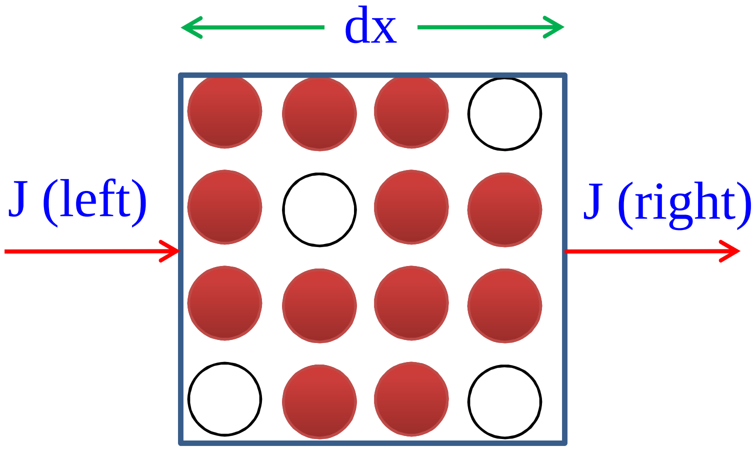
Steady State : Concentration profile not changing with time.



Concentration 'C' in the box doesn't change with time

Steady State
J(x) Left = J(x) Right

Non-Steady State : Concentration profile changes with time.



Concentration accumulating in the box

Non-Steady State
J(x) Left ≠J(x) Right

Fick's I Law

- Steady-state diffusion is described by Fick's first law which states that flux, J, is proportional to the concentration gradient.
- The constant of proportionality is called diffusion coefficient (diffusivity), D (cm^2/sec). diffusivity is characteristic of the system and depends on the nature of the diffusing species, the matrix in which it is diffusing, and the temperature at which diffusion occurs.
- Thus under steady-state flow, the flux is independent of time and remains the same at any cross-sectional plane along the diffusion direction. for the one-dimensional case, Fick's first law is given by

$$\boxed{J \equiv atoms / area / time \propto concentration\ gradient}$$

$$\boxed{J \propto \frac{dc}{dx}} \longrightarrow \boxed{J = -D\frac{dc}{dx}} \longrightarrow \boxed{J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}}$$

$$\frac{dn}{dt} = -DA\frac{dc}{dx}$$

No. of atoms crossing area A per unit time

Diffusion coefficient/ diffusivity

Concentration gradient

Cross-sectional area

Steady state

$J \neq f(x,t)$

The minus sign in the equation means that diffusion occurs down the concentration gradient

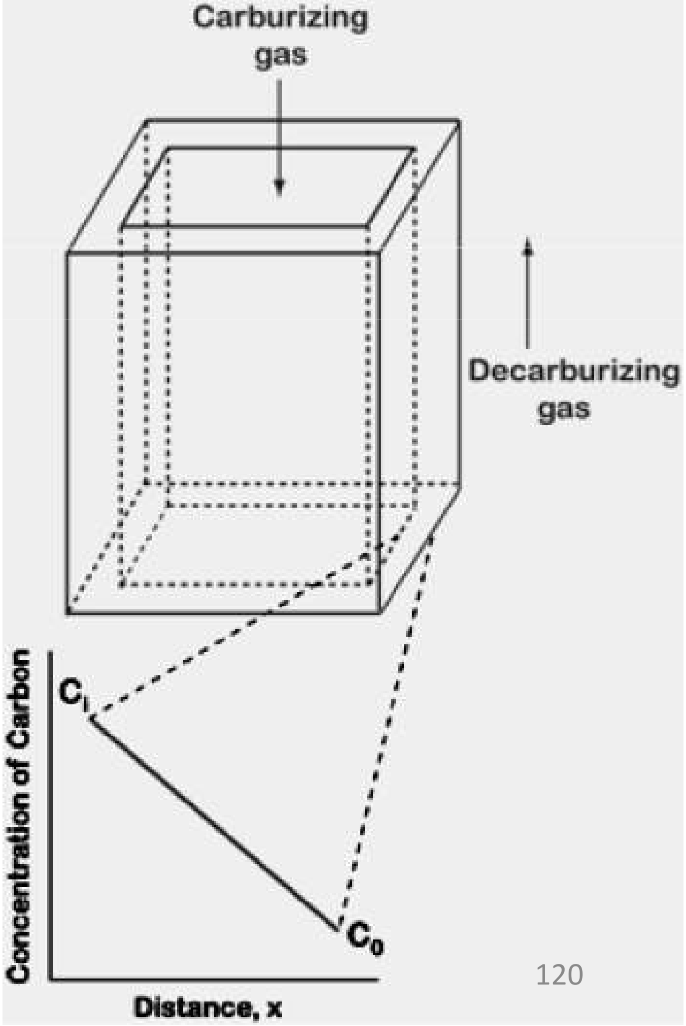
Fick’s I Law

- ❑ In Ficks I law, minus sign comes from the fact that matter flows down the concentration gradient. It is not necessarily true in all the cases.
- ❑ Matter may also diffuse up the concentration gradient, which is called uphill diffusion.

- ❑ Fick’s first law can directly be applied in the case of steady state, as shown in the example below.
- ❑ Steady state means that there will not be any change in the composition profile with time.
- ❑ If we pass carburizing gas through the pipe as shown in the figure and decarburizing gas outside the pipe, a steady composition profile may develop.
- ❑ Concentration gradient can be calculated following:

$$\frac{dc}{dx} = -\frac{C_i - C_0}{d} = -\frac{C_0 - C_i}{d}$$

- ❑ From this, one can calculate the flux from the known diffusion coefficients of carbon or the diffusion coefficient from the flux determined.



Solved Example -1

The steady-state diffusion is found in the purification of hydrogen gas. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm-thick sheet of palladium having an area of 0.25 m^2 at 600°C. Assume a diffusion coefficient of 1.7×10^{-8} m^2 / s, that the concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.

This Problem calls for the mass of hydrogen, per hour, that diffuses through a pd sheet.

From the Fick's I law:

$$\boxed{M = JAt = -DAt\frac{\Delta c}{\Delta x}}$$

$$\boxed{= -(1.7\times10^{-8} m^2/s)(0.25m^2)(3600s/h)\left[\frac{0.4-2.0kg/m^3}{6\times10^{-3}s}\right]}$$

$$\boxed{= 4.1\times10^{-3} kg/h}$$

Solved Example -2

A sheet of BCC iron 2 mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at *675ºC*. After having reached steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%. Compute the diffusion coefficient if the diffusion flux is 7.36 × 10^{-9} kg/m^2-s *(Hint : convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.*

This problem calls for computation of the diffusion coefficient for a steady-state diffusion situation. Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using below equation.

For 0.015 wt% C

$$C'_C = \left[\frac{C_C}{\frac{C_C}{\rho_C} + \frac{C_C}{\rho_{Fe}}} \times 10^3 \right]$$

$$C'_C = \left[\frac{0.015}{\frac{0.015}{2.25} + \frac{99.985}{7.87}} \times 10^3 \right]$$

$$= 1.18 kgC / m^3$$

Similarly, for 0.0068 wt% C

$$C''_C = \left[\frac{0.0068}{\frac{0.0068}{2.25} + \frac{99.9932}{7.87}} \times 10^3 \right]$$

$$= 0.535 kgC / m^3$$

$$D = -J \frac{X_A - X_B}{C_A - C_B}$$

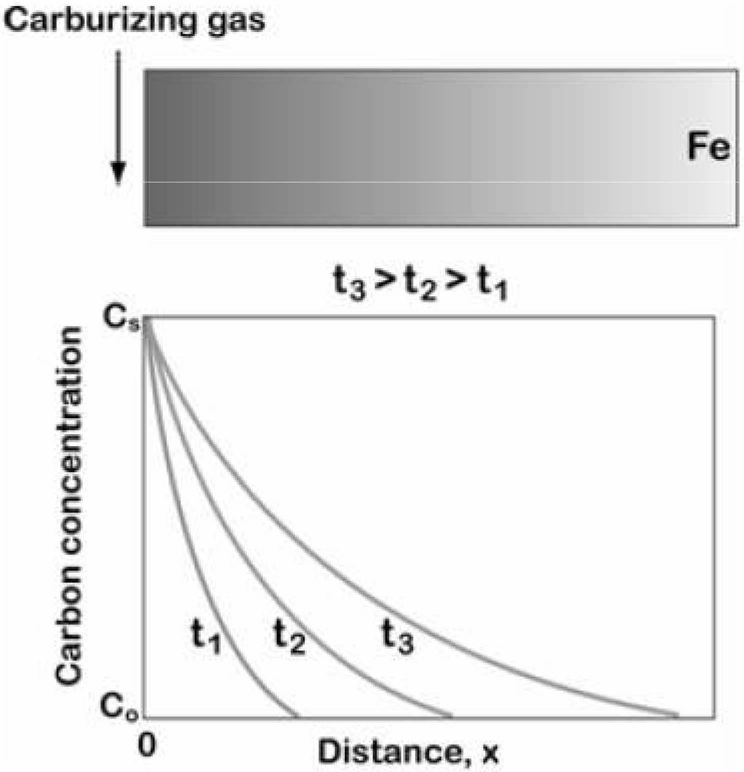
$$= -(7.36 \times 10^{-9} Kg / m^2 - s) \left[\frac{-2 \times 10^{-3} m}{1.18 Kg / m^3 - 0.535 Kg / m^3} \right]$$

$$= 2.3 \times 10^{-11} m^2 / s$$

Fick's II Law

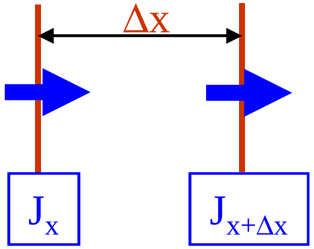
- ❑ However, just the Fick's first law may not be useful to relate the flux and the concentration profile, since, in most of the cases, systems develop non steady state concentration profile.
- ❑ It means that concentration at a particular position changes with time.
- ❑ For example, if we keep concentration of carbon on one of the Fe surfaces anneal, composition profile will change with time , as shown in the figure.

- ❑ We can't apply Fick's first law directly to evaluate the concentration profile that develops during diffusion in this case, since, as shown in the figure, composition changes with annealing time at a particular position.
- ❑ So we need to have a relation, which can relate time along with the concentration and the position.
- ❑ For that Fick's second law is derived. It is derived using conservation of mass and Fick's first law.



Fick’s II Law

- ❑ Most interesting cases of diffusion are non-steady-state processes since the concentration at a given position changes with time, and thus the flux changes with time.
- ❑ This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or depleted from a region (which may cause them to accumulate in another region). *Fick’s second law characterizes these processes, which is expressed as:*



$$Accumulation = J_x - J_{x+\Delta x}$$

$$Accumulation = J_x - \left\{ J_x + \frac{\partial J}{\partial x}\Delta x \right\}$$

$$\left(\frac{\partial c}{\partial t}\right)\Delta x = J_x - \left\{ J_x + \frac{\partial J}{\partial x}\Delta x \right\}$$

$$\left[\left(\frac{Atoms}{m^3}\frac{1}{s}\right).m\right] = \left[\frac{Atoms}{m^2 s}\right] \equiv [J]$$

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

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

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

$$\left(\frac{\partial c}{\partial t}\right) = D\frac{\partial^2 c}{\partial x^2}$$

Fick’s II law

Non-steady state

J = f(x,t)

Solutions to Fick’s second Law

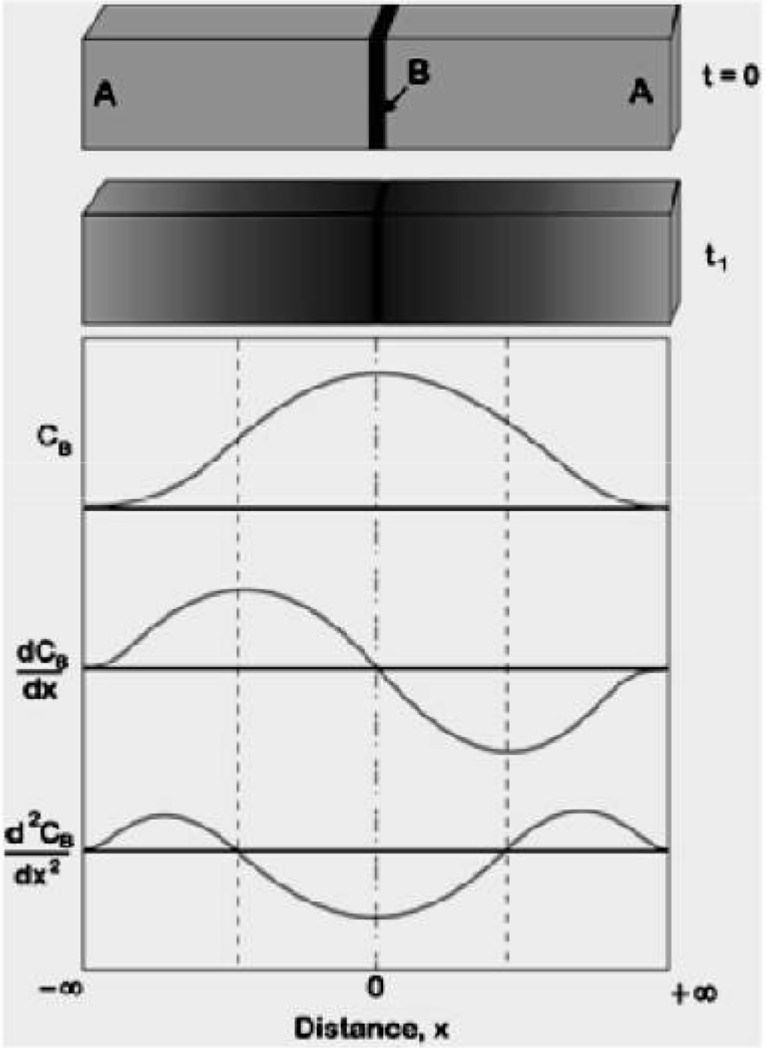
- Solution of the Fick’s second law depends on initial and boundary conditions.
- Further, D, in some cases, may be considered constant. That means D does not change with concentration or position.
- However, this condition meets only in very limited cases.
- In most of the practical examples, D is a function of concentration. In this case, solution to the Fick’s second law is complicated.
- So in the beginning, we shall solve the Fick’s second law for constant D.
- Solutions are mainly for two different types of conditions, small and large time values.
- When diffusion annealing time is small, solution is expressed with integrals or error functions. For long annealing time, it is expressed in terms of trigonometrical series.
- Note that the long or short annealing time is rather relative. By saying long annealing time, we mean that the complete sample is affected by the diffusion process and may lead to homogenization.
- By saying short annealing time, we mean that experiments are conducted such that whole material is not affected by the diffusion process.

Solution for a thin film source

- Let us consider that D is constant. That means D does not change with the composition. Since at a particular location C changes continuously with annealing time, t or a particular C changes its location continuously. From the assumption, we can state that D is the same at any location.
- The meaning of the above statement will be more clear, when we shall consider the change of D with the change in C concentration.
- Let us consider the situation, when a very thin film of element B is sandwiched between material A and then annealed at elevated temperature.

Note: One might ask, how thin it is?

- By saying “thin” we mean that the amount of material B is very low and even after total mixing (full homogenization) element B can be considered as impurities in the material A.
- That means, after deposition of B on A, the chemical potential gradient is negligible.



Solution for a thin film source

- In other sense, we can consider this as an example of diffusion in the absence of any driving force (although small driving force will be there from entropy of mixing)
- Actual meaning will be clear, when we discuss about the atomic mechanism of diffusion!
- We can consider that D is constant, since the material in which it diffuses has fixed composition.
- For constant D, the Fick's II law can be written as $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} \right) = D\frac{\partial^2 C}{\partial x^2}$
- As shown in the previous slide, it is seen that the element distribution after the diffusion can be expressed by exponential relation.
- Following the Fick's second law the distribution of element B in A can be expressed as

$$C_B(x) = \frac{C_0}{t^{1/2}}\exp\left(-\frac{x^2}{4D_B t} \right)$$ where C_o is a constant

- This relation is developed based on the fact that composition profile shows exponential decay from thin film source.
- The correctness of the solution can be checked by differentiation of the equation with respect to t and x and then using them in the Fick's second law to find the equal values on both the sides.

Solution for a thin film source

- Further, the boundary condition that $C_B = 0$, at $x = \infty$ at t = 0 and $C_B = \infty, at$ x = 0 at t = 0 also meet.
- Now one might get confused, when we say $C_B = \infty$, since concentration of element B (= X_B / V_m = 1/ V_m) can't be infinite any time and will have some definite value even at completely pure state.
- Here $C_B = \infty$ is notional and means that the element B is not diluted by any other element, which further means that it is in pure state and for system it means that it has infinite source of element B before starting the experiment.
- We shall show that the absolute values of C_B (x) or C_0 are not important but the ratio $C_B(x)/C_0$ is important, where this solution is actually used to calculate the tracer or impurity diffusion coefficient of the species.
- Total material B (mole/m^2) that was sandwiched before annealing can be found following.

$$M_B = \int_{-\infty}^{+\infty} C_B$$

- So we can write $$M_B = \int_{-\infty}^{+\infty} \frac{C_B}{t^{1/2}} \exp\left(-\frac{x^2}{4D_B t}\right) dx$$
- Further, we consider $\lambda = \frac{x}{2\sqrt{D_B t}}$ means $dx = (2\sqrt{D_B t})d\lambda$

Solution for a thin film source

- ❑ Since integration gives √Π, we get

$$M_B = 2C_0\sqrt{D_B}\int_{-\infty}^{+\infty}\exp(-\lambda^2)d\lambda = 2C_0\sqrt{\pi D_B}$$

- ❑ Replacing this for M_B we find

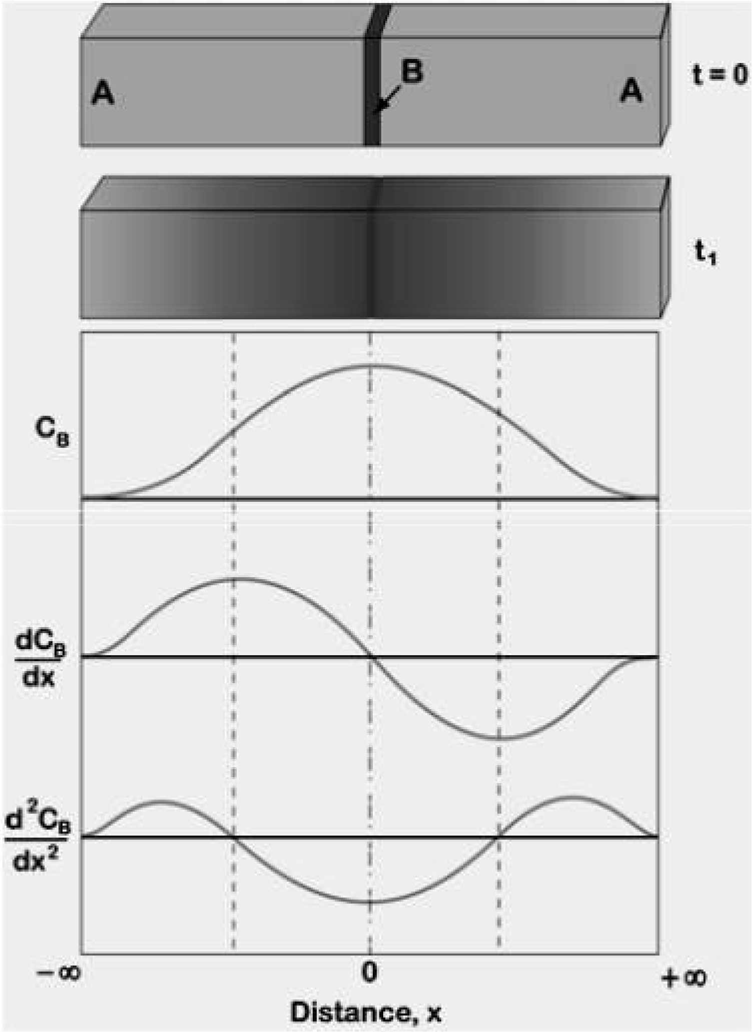
$$C_B(x) = \frac{M_B}{2\sqrt{\pi D_B t}}\exp\left(-\frac{x^2}{4D_B t}\right)$$

- ❑ C_B vs. x describes the distribution of elements B.
- ❑ dC_B /dx describes (following the Fick's law) the change in flux with respect to distance at a particular annealing time.

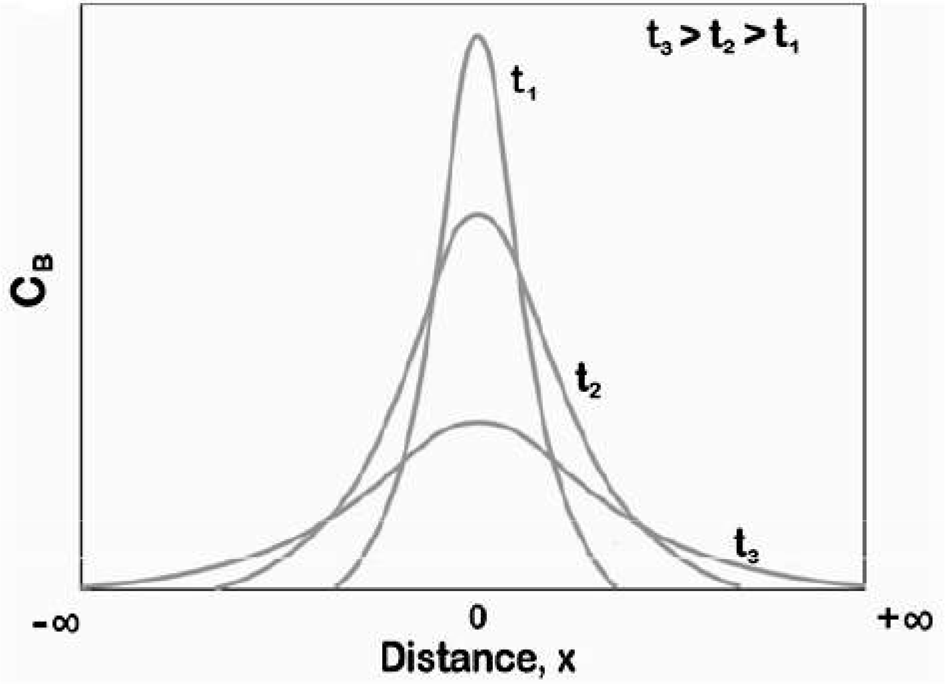
$$\frac{d^2C_B}{dx^2} = \frac{dC_B}{dt} vs.x$$

It explains the rate of change of element B

- ❑ The negative values indicate the region, where it loses the element B and positive value indicates that the region where it gains the element B. Note that the region where it is losing or gaining the element B depends on the time of annealing.



Solution for a thin film source



- The change in distribution of elements B with the increase in time is shown in the figure.

$$C_B(x) = \frac{M_B}{\boxed{2}\sqrt{\pi D_B t}} \exp\left(-\frac{x^2}{4D_B t}\right)$$

- Factor 2 comes from the fact that elements diffuse both the sides from the source

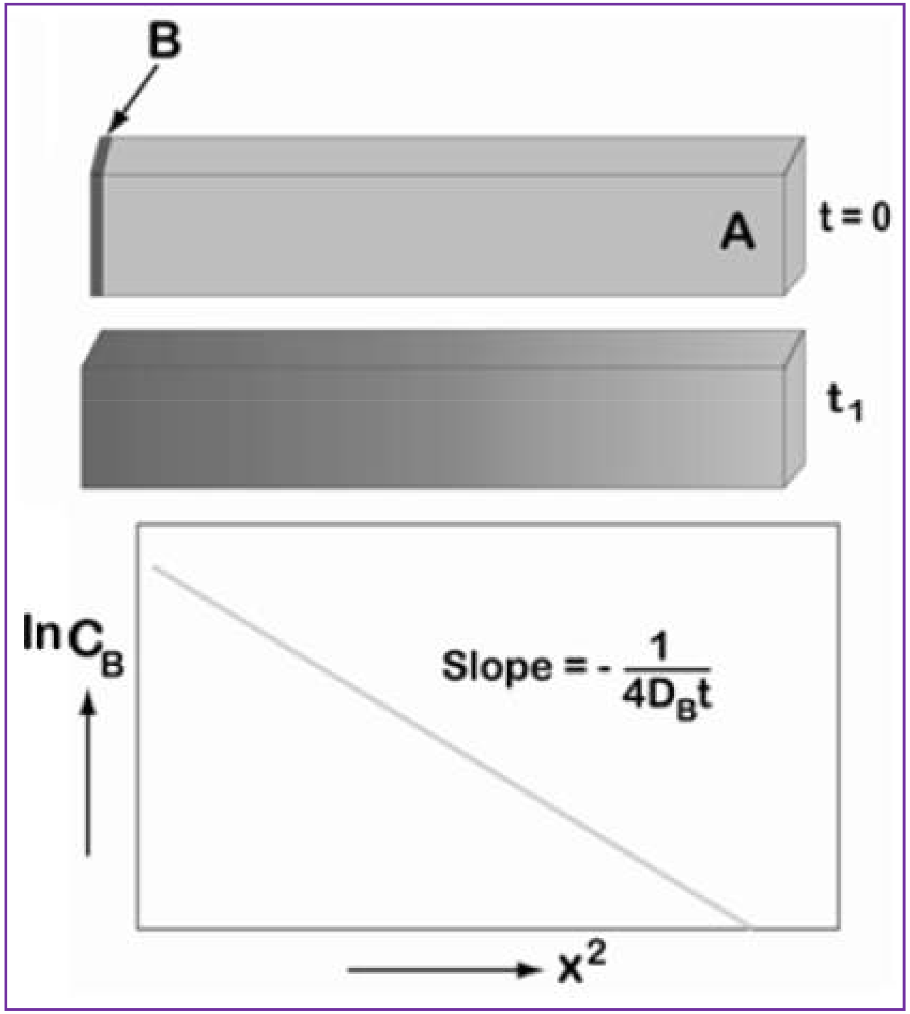
Solution for a thin film source

- ❑ If the element B diffuses to one direction then the factor 2 should not be considered.

$$C_B(x) = \frac{M_B}{\sqrt{\pi D_B t}} \exp\left(-\frac{x^2}{4D_B t}\right)$$

$$\ln C_B(x) = \ln \frac{M_B}{\sqrt{\pi D_B t}} - \frac{x^2}{4D_B t}$$

- ❑ From the calculated slope, one can determine the diffusion coefficient from the known annealing time.

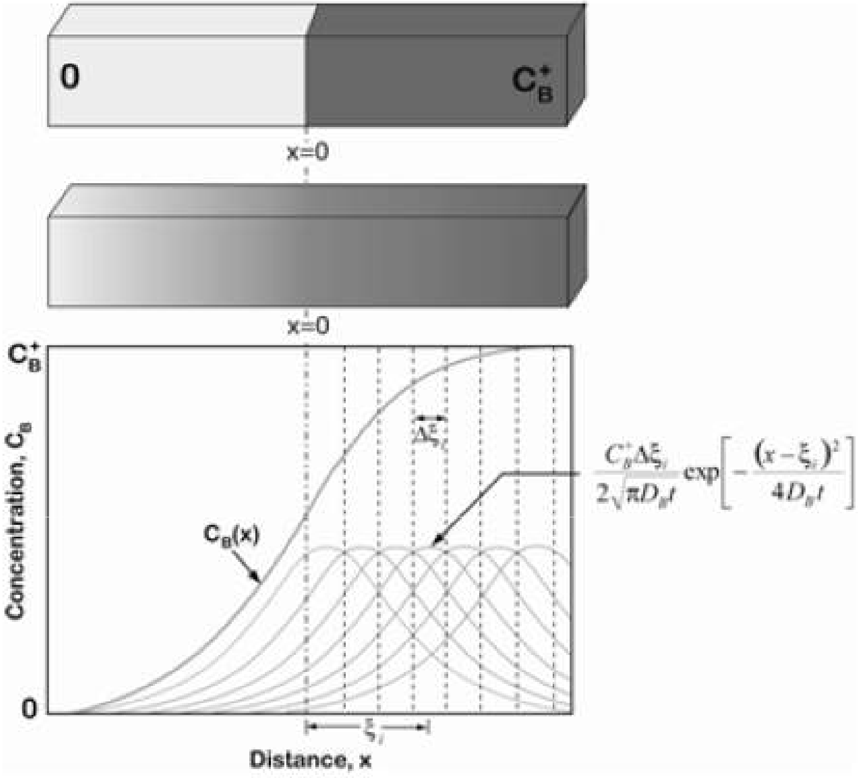


Solution in semi infinite diffusion couples (error function analysis)

- ☐ Let us consider now the semi infinite diffusion couple of two blocks with concentration of

$$C_B = 0 \quad and \quad C_B = C_B^+$$

- ☐ It means that, in a A-B binary system, it is bonding between two blocks made of pure A and an alloy of AB.
- ☐ Unlike the previous case, here, because of the difference in the composition, diffusion will be driven by the chemical potential gradient.



- ☐ However, we shall show later that the solution we are going to derive, can be used only in the case where the concentration and the chemical potential difference of the end members is not much. That means diffusion coefficients do not vary significantly with the composition.
- ☐ Semi infinite means that, we anneal for a certain annealing time such that the end of the initial materials are not affected by the diffusion of elements.

Solution in semi infinite diffusion couples (error function analysis)

- ☐ Although the meaning of the semi infinite indicates that a good part of the end of the diffusion couple should not be affected but actually even with one unaffected atomic layer in the end is sufficient to consider the system as semi infinite diffusion couple!
- ☐ This is important since otherwise we can't apply the relation derived here to determine the diffusion parameter or to calculate the concentration profile from the known diffusion parameter.
- ☐ For the sake of solving the Fick's second law, we divide the alloy with the composition C_B^+ into n numbers of very thin slices.
- ☐ We consider the distribution of element B from one slice. Suppose from the slice, *i*, which is at the distance of ξ_i from the initial contact plane, x=0. Then the distribution of element B following the solution for thin film, we can write

$$C_B(x) = \frac{C_B^+ \Delta\xi_i}{2\sqrt{\pi D_B t}} \exp\left[-\frac{(x-\xi_i)^2}{4D_B t}\right]$$

Where $M_B(mole/m^2) = C_B^+ \Delta\xi_i$

- ☐ Similarly, if we consider the distribution of elements B from all the slices and superimpose, we shall get the total distribution of element B at a particular position as

$$C_B(x) = \frac{C_B^+}{2\sqrt{\pi D_B t}} \sum_{i=1}^{n} \exp\left[-\frac{(x-\xi_i)^2}{4D_B t}\right] \Delta\xi_i$$

Solution in semi infinite diffusion couples (error function analysis)

Since we have considered very thin slices, we can write

$$C_B(x) = \frac{C_B^+}{2\sqrt{\pi D_B t}} \int_0^{\infty} \exp\left(-\frac{x-\xi}{4D_B t}\right) d\xi$$

Further consider $\eta = \dfrac{x-\xi}{2\sqrt{D_B t}}$

That means $d\eta = -\dfrac{d\xi}{2\sqrt{D_B t}}$

When $\xi = 0$ $\eta = \dfrac{x}{2\sqrt{D_B t}}$ ***and when*** $\xi = \infty$ $\eta = -\infty$

By replacing

$$C_B(x) = -\frac{C_B^+}{\sqrt{\pi}} \int_{x/(2\sqrt{D_B t}}^{-\infty} \exp(-\eta^2)\, d\eta = \frac{C_B^+}{\sqrt{\pi}} \int_{-\infty}^{x/(2\sqrt{D_B t}} \exp(-\eta^2)\, d\eta$$

Solution in semi infinite diffusion couples (error function analysis)

- Since this integration is not very straightforward and takes very long time to determine one single value, it is expressed in terms of error function. Advantage of using this error function is that one can determine the values from a table.
- Error function of Z is defined as

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^{Z} \exp(-\eta^2) d\eta$$

- Note here that z is actually the upper limit of the integration. Lower limit of the integration should be zero.
- So the expression in the previous slide should be rewritten such that it can be replaced by the error function

$$C_B(x) = \frac{C_B^+}{\sqrt{\pi}} \left[\int_{-\infty}^{0} \exp(-\eta^2) d\eta + \int_{0}^{x/2\sqrt{D_B t}} \exp(-\eta^2) d\eta \right]$$

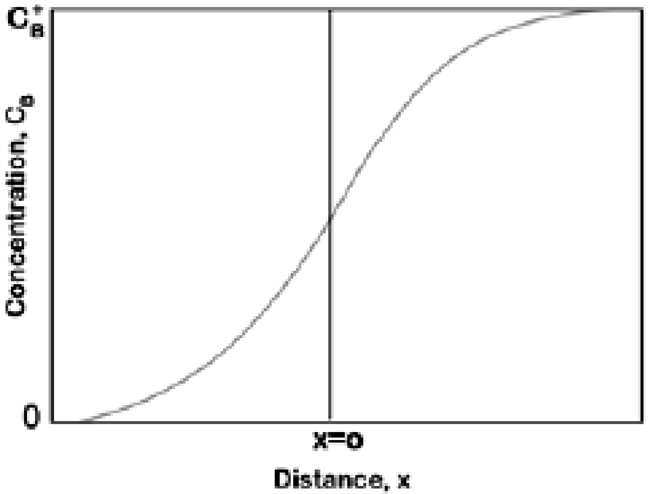
- Following, we can write it in terms of error function as

$$C_B(x) = \frac{C_B^+}{2} \left[-erf(-\infty) + erf\left(\frac{x}{2\sqrt{D_B t}} \right) \right]$$

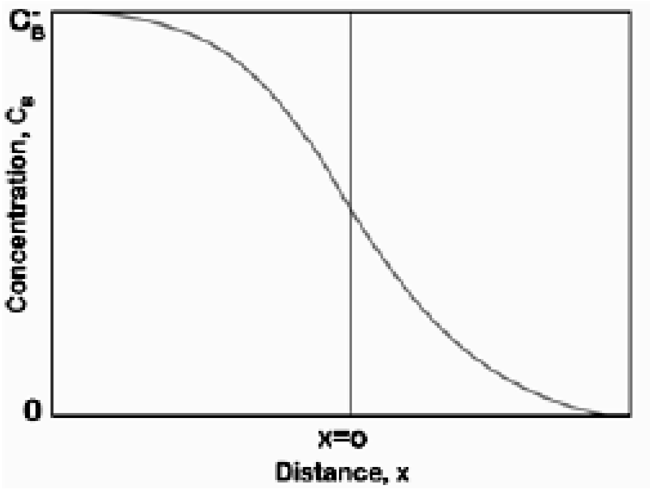
since $erf(-z) = erf(z)$

$$C_B(x) = \frac{C_B^+}{2} \left[1 + erf\left(\frac{x}{2\sqrt{D_B t}} \right) \right]$$

Solution in semi infinite diffusion couples (error function analysis)



$$\frac{C_B(x)}{C_B^+} = \frac{1}{2}\left[1 + erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$



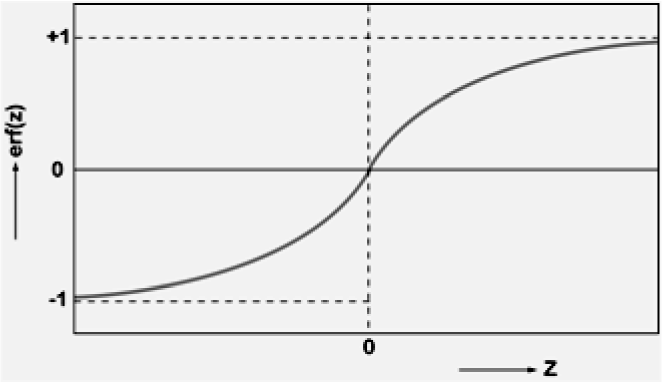
$$\frac{C_B(x)}{C_B^-} = \frac{1}{2}\left[1 - erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

- ❑ So from the previous relation, it is apparent that the sign of x will depend on which side of the x = 0, we are interested to calculate.
- ❑ Further, if the composition profile is just the opposite compared to the first example, it can be shown that the relation becomes $\frac{C_B(x)}{C_B^-} = \frac{1}{2}\left[1 - erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$

Note: We always use "+" at superscript for the concentration to denote right hand side of the couple and "-" for the left hand side of the couple.

Tabulated error function values

z	erf(z)	z	erf(z)	z	erf(z)	z	erf(z)	z	erf(z)
0	0	0.5	0.5204999	1	0.8427007	1.5	0.9661051	2	0.9953223
0.01	0.0112834	0.51	0.5292436	1.01	0.8468104	1.51	0.9672767	2.01	0.9955248
0.02	0.0225646	0.52	0.5378986	1.02	0.850838	1.52	0.9684135	2.02	0.9957195
0.03	0.0338412	0.53	0.5464641	1.03	0.8547842	1.53	0.9695162	2.03	0.9959063
0.04	0.0451111	0.54	0.5549392	1.04	0.8586499	1.54	0.9705857	2.04	0.9960858
0.05	0.056372	0.55	0.5633234	1.05	0.8624361	1.55	0.9716227	2.05	0.9962581
0.06	0.0676216	0.56	0.5716158	1.06	0.8661435	1.56	0.9726281	2.06	0.9964235
0.07	0.0788577	0.57	0.5798158	1.07	0.8697733	1.57	0.9736026	2.07	0.9965822
0.08	0.0900781	0.58	0.5879229	1.08	0.8733261	1.58	0.974547	2.08	0.9967344
0.09	0.1012806	0.59	0.5959365	1.09	0.8768031	1.59	0.975462	2.09	0.9968805
0.1	0.1124629	0.6	0.6038561	1.1	0.880205	1.6	0.9763484	2.1	0.9970205
0.11	0.1236229	0.61	0.6116812	1.11	0.883533	1.61	0.9772068	2.11	0.9971548
0.12	0.1347584	0.62	0.6194115	1.12	0.8867879	1.62	0.9780381	2.12	0.9972836
0.13	0.1458671	0.63	0.6270464	1.13	0.8899706	1.63	0.9788428	2.13	0.997407
0.14	0.156947	0.64	0.6345858	1.14	0.8930823	1.64	0.9796218	2.14	0.9975253
0.15	0.167996	0.65	0.6420293	1.15	0.8961238	1.65	0.9803756	2.15	0.9976386
0.16	0.1790118	0.66	0.6493767	1.16	0.8990962	1.66	0.9811049	2.16	0.9977472
0.17	0.1899925	0.67	0.6566277	1.17	0.9020004	1.67	0.9818104	2.17	0.9978511
0.18	0.2009358	0.68	0.6637822	1.18	0.9048374	1.68	0.9824928	2.18	0.9979506
0.19	0.2118399	0.69	0.6708401	1.19	0.9076083	1.69	0.9831526	2.19	0.9980459
0.2	0.2227026	0.7	0.6778012	1.2	0.910314	1.7	0.9837905	2.2	0.9981372
0.21	0.2335219	0.71	0.6846653	1.21	0.9129555	1.71	0.984407	2.21	0.9982244
0.22	0.2442959	0.72	0.6914328	1.22	0.9155339	1.72	0.9850028	2.22	0.9983079
0.23	0.2550226	0.73	0.6981037	1.23	0.9180501	1.73	0.9855785	2.23	0.9983878
0.24	0.2657001	0.74	0.7046778	1.24	0.9205052	1.74	0.9861346	2.24	0.9984642
0.25	0.2763264	0.75	0.7111554	1.25	0.9229001	1.75	0.9866717	2.25	0.9985373
0.26	0.2868997	0.76	0.7175365	1.26	0.9252359	1.76	0.9871903	2.26	0.9986071
0.27	0.2974182	0.77	0.7238214	1.27	0.9275136	1.77	0.9876909	2.27	0.9986739
0.28	0.3078801	0.78	0.7300102	1.28	0.9297342	1.78	0.9881742	2.28	0.9987377
0.29	0.3182835	0.79	0.7361032	1.29	0.9318986	1.79	0.9886405	2.29	0.9987986
0.3	0.3286268	0.8	0.7421008	1.3	0.9340079	1.8	0.9890905	2.3	0.9988568
0.31	0.3389082	0.81	0.7480031	1.31	0.9360631	1.81	0.9895245	2.31	0.9989124
0.32	0.349126	0.82	0.7538106	1.32	0.9380651	1.82	0.9899432	2.32	0.9989655
0.33	0.3592787	0.83	0.7595236	1.33	0.940015	1.83	0.9903468	2.33	0.9990162
0.34	0.3693645	0.84	0.7651426	1.34	0.9419137	1.84	0.9907359	2.34	0.9990646
0.35	0.3793821	0.85	0.7706679	1.35	0.9437622	1.85	0.991111	2.35	0.9991107
0.36	0.3893297	0.86	0.7761001	1.36	0.9455614	1.86	0.9914725	2.36	0.9991548
0.37	0.399206	0.87	0.7814397	1.37	0.9473124	1.87	0.9918207	2.37	0.9991968
0.38	0.4090095	0.88	0.7866872	1.38	0.949016	1.88	0.9921562	2.38	0.9992369
0.39	0.4187387	0.89	0.7918431	1.39	0.9506733	1.89	0.9924793	2.39	0.9992751
0.4	0.4283924	0.9	0.7969081	1.4	0.9522851	1.9	0.9927904	2.4	0.9993115
0.41	0.4379691	0.91	0.8018827	1.41	0.9538524	1.91	0.9930899	2.41	0.9993462
0.42	0.4474676	0.92	0.8067676	1.42	0.9553762	1.92	0.9933782	2.42	0.9993793
0.43	0.4568867	0.93	0.8115635	1.43	0.9568572	1.93	0.9936556	2.43	0.9994108
0.44	0.4662251	0.94	0.8162709	1.44	0.9582966	1.94	0.9939226	2.44	0.9994408
0.45	0.4754817	0.95	0.8208907	1.45	0.959695	1.95	0.9941793	2.45	0.9994694
0.46	0.4846554	0.96	0.8254236	1.46	0.9610535	1.96	0.9944263	2.46	0.9994966
0.47	0.4937451	0.97	0.8298702	1.47	0.9623729	1.97	0.9946637	2.47	0.9995226
0.48	0.5027497	0.98	0.8342314	1.48	0.9636541	1.98	0.994892	2.48	0.9995472
0.49	0.5116683	0.99	0.838508	1.49	0.9648979	1.99	0.9951114	2.49	0.9995707



$$erf\,(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-\eta^2)\,d\eta$$

$$= \frac{2}{\sqrt{\pi}} \left[z - \frac{z^3}{3\times 1!} + \frac{z^5}{5\times 2!} - \frac{z^7}{7\times 3!} \ldots\ldots \right]$$

$$erf\,(-z) = -erf\,(z)$$

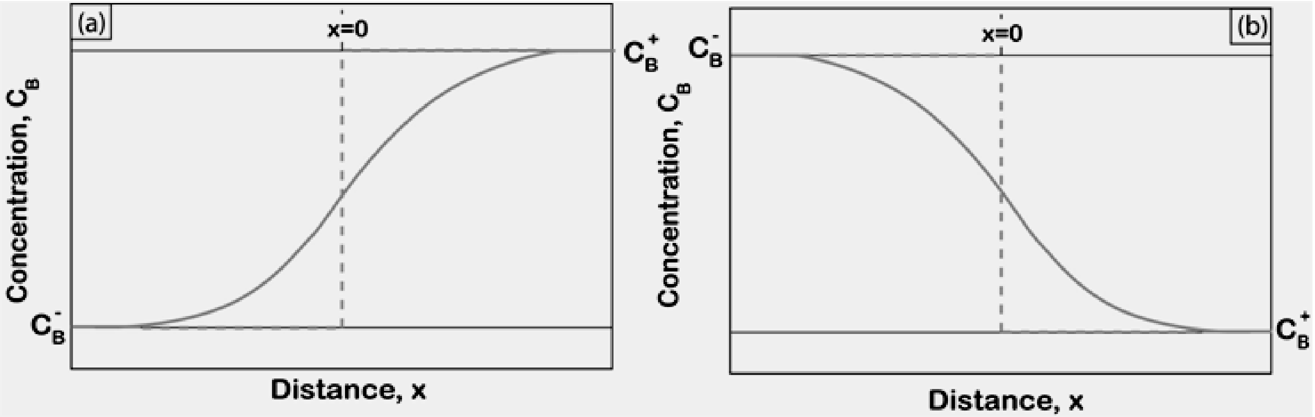
Solution in semi infinite diffusion couples (error function analysis)

- ☐ In the previous case, we considered the diffusion between the diffusion couple of two different blocks with composition $C_B = 0$, and C_B^+ or otherwise $C_B = C_B^-$ and 0.
- ☐ That means in both the cases, it was a couple between one pure element and an alloy of AB.
- ☐ Error function solutions given previously can be rewritten interms of normalized concentration profiles as

$$\frac{C_B(x)-0}{C_B^- - 0} = \frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \qquad \frac{C_B(x)-0}{C_B^- - 0} = \frac{1}{2}\left[1-erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]$$

- ☐ In some cases, it is possible that two alloys of AB are couples.
- ☐ Now if we consider the diffusion couple between C_B^- and C_B^+, where $C_B^+ > C_B^-$ the relation can be written as shown in Fig a.

$$\frac{C_B(x)-C_B^-}{C_B^+ - C_B^-} = \frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \quad or \quad C_B(x) = \frac{C_B^+ + C_B^-}{2} + \frac{C_B^+ - C_B^-}{2}\,erf\left(\frac{x}{2\sqrt{D_B t}}\right)$$

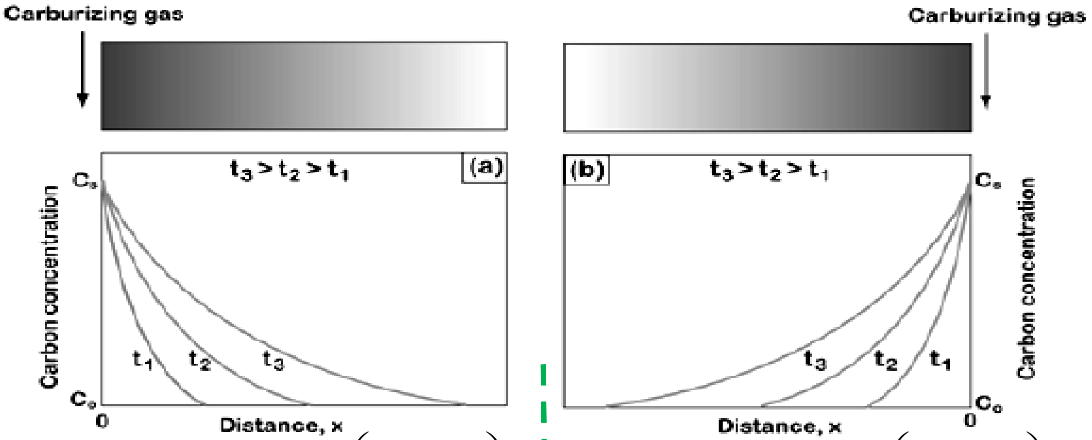


Solution in semi infinite diffusion couples (error function analysis)

- ❑ Further, the relation in the case of diffusion couple, where C_B^- and C_B^+ and $C_B^- > C_B^+$ as shown in figure b. (in the previous slide), it can be expressed as

$$\frac{C_B(x)-C_B^+}{C_B^- - C_B^+} = \frac{1}{2}\left[1-erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right] \quad Or \quad C_B(x) = \frac{C_B^- + C_B^+}{2} - \frac{C_B^- - C_B^+}{2} erf\left(\frac{x}{2\sqrt{D_B t}}\right)$$

- ❑ In the case of carburizing, we can see that the relation will be the same, irrespective of the side on which carburizing is done, since in the case of Fig. a, x is positive but in Fig. b, x is negative



$$\frac{C(x)-C_0}{C_S - C_0} = 1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x)-C_0}{C_S - C_0} = 1+erf\left(\frac{-x}{2\sqrt{Dt}}\right) = 1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x) = C_S - (C_S - C_0) erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x) = C_S\left[1-erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad for \quad C_0 = 0$$

Few important notes

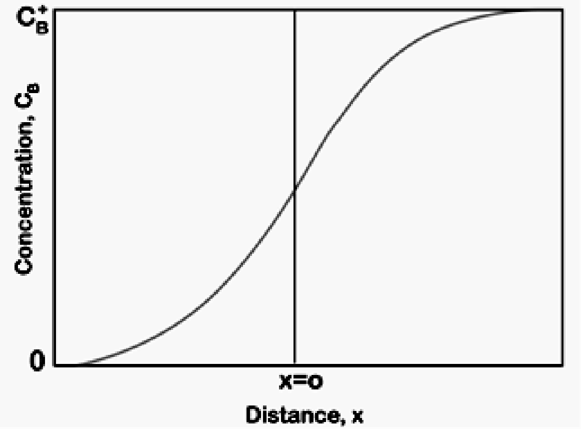
- So from the previous relations, it is apparent that the sign of x (whether positive or negative) will depend on in which side of the x = 0, we are interested to calculate.
- Note again that D will be more or less the constant at any position it is calculated. It was also one of the assumptions for this derivation.
- From the error function analysis above, we can see that, at x =0

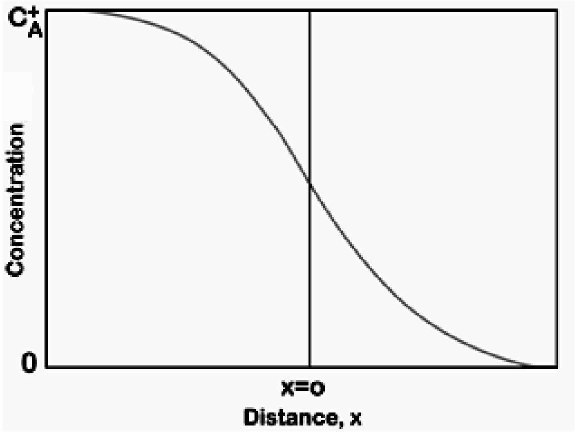
$$\textit{from the relation}\quad \frac{C_B(x)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\left[1+erf\left(\frac{x}{2\sqrt{D_B t}}\right)\right]\quad \textbf{\textit{it comes}}\quad \frac{C_B(x=0)-C_B^-}{C_B^+-C_B^-}=\frac{1}{2}\Rightarrow C_B(x=0)=\frac{1}{2}(C_B^+ + C_B^-)$$

$$\textit{from the relation}\quad C(x)=C_S-(C_S-C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right)\quad \textbf{\textit{it comes}}\quad C(x=0)=C_S$$

- It indicates that in a system, where two blocks with different concentrations are coupled, at x =0, which is basically the initial contact plane, the concentration will be always average of the concentration of the initial materials.
- Note that we need to locate anyway the initial contact plane after the diffusion process, since x in the equation is actually measured from the location of the initial contact plane.
- This also indicates that this equation can only be used when end parts of the couple is not affected by the diffusion process, since otherwise at x =0, it will have another average value depending on how much of the end members are affected.

Few important notes





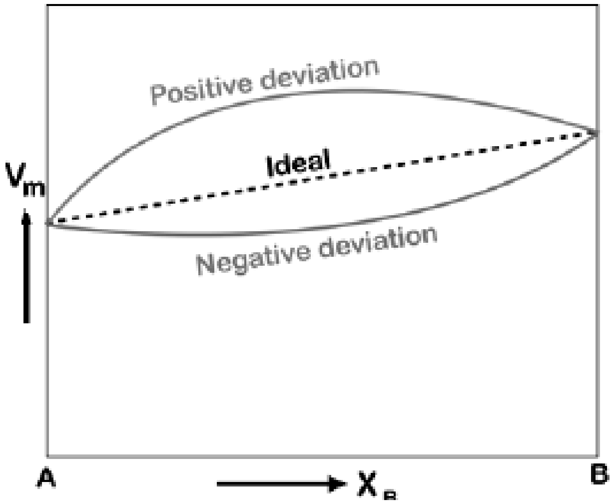
- In the case of carburizing, the surface concentration should always be the same.
- Note again that D will be more or less the constant at any position it is calculated. It was also one of the assumptions for this derivation.
- Before proceeding further for calculation using error function, one needs to check if indeed you can locate the position of x = 0 by taking average of the end member concentrations.
- This position should be possible to locate even by equalizing the areas P and Q (since the loss from one side of the couple should be equal to the gain in another side).
- If the composition profile is not symmetric, it can be found mathematically by

$$\int_{-\infty}^{x} C_B dx = \int_{x}^{-\infty} (C_B^+ - C_B) dx$$

- When for a particular x the integrals have the same values, it should be fixed as 0 position.

Few important notes

- Although it looks very trivial, finding this plane may not be that easy in most of the cases.
- Since initial contact plane x=0 is an unique plane (only one value is possible), it should be possible to find from any of the concentration profiles of elements A or B, as shown in the previous slide. However, from our experience, we have seen that it is possible to locate or find a single value from any of the profiles, only when molar volume changes ideally in the system, as shown in the figure above.



- Note that the molar volume data are required to calculate the concentration.
- When it deviates (positively or negatively) from the ideality, one finds two different values from two different composition profiles.
- Difference depends on the deviation from the ideality.
- It feels as if the system lost its initial contact plane. It will be discussed further in details at later stage, with examples.
- So the limitation of the error function analysis is not only that diffusion coefficient is more or less the constant but also the molar volume does not change much with the composition or changes ideally.

Summary on Fick’s II Law

Process	Solution
Carburisation	$C = C_S - (C_S - C_0)\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$ Cs = Surface concentration C0 = Bulk concentration
Decarburisation	$C = C_0\,erf\left(\frac{x}{2\sqrt{Dt}}\right)$ C0 =Initial Bulk concentration
Diffusion couple	$C = \left(\frac{C_1 + C_2}{2}\right) - \left(\frac{C_1 - C_2}{2}\right) erf\left(\frac{x}{2\sqrt{Dt}}\right)$ C1 = Concentration of steel 1 C2 = Concentration of steel 2
Homogenisation	$C = C_{mean} + \beta_0 \sin\left(\frac{\pi x}{\lambda}\right) \exp\left(-\frac{t}{\tau}\right)$ Cmean = Mean concentration β0 = Initial concentration amplitude λ = half wavelength t = relaxation time

Solved Example - 3

An FCC iron–carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052ºC). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere; that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed *decarburization.) At what position will the* carbon concentration be 0.25 wt% after a 10-h treatment? The value of *D at 1325 K is* 4.3 $\times 10^{-11}$ m^2/s.

This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10-h heat treatment at 1325 K when C_o = 0.55 wt% C.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

Z	Erf (Z)
0.40	0.4284
Z	0.4545
0.45	0.4755

Using tabulation of error function values and linear interpretation

$$\frac{Z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284}$$

$$Z = 0.4277$$

$$\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4277$$

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.6\times10^{4}\,s)(4.3\times10^{-11}\,m^2/s)}$$

$$= 1.06\times10^{-3}\,m = 1.06\,mm$$

Solved Example - 4

Nitrogen from a gaseous phase is to be diffused into pure iron at 675°C. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675°C is 1.9×10^{-11} m^2/s .

This problem asks us to compute the nitrogen concentration C_x at the 2 mm position after a 25 h diffusion time, when diffusion is non steady-state.

$$\frac{C_x - C_o}{C_s - C_o} = \frac{C_x - 0}{0.2 - 0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \mathrm{erf}\left(\frac{2\times10^{-3} m}{2\sqrt{(1.9\times10^{-11} m^2/s)(25h)(3600s/h)}}\right)$$

$$= 1 - erf(0.765)$$

Using tabulation of error function values and linear interpretation

Z	Erf (Z)
0.750	0.7112
0.765	y
0.800	0.7421

$$\frac{0.765 - 0.750}{0.800 - 0.750} = \frac{y - 0.7112}{0.7421 - 0.7112}$$

$$y = erf(0.765) = 0.7205$$

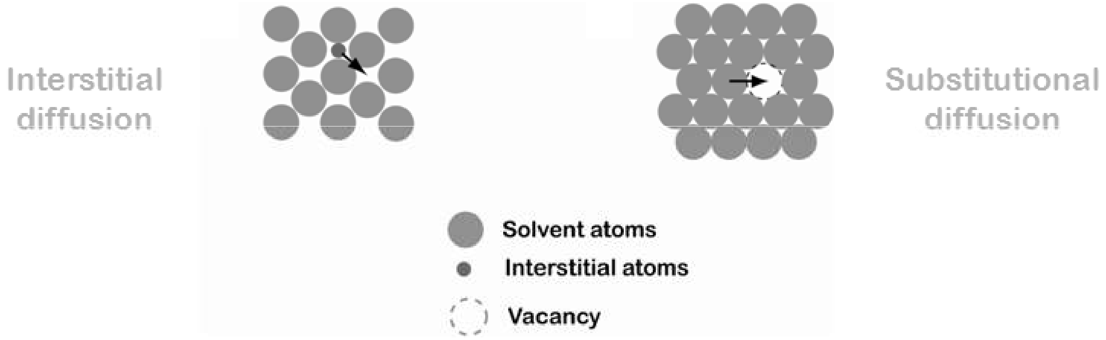
$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.7205$$

$$C_x = 0.056 wt\% N$$

Atomic mechanism of diffusion

- Till now, we discussed the diffusion process without going to the atomic level. By measuring concentration profile, one can measure the diffusion coefficients.
- However, to get further insights on the diffusion process, we need to understand the atomic mechanism.
- It is almost impossible to track the jump of any particular atom. However, based on the experimental results, we can use logical arguments to explain the process in the atomic level.

Mainly there can be two types of diffusion:

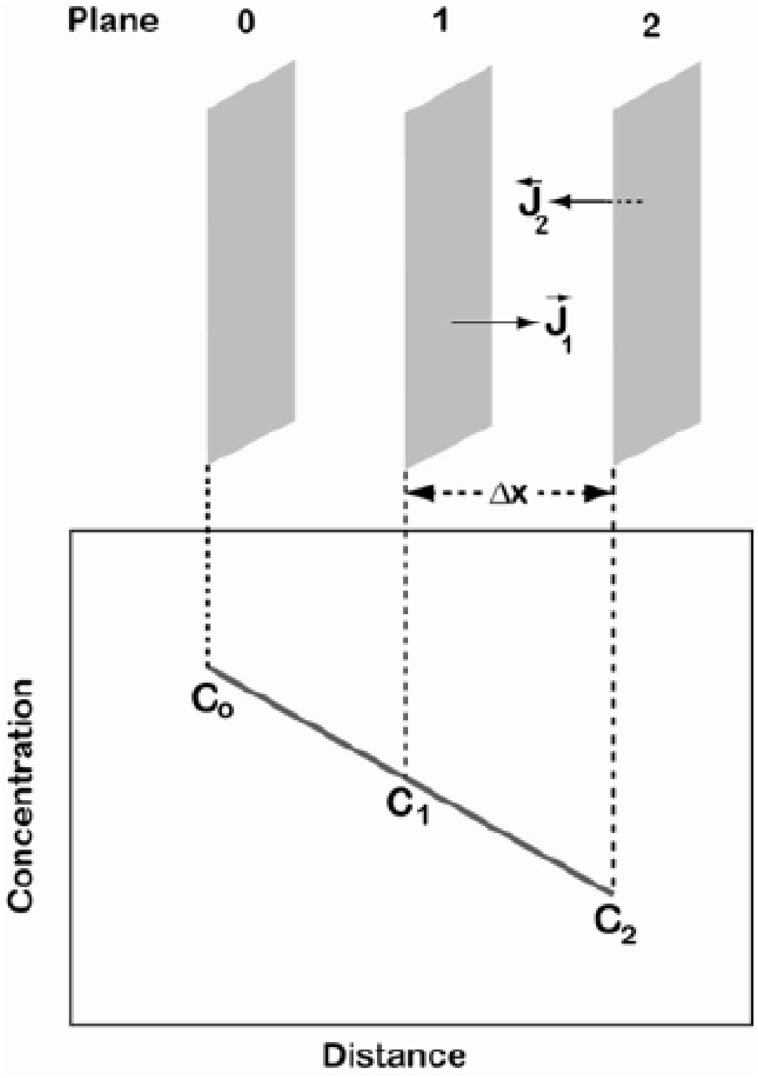


- As we have seen before that all elements will have some impurities. C, O, H etc. are present in most of the metals in interstitial voids. So, here diffusion occurs by interstitial diffusion mechanism.
- Similarly vacancies are also always present. So substitutional diffusion is possible because of presence of vacancies.
- *Let us first consider random jump of atoms that is diffusion without the presence of any driving force.*

Interstitial Diffusion

- Atoms vibrate with Debye frequency at their positions with an average energy of 3kT.
- Because of violent oscillation, sometimes it can acquire enough energy to cross the activation barrier to jump to another position.
- In this context atoms can be considered as restless, aimless, brainless matter, which tries to jump even without any gain or purpose.
- In the case of interstitial diffusion, if the concentration of atoms is very less, atom can jump randomly to any other position, since as discussed before that most of the interstitial voids will be vacant.
- For example, as shown before, at maximum composition of C in α-Fe, only one octahedral void is occupied out of 3000 voids.
- In substitutional diffusion, however, the diffusion process is rather complicated since one particular atom can exchange position on the condition that vacancy is available next to it.
- We have shown before that, on average, near the melting point, only one vacancy is available out of 1000 atoms. So in general substitutional diffusion rate is much lower compared to the rate of interstitial diffusion.
- Let us consider three adjacent planes of the host element, denoted as 0, 1 and 2.
- These planes have many voids. Few voids are occupied by interstitial atoms.
- Let us consider that concentration of interstitial atoms $C_0 > C_1 > C_2$

Interstitial Diffusion



- That means number of atoms decrease as we move from plane 0 to 2.
- The distance between different planes is Δx, which could be related to the lattice parameter of the crystal depending on the orientation of the planes.
- Remember again that there is no driving force, like chemical and electrical potential gradient, present.
- Let us consider the jump of atoms between plane 1 and 2
- The flux of atoms from the plane 1 to plane 2 can be written as

$$J_1 = \frac{1}{2} n_1 \Gamma_1$$

- The flux of atoms from the plane 1 to plane 2 can be written as

$$J_2 = \frac{1}{2} n_2 \Gamma_2$$

Interstitial Diffusion

- ✓ Γ_1 : Jump frequency per second from plane 1
- ✓ Γ_2 : Jump frequency from plane 2
- ✓ n_1 and n_2 are the number of atoms/area in plane 1 and 2 ($n_1 > n_2$).

- ☐ Factor ½ comes from the fact that only half of the atoms might jump from plane 1 to 2 and another half might jump from plane 1 to plane 0.
- ☐ So the resultant flux from the plane 1 to 2 can be written as

$$\vec{J} = \vec{J}_1 - \overleftarrow{J}_2 = \frac{1}{2}(n_1\Gamma_1 - n_2\Gamma_2)$$

- ☐ Now we consider random jump of atoms: $\Gamma_1 = \Gamma_2 = \Gamma$
- ☐ This is a fair assumption since the possibility of each atom to jump to any of the adjacent planes is equal. Note that we are considering here cubic crystal, where barrier for jump (because of presence of neighbouring host atoms) to any direction is the same.
- ☐ Further, the concentration of atoms (mole/m^3) in different planes can be written as:

$$C_1 = n_1 / \Delta x$$

$$C_2 = n_2 / \Delta x$$

- ☐ So the flux of atoms from the plane 1 to plane 2 can be written as

$$\vec{J} = \frac{1}{2}(C_1 - C_2)\Delta x\Gamma$$

Interstitial Diffusion

- Further the concentration gradient can be written as

$$\frac{dc}{dx} = \frac{(C_2 - C_1)}{\Delta x} = -\frac{(C_1 - C_2)}{\Delta x} \quad \textit{Since the distance between the planes is very small.}$$

- So the flux of atoms from the plane 1 to plane 2 can be written as

$$\vec{J} = -\frac{1}{2}\Delta x^2 \Gamma \frac{dc}{dx}$$

- Comparing with Fick's first law, we can write

$$D = \frac{1}{2}\Gamma \Delta x^2$$

- We considered that the atoms can jump to only two directions. However, in three dimension atoms can jump to any of the nearest neighbor positions and we can write

$$D = \frac{1}{Z}\Gamma \Delta x^2$$

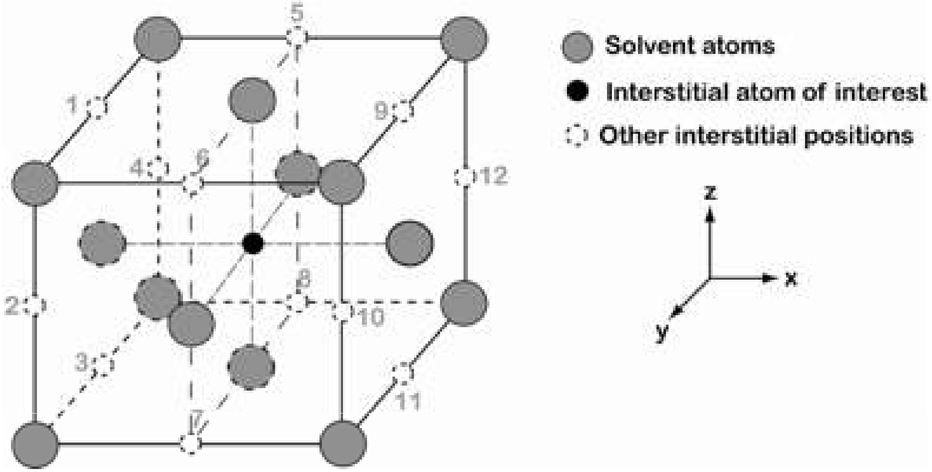
  where Z is the coordination number that is the number of nearest neighbor voids in this case.

- In FCC crystal, diffusion coefficient, in general, can be written as

$$D = \frac{1}{12}\Gamma \Delta x^2$$

Interstitial Diffusion

- Note that the activation barrier, as considered, for the jump to any point should be the same, since it is isotropic.

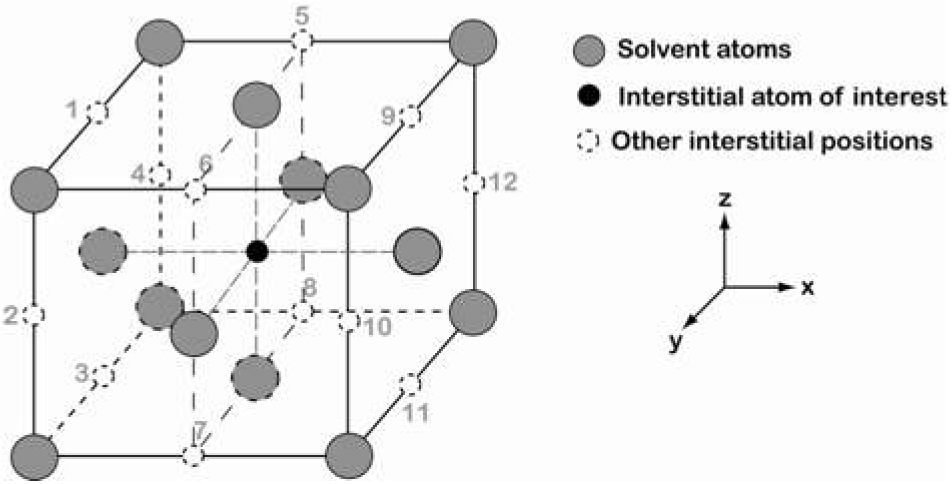


- If we consider the diffusion to a particular point only then we can write

$$D = \Gamma_i \Delta x_i^2 \quad \text{where} \quad \Gamma = Z\Gamma_i$$

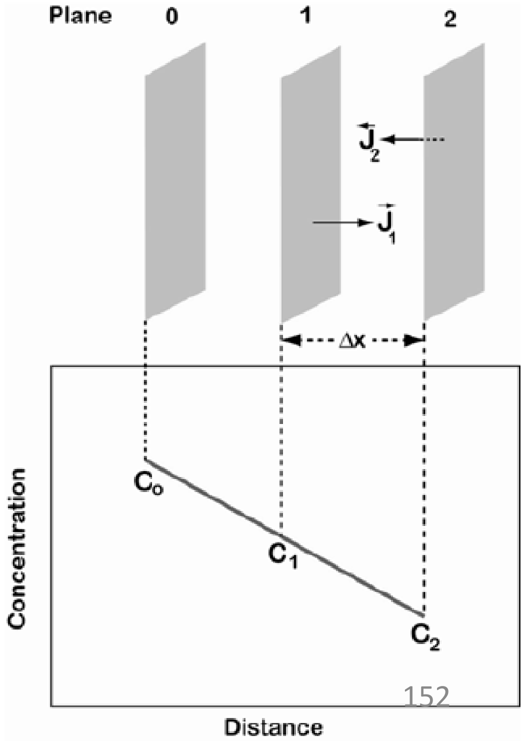
Relation of jump frequency with the diffusion coefficient in a FCC lattice

- Now let us consider the diffusion in a FCC lattice.
- We assume that voids 1, 2,3 and 4 are present on plane 0, voids 5,6,7,8 and the interstitial atom are present on plane 1 and voids 9,10,11,12 are present on plane 2



- The interstitial atoms can jump to any of the positions, without any preference
- Diffusion coefficient should be considered from the jump of many atoms together.
- There will be many atoms present on plane 1 (as previously we considered n_1)
- So different atoms from plane 1 can jump to different voids between 1 to 12.
- So the average diffusion coefficient can be written as

$$D = \frac{1}{Z}\sum_{i=1}^{Z}\Gamma_i \Delta x_i^2$$



Relation of jump frequency with the diffusion coefficient in a FCC lattice

- ❑ In a FCC crystal

$$D = \frac{1}{12}\sum_{i=1}^{i=12}\Gamma_i \Delta x_i^2$$

- ❑ Let us consider the jump to x direction (both positive and negative)
- ❑ jump to the positions 5,6,7 and 8 does not make any effective jump, since $\Delta x_i = 0$
- ❑ Effective jump length to the positions 1,2,3 and 4 is $\Delta x_i = -a/2$
- ❑ Effective jump length to the positions 9,10,11 and 12 is $\Delta x_i = +a/2$
- ❑ Jump frequency $\Gamma_i = \Gamma$ since the activation energy for jump to any positions will be the same
- ❑ So diffusion coefficient can be written as

$$D = \frac{1}{12}\left(\sum_{i=1}^{4}\Gamma\Delta x_i^2 + \sum_{i=5}^{8}\Gamma\Delta x_i^2 + \sum_{i=9}^{12}\Gamma\Delta x_i^2\right) = \frac{1}{12}\left[4\Gamma\left(-\frac{a}{2}\right)^2 + 4\Gamma(0) + 4\Gamma\left(\frac{a}{2}\right)^2\right]$$

$$= \frac{1}{6}\Gamma a^2$$

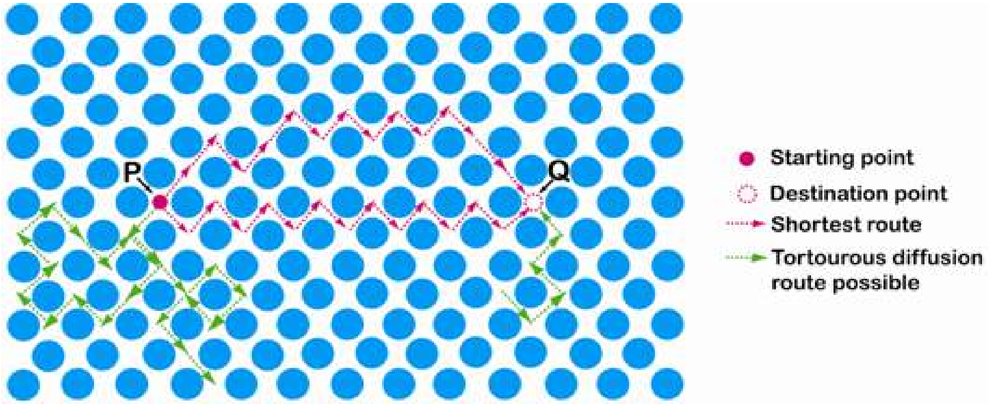
- ❑ Note that it will be the same even if we consider y or z direction in this cubic lattice

Concept of random walk

- We related the jump frequency without going into details of the possibility of next jump after making a successful jump.
- However, we find a very strange fact when we try to relate diffusion coefficient with the jump distance.
- The diffusion coefficient of carbon in γ- iron with FCC structure at 1100°C is in the order of 10^{-10} m^2/s.
- The jump distance can approximately be considered as $\Delta x \approx 10^{-10}$ m
- From the relation derived between diffusion coefficient and the jump frequency, we can write $\Gamma \approx 10^{10}$ /s
- This means, atoms change their position in the order of 10^{10} times per second!
- This number sounds very high, however, if we consider Debye frequency, it sounds reasonable.
- That means atoms make successful jump one out of 10^3 attempts only, since vibration frequency or Debye frequency is roughly in the order of 10^{13}/s.
- Now suppose for the sake of explanation, we consider that atom can jump on a straight line and always goes forward.
- Then after 1 hour, jump distance will be $10^{-10} \times 10^{10} \times 60 \times 60 = 3.6$ kms! The same after 10 hrs will be 36 kms!

Concept of random walk

- ☐ However, previously we have seen that the typical diffusion length is in micron.
- ☐ This indicates that jump of atom is not linear and possibly many times jumps back to previous position to have resultant jump distance zero.
- ☐ Jump is random, as we are considering the jump of atom without any driving force, the jump of atoms will be random.
- ☐ This must be the reason to find much smaller diffusion length in practice.
- ☐ This is the reason to say that when there is no driving force atoms go through a random walk.
- ☐ So we need to relate this random walk with the actual jump distance and the diffusion coefficient of atoms.
- ☐ This sounds very difficult, but can be done following simple approach, without making too many assumptions.



Concept of random walk

- For the sake of explanation, let us consider first atomic arrangement in two dimension.
- Host atoms are shown as blue balls and the interstitial atom as small red ball.
- As mentioned previously, we are considering very small concentration of interstitial atoms (one in few thousands voids) and we may assume that no other interstitial atom is present in the close vicinity.
- Let us consider that the interstitial atom reaches to the point Q from P after certain number of jumps.
- Now question is after how many jumps one atom will reach to that point.
- One can easily count that there are few paths (shown by red arrows) through which it can reach to Q after 14 jumps.
- However, actually, chance is very less that atoms will follow this route.
- It can follow a very torturous long route, as shown by green arrows, to arrive at Q.
- For a number of random jumps, n, the mean distance x, after time ‘t’ is given by

$$x = \lambda\sqrt{n} \Rightarrow \lambda\sqrt{\nu t}$$

- Hence the diffusion distance is proportional to $\sqrt{t}$
- Since the jump of atoms is random in nature, there can be huge difference in the number of jumps that different atoms will make to reach to a particular distance.

Concept of random walk

- Now let us go back to our discussion on diffusion of carbon in iron.
- We have calculated that the average jump of carbon atoms in g-iron at 1100°C is 10^{10} /s.
- If we consider that each jump distance is about 10^{-10} m, then each carbon atom travels total distance of 3.6 kilometers in 1 hr .
- However, because of random nature of jump, on average, atoms will travel the effective distance of

$$x = \sqrt{10^{10} \times 3600} \times 10^{-10} m = 6 \times 10^{6} \times 10^{-10} m = 0.6mm = 600\mu m$$

- Note that this is the order of diffusion length we actually see in carburized steel.

Substitutional diffusion

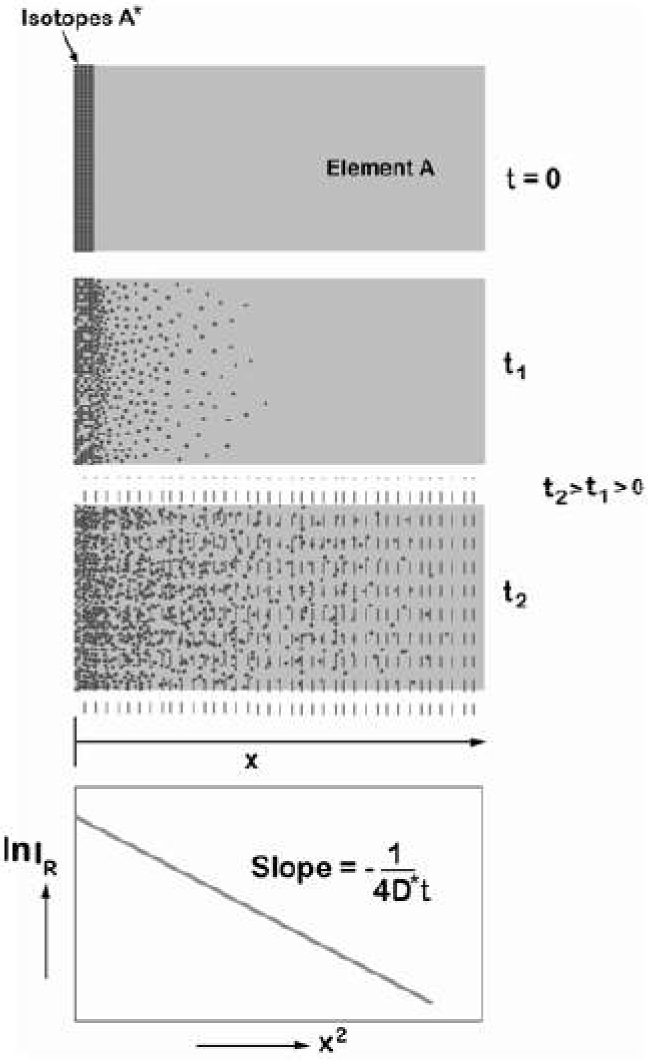
- Previously we discussed about the interstitial atomic mechanism of diffusion.
- Now we shall discuss atomic mechanism of substitutional diffusion, which is very different in nature.
- As explained earlier tracer diffusion method that is monitoring the diffusion of atoms that are detectable is the way to measure self diffusion coefficient.
- First we need to understand the tracer diffusion method and then we shall develop the relation between tracer and self diffusion coefficient.
- As mentioned earlier, we actually determine the tracer diffusion coefficients to understand the self diffusion.
- Unlike previous case, there is difference between these two diffusion coefficients in substitutional diffusion.
- So first let us discuss about the tracer diffusion mechanism, following which self diffusion will be discussed.

Substitutional diffusion

- Suppose we want to measure tracer diffusion of A in the same material A.
- Radio tracer atoms A* are deposited on the surface of an element A and then allowed to diffuse in the substrate.

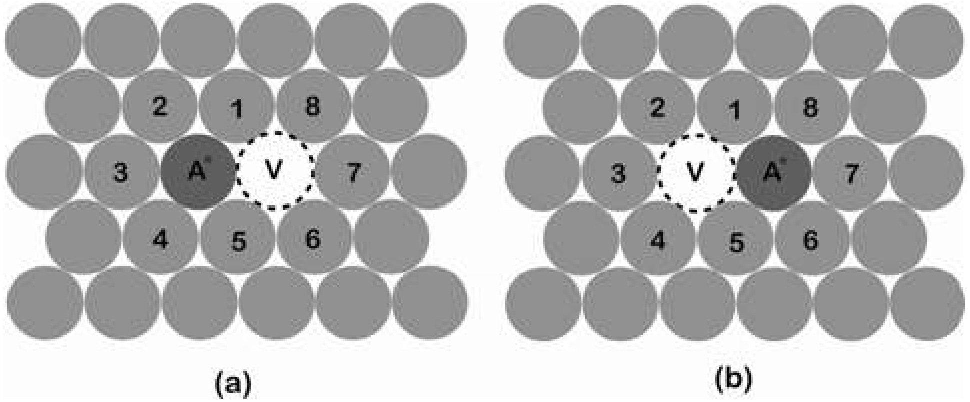
$$\ln I_R = \ln\left(\frac{1}{\sqrt{\pi D_A^* t}}\right) - \frac{x^2}{4D_A^* t}$$

- As explained previously, from the values of slope, we can determine the tracer diffusion coefficient.
- We have discussed before that even almost near the melting point, there could be maximum one vacancy available out of 1000 atoms.
- That means one vacancy is available in a cube of 10 atoms each side. So, we can neglect the interaction between vacancies (That means we are neglecting the contribution from divacancies).
- Now the vacancy can exchange position with any atoms surrounding it. We consider that the tracer atom, with its own probability has changed the position with vacancy.



Substitutional diffusion

- ❑ Further question is that what will be the next position for the tracer atom.
- ❑ The next most probable jump is jumping back to the previous position, since vacancy is available at that site and vacancies are not available at any other sites!
- ❑ Then two successive jumps will cancel the diffusion of the tracer atoms.



(a) (b)

- ❑ However, our experiments reflect that the tracer atoms jump to different distance after a particular time. This further indicates that there should be a possibility for the tracer atom to go forward.
- ❑ This is possible because, the jump of the tracer atoms is dependent on the availability of vacancies, however, a vacancy can exchange position with another atoms.
- ❑ So the vacancy has an equal probability to exchange position with other atoms, for example 1 or 5
- ❑ So the next possible jump of the tracer atom is to 1 or 5, on the condition that vacancy has already exchanged the position with atoms at 1 or 5.

Substitutional diffusion

- ☐ The next possible jump for the tracer atom is to 6 or 8, on the condition that the vacancy has arrived there.
- ☐ The chance for tracer atom to reach to the point 7 is the least since first the vacancy after few jumps has to reach to that position.
- ☐ So on broader sense, we can say that the jump of tracer atom is correlated (unlike jump of interstitial atoms). That means, the jump of a tracer atom is dependent on the other jumps. That further means that the tracer atom does not have true random jump. So the average jump length of the tracer atom should be written as

$$\bar{L}_t^{\,2} = nl^2\left(1 + \frac{2}{n}\sum_{j=1}^{n-1}\sum_{i=1}^{n-j}\cos\theta_{i,i+j}\right)$$ *Second part cannot be taken as zero*

- ☐ On the other hand vacancies can go through a random jump process, since it can exchange position with any atom. So the average jump distance of the vacancies can be written as

$$\bar{L}_v^{\,2} = nl^2$$

- ☐ If we take the ratio of the square of the average jump distance, the value indicates the fraction of the jump of tracer atoms compared to the jump of vacancies.

Substitutional diffusion

- ❑ The ratio is called the correlation factor and expressed as

$$f = n \xrightarrow{\lim} \infty \frac{\overline{L_t}^{2}}{\overline{L_v}^{2}} = n \xrightarrow{\lim} \infty \left(1 + \frac{2}{n} \sum_{j=1}^{n-1} \sum_{i=1}^{n-j} \cos \theta_{i,i+j} \right)$$

- ❑ Since diffusion coefficient is proportional to the square of the jump distance, we can write

$$D^{*} = fD^{V}$$

- ❑ Further since a single vacancy even involves jump of many atoms and again because we calculate the diffusion rate from the jump of many atoms together, we can say that the self diffusion coefficient of the elements is the same as the diffusion coefficient of the vacancies. So we can write

$$D^{*} = fD^{s}$$

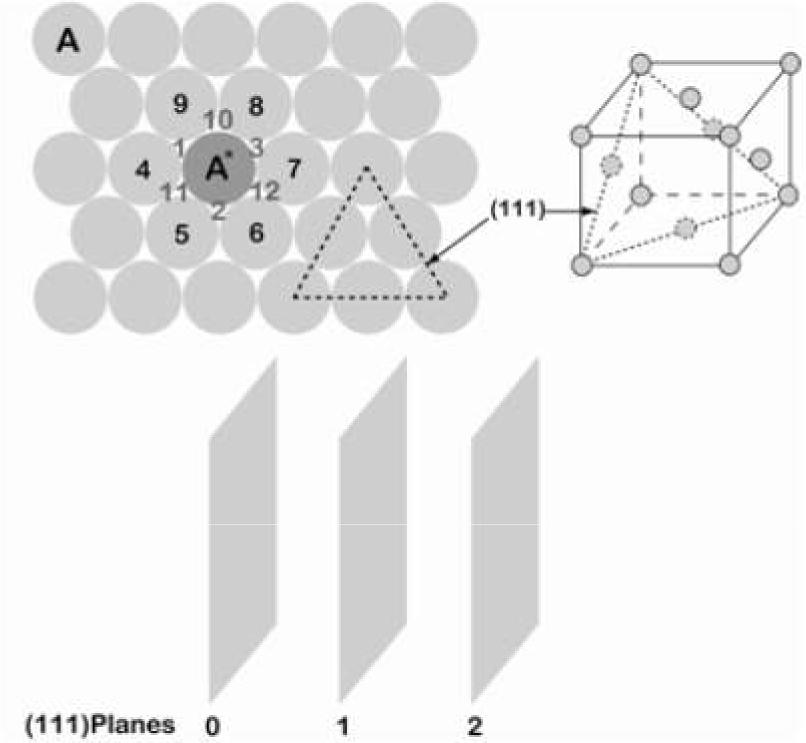
- ❑ The correlation factor in different crystal structure is calculated as

Crystal Structure	***Z***	***f***
Simple cubic	6	0.65549
Body centered cubic	8	0.72149
Face centered cubic	12	0.78145

- ❑ Note: Correlation factor in interstitial diffusion is 1, since we consider that the concentration of interstitial atoms is very low to make random jump possible because of availability of free sites to jump.

Substitutional diffusion

- Now, let us do the similar analysis what we did for the interstitial diffusion to find the relation between the self diffusion coefficient with the jump frequency. However, the starting point will be again the tracer diffusion, since we measure the diffusion of tracer atoms.
- We consider the (111) plane of a FCC crystal. Further we assume that the tracer atom and the atoms 4-9 are sitting on the plane 1.
- Similarly, atoms in voids 1,2 and 3 are sitting on plane 0. That means we can consider that atoms in voids 10,11 and 12 are sitting on plane 2.



- Let us consider the diffusion between plane 1 and 2 only, in the x direction.
- It must be clear that if we consider the jump of the tracer atom from the plane 1 to the plane 2, then it can jump to any of the positions occupied by the three atoms 10, 11 and 12, on the condition that vacancy is available there.
- So the flux of tracer atoms from the plane 1 to the plane 2 can be written as

Substitutional diffusion

- So the flux of tracer atoms from the plane 1 to the plane 2 can be written as

$$\vec{J}{}^{*}_{A} = \frac{3}{12} n_1 f p_v \Gamma_1 = \frac{1}{4} n_1 f p_v \Gamma_1$$

- Γ_1 : Jump frequency per second from plane 1
- Γ_2 : Jump frequency from plane 2
- n_1 and n_2 are the number of tracer atoms/area in plane 1 and 2
- *f* is the correlation factor,
- p_v is the probability that tracer atom will find a vacancy to exchange the position, which should be equal to the fraction of vacancy, X_v present
- Flux of tracer atoms from plane 2 to 1

$$\overset{\leftarrow}{J}{}^{*}_{A} = \frac{3}{12} n_2 f p_v \Gamma_2 = \frac{1}{4} n_2 f p_v \Gamma_2$$

- Following similar analysis, as we did for interstitial diffusion, we can write the resultant flux as

$$J_A^{*} = \frac{1}{4} f X_v \Gamma (n_2 - n_1)$$

$$J_A^{*} = -\frac{1}{4} f p_v \Gamma \Delta x^2 \frac{dc}{dx}$$

Substitutional diffusion

$$D_A^* = \frac{1}{4} f p_v \Gamma \Delta x^2$$

$$D_A^* = \frac{1}{4} f X_v \Gamma \Delta x^2$$

- Further, if we consider the jump to any of the nearest neighbor and considering many atoms together, we can write

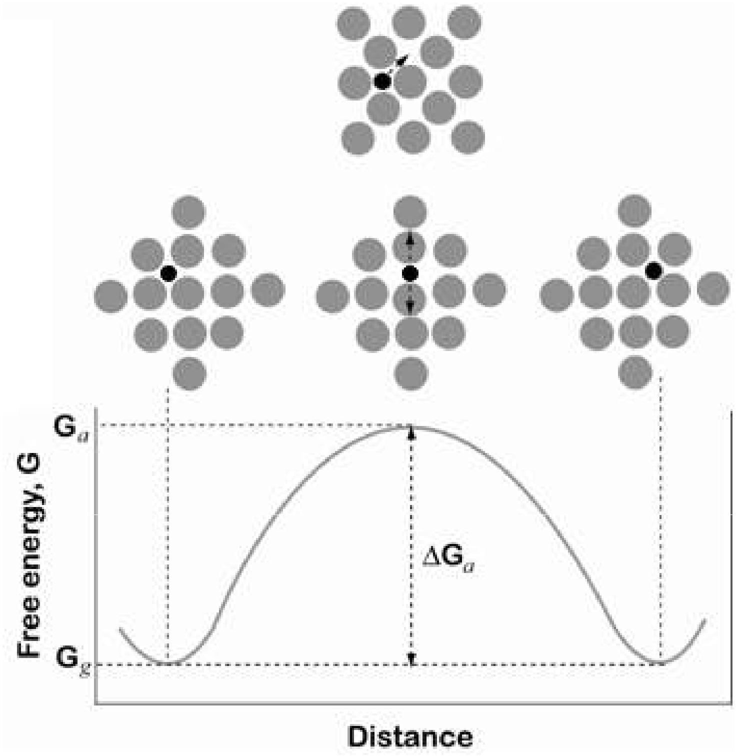
$$D_A^* = f X_v \frac{1}{Z} \sum_{Z=1}^{Z} \Gamma_i \Delta x_i^2$$

- So the self diffusion coefficient can be written as

$$D_A^S = X_v \frac{1}{Z} \sum_{Z=1}^{Z} \Gamma_i \Delta x_i^2$$

Activation energy for diffusion

- We have now seen that atoms jump to the next neighboring position because of thermal vibration.
- In interstitial diffusion there is a chance that the neighboring sites are vacant.
- However, in substitutional diffusion, it is bit complicated, since vacancy should be present in the next neighbor position and then only there will be a possibility of jump.
- First we shall discuss the activation energy required for interstitial self diffusion.
- Atom from ground state, G_g jumps to another ground state but go through an activated state, G_a, where it has to move its neighboring atoms elastically.



- As shown in the figure, atom cannot just exchange the place very smoothly. It has to move the neighbouring elements to clear the passage, since the size of the atom is bigger than the void through which it will diffuse.
- So the energy is required to move the neighboring atoms elastically. Atoms vibrate with average energy and certain number of vibrations can have enough energy to cross the barrier.

Activation energy for diffusion

- Average fraction or probability that atom will cross the barrier is $\exp(-\Delta G_a / RT)$
- Jump frequency can be expressed as $\Gamma_i = \nu \exp\left(\frac{-\Delta G_a}{RT}\right)$
- Diffusion coefficient is expressed as $D = \Gamma_i (\Delta x_i)^2$

$$D = \nu \Delta x^2 \exp\left(\frac{-\Delta G_a}{RT}\right) = \nu \Delta x^2 \exp\left(\frac{-\Delta G_m}{RT}\right) = \nu \Delta x^2 \exp\left(\frac{-Q}{RT}\right) = D_0 \exp\left(-\frac{Q}{RT}\right)$$

- Now $Q = \Delta G_m = \Delta H_m - T\Delta S_m$ activation energy for migration.

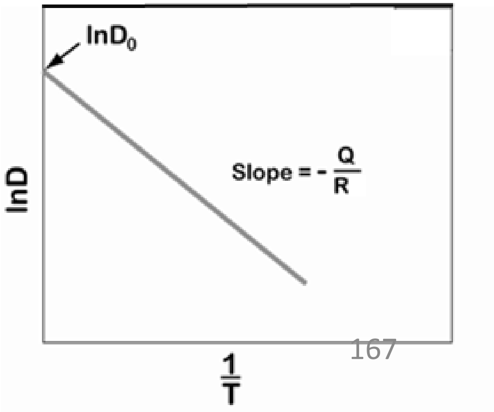
$$D = D_0 \exp\left(-\frac{\Delta H_m}{RT}\right) \quad \textit{where} \quad D_0 = \nu \Delta x^2 \exp\left(-\frac{\Delta S_m}{R}\right) \quad \textit{pre exponential factor}$$

ΔH_m *activation enthalpy for migration*

- Activation energy can be determined from the diffusion coefficients calculated at different temperatures.

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \Rightarrow \ln D = \ln D_0 - \frac{Q}{RT}$$

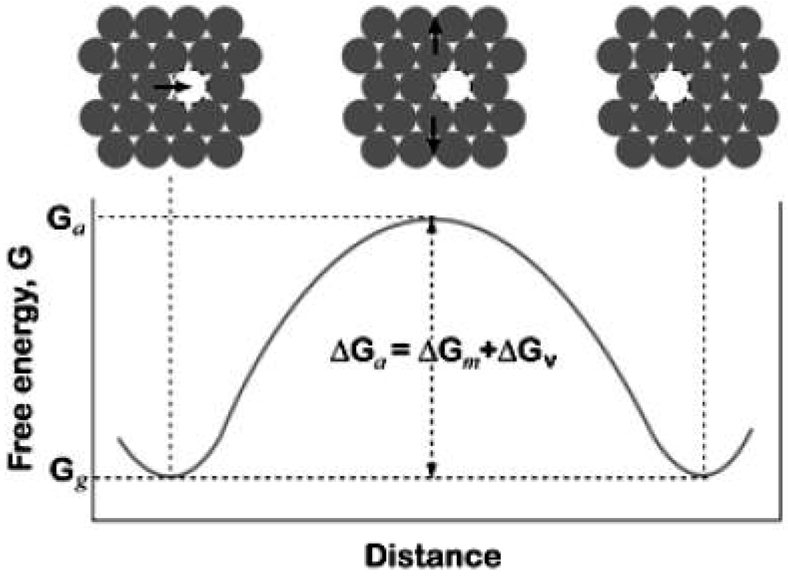
- So if we plot lnD vs. 1/T, we can determine the activation energy for diffusion, Q.



Activation energy for Substitutional diffusion

- Here the main difference between the substitutional and interstitial diffusion is that atom can exchange position only if vacancy is available next to it with its own probability.
- Average fraction of atoms, which will cross the barrier is

$$X_V \exp\left(\frac{-\Delta G_m}{RT}\right)$$



- Jump frequency can be expressed as

$$\Gamma_i = \nu X_V \exp\left(-\frac{\Delta G_m}{RT}\right)$$

- Diffusion coefficient to a particular direction is expressed as

$$D = \Gamma_i (\Delta x)^2$$

$$D = \nu X_V \Delta x^2 \exp\left(-\frac{\Delta G_m}{RT}\right)$$

Substitutional diffusion

- Equilibrium concentration of vacancies

$$X_V = \exp\left(-\frac{\Delta G_V}{RT}\right)$$

$$D = \nu\Delta x^2 \exp\left(-\frac{\Delta G_m + \Delta G_V}{RT}\right) = \nu\Delta x^2 \exp\left(-\frac{\Delta G_a}{RT}\right) = D_0 \exp\left(-\frac{\Delta G_a}{RT}\right)$$

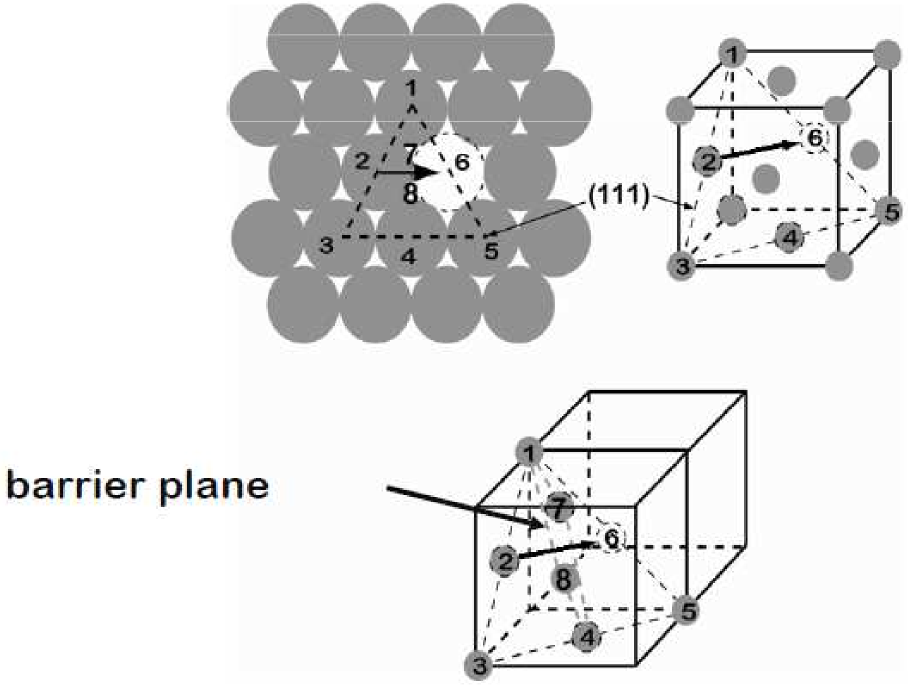
- So G_a is the activation energy for self diffusion. It has two components; activation energy for migration and activation energy for vacancy formation.

$$D = \nu\Delta x^2 \exp\left(\frac{\Delta S_a}{R}\right)\exp\left(\frac{\Delta H_a}{RT}\right) = D_0 \exp\left(-\frac{\Delta H_a}{RT}\right)$$

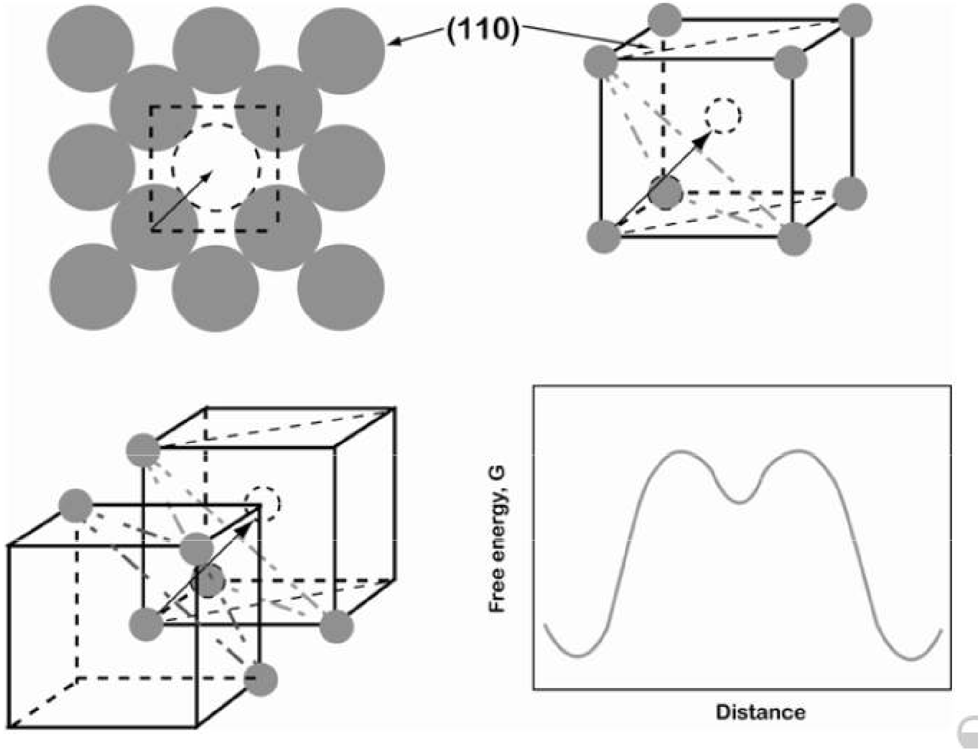
- The same way again, as explained previously about the interstitial diffusion, we can determine the activation energy.

Activation barrier in FCC crystal

- To understand the actual activation barrier, we need to consider the atomic arrangement in three dimension.
- Let us consider atomic arrangement of (111) plane of a FCC unit cell.
- Suppose atoms 1-5 and vacancy at lattice point 6 are on the same plane. If atom 7 is located on the plane below this then atom 8 is located on the plane above it.
- So if atom 2 jumps to 6, then it will have barrier plane with atoms 1, 7, 4 and 8.

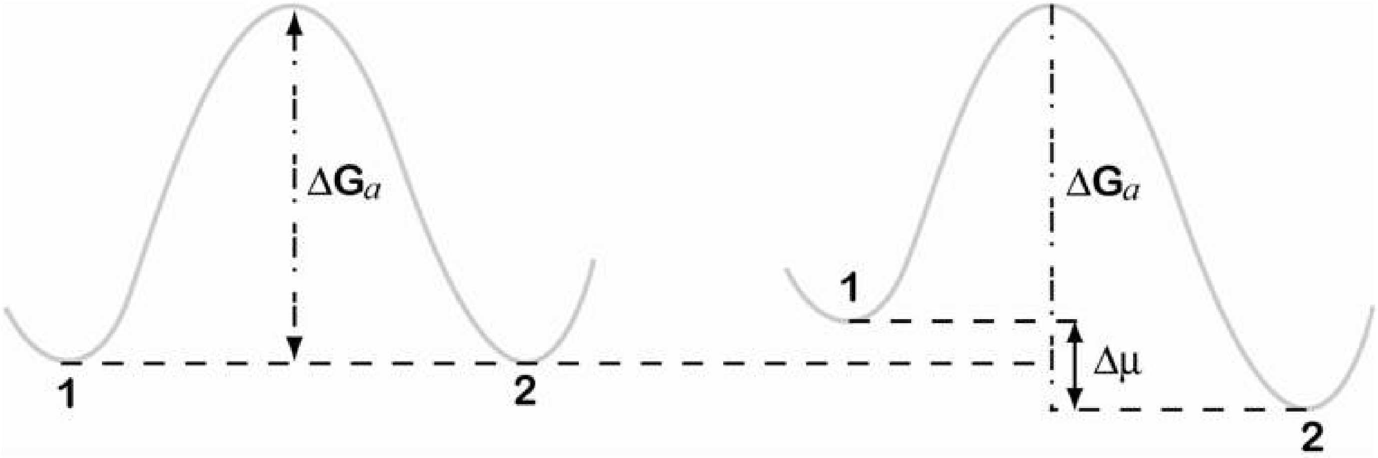


Activation barrier in BCC crystal



- ❑ If the (100) plane is seen, the activation barrier is not clear.
- ❑ Looking at one unit cell, it feels like it has one barrier plane.
- ❑ However, actually it has two barrier planes and that is why it shows two humps in the activation barrier plot

Diffusion under chemical potential gradient



- ☐ In self diffusion, suppose in a cubic crystal, when there is no concentration gradient, the activation barrier for jump of atoms from plane 1 to 2 or plane 2 to 1 is the same and we can write

$$\Gamma_{1\to 2} = \Gamma_{2\to 1} = \nu \exp\left(-\frac{\Delta G_a}{RT}\right)$$

- ☐ Now suppose, we consider a system with chemical potential gradient between plane 1 and 2 by $\frac{d\mu}{dx} = \frac{\Delta\mu}{\Delta x}$ Interplanar distance is Δx
- ☐ Then we can write $\Gamma_{1\to 2} = \nu \exp\left(-\frac{[\Delta G_a - \Delta\mu/2]}{RT}\right)$ $\Gamma_{2\to 1} = \nu \exp\left(-\frac{[\Delta G_a + \Delta\mu/2}{RT}\right)$
- ☐ So we can write that diffusion rate under chemical potential gradient will be higher than self diffusion, since $\Gamma_{1\to 2} > \Gamma_{2\to 1}$

Factors affecting Diffusion

Ease of a diffusion process is characterized by the parameter *D*, *diffusivity.* The value of diffusivity for a particular system depends on many factors as many mechanisms could be operative.

Diffusing species

If the diffusing species is able to occupy interstitial sites, then it can easily diffuse through the parent matrix. On the other hand if the size of substitutional species is almost equal to that of parent atomic size, substitutional diffusion would be easier. Thus size of diffusing species will have great influence on diffusivity of the system.

Lattice structure

Diffusion is faster in open lattices or in open directions than in closed directions.

Presence of defects

As mentioned in earlier section, defects like dislocations, grain boundaries act as short-circuit paths for diffusing species, where the activation energy is diffusion is less. Thus the presence of defects enhances the diffusivity of diffusing species.

Factors affecting Diffusion

Temperature

- Temperature has a most profound influence on the diffusivity and diffusion rates. It is known that there is a barrier to diffusion created by neighboring atoms those need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion.
- Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature.

$$D = D_0 \, e^{\left(-\frac{Q}{kT}\right)}$$

- Where D_0 is a pre-exponential constant, Q is the activation energy for diffusion, R is gas constant (Boltzmann's constant) and T is absolute temperature.
- From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient. It can also be observed that there exists a linear proportional relation between (lnD) and (1/T). Thus by plotting and considering the intercepts, values of Q and D_0 can be found experimentally (*see in next slide for clear understanding*).

Diffusion paths with lesser resistance

Experimentally determined activation energies for diffusion…!

$$Q_{surface} < Q_{grain\ boundary} < Q_{pipe} < Q_{lattice}$$

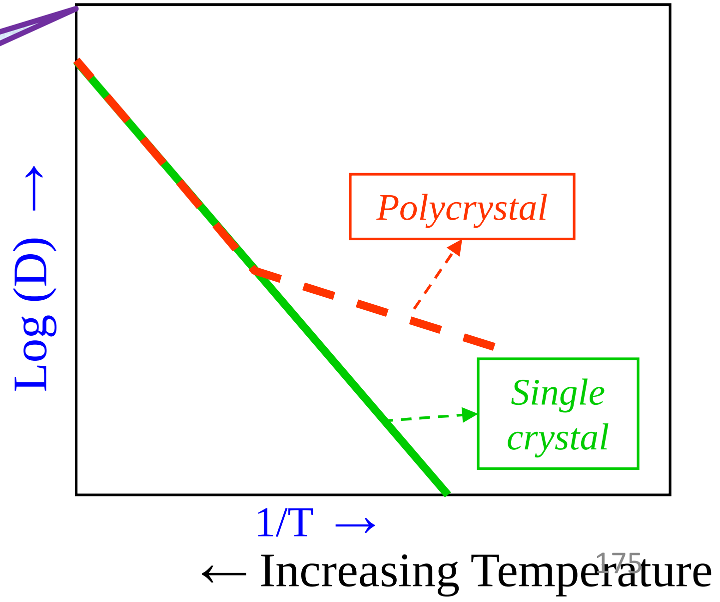
Lower activation energy automatically implies higher diffusivity

Core of dislocation lines offer paths of lower resistance PIPE DIFFUSION

Diffusivity for a given path along with the available cross-section for the path will determine the diffusion rate for that path

Comparison of Diffusivity for self-diffusion of Ag → Single crystal vs. polycrystal

- $Q_{grain\ boundary}$ = *110 kJ /mole*
- $Q_{Lattice}$ = *192 kJ /mole*



Solved Example - 5

Using the following diffusion data, compute the value of D for the diffusion of magnesium in aluminum at 400ºC.

$D_{o(\text{Mg in Al})} = 1.2 \times 10^{-4}$ m²/s Q_d=131 KJ/mol

This problem asks us to compute the magnitude of D for the diffusion of Mg in Al at 400ºC (673K).

$$D = (1.2\times10^{-4}\, m^2/s)\exp\left[-\frac{131{,}000\, J/mol}{(8.31\, J/mol-k)(673k)}\right]$$

$$= 8.1\times10^{-15}\, m^2/s$$

Solved Example - 6

At what temperature will the difusion coefficient for the diffusion of zinc in copper have a value of 2.6×10^{-16} m^2/s
D_o =2.4×10^{-5} m^2/s Q_d=189 KJ/mol

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Zn in Cu has a value of 2.6×10^{-16} m^2/s. Solving for T from below equation

$$\boxed{T = -\frac{Q_d}{R(\ln D_o - \ln D)}}$$

By using the given data we can get

$$\boxed{T = \left[-\frac{189{,}000 J/mol}{(8.31 J/mol-k)[\ln(2.6\times10^{-16} m^2/s) - \ln(2.4\times10^{-5} m^2/s)} \right]}$$

$$\boxed{= 901K = 628^0 C}$$

Solved Example - 7

The diffusion coefficients for nickel in iron are given at two temperatures:

At 1473K 2.2×10^{-15} m^2/s

At 1673K 4.8×10^{-14} m^2/s

a) Determine the values of D_o and the activation energy Q_d.

b) What is the magnitude of D at 1300ºC (1573K)

$$T = -\frac{Q_d}{R(\ln D_o - \ln D\ )}$$

From this equation we can compute two simultaneous equations they are

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_1}\}$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\{\frac{1}{T_2}\}$$

⇨

$$Q_d = -R\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$Q_d = -(8.314 J/mol-K)\frac{[\ln(2.2\times10^{-15}) - \ln(4.8\times10^{-14})}{\frac{1}{1473K} - \frac{1}{1673K}}$$

$$\boxed{= 315{,}700 J/mol}$$

Now we can solve D_o from this equation

$$D_0 = D_1 \, e^{\left(-\frac{Q_d}{RT_1} \right)}$$

$$= (2.2 \times 10^{-15} m^2 / s) \exp\left[\frac{315{,}700 J / mol}{(8.31 J / mol - k)(1473 k)} \right]$$

$$= 3.5 \times 10^{-4} m^2 / s$$

(b) Using these values of D_o and $Q_{d,}$ D $_{at}$ 1573K is just

$$D = (3.5 \times 10^{-4} m^2 / s) \exp\left[-\frac{315{,}700 J / mol}{(8.31 J / mol - k)(1573 k)} \right]$$

$$= 1.1 \times 10^{-14} m^2 / s$$

Summary

Diffusion Faster for	Diffusion Slower for
Open crystal structures	Close packed structures
Lower melting temperature materials.	Higher melting temperature materials
Smaller diffusing atoms	Larger diffusing atoms
Cations	Anions
Materials with secondary bonding	Materials with covalent bonding
Lower density materials	Higher density materials

Interfaces in materials

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Introduction

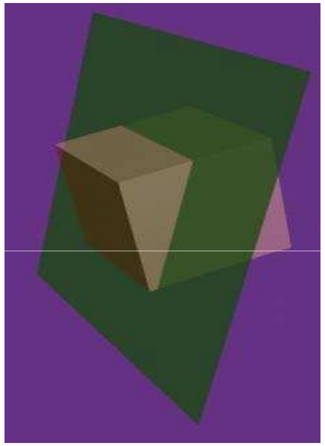
- Nature of interfaces and their energies play an important role during phase transformation in materials.
- During nucleation of a new phase in a metastable parent phase , the interface created between nucleus and the parent phase contributes to an increase in Gibbs energy of the system. This leads to an activation barrier for nucleation of the new phase, whose magnitude, among other factors, also depends on the energy of such an interface.
- Interfaces between the product and parent phases also play significant role during the growth of stable nuclei. Growth occurs by movement of product/parent interfaces, and the mobility of an interface (*the rate at which an interface moves under the influence of a driving force)* depends to a large extent on its structure *(nature).*
- Basically three different types of interface are important in metallic systems.
    - The free surface of a crystal (*solid/vapor interface*) : All crystals possess this type of interface.
    - Grain boundaries (*α / α interface)* : This type separates crystals with essentially the same composition and crystal structure, but a different orientation in space.
    - Interphase interfaces (*α / β interfaces*) : This type of interface separates two different phases that can have different crystal structures or compositions and therefore also includes solid/liquid interfaces.

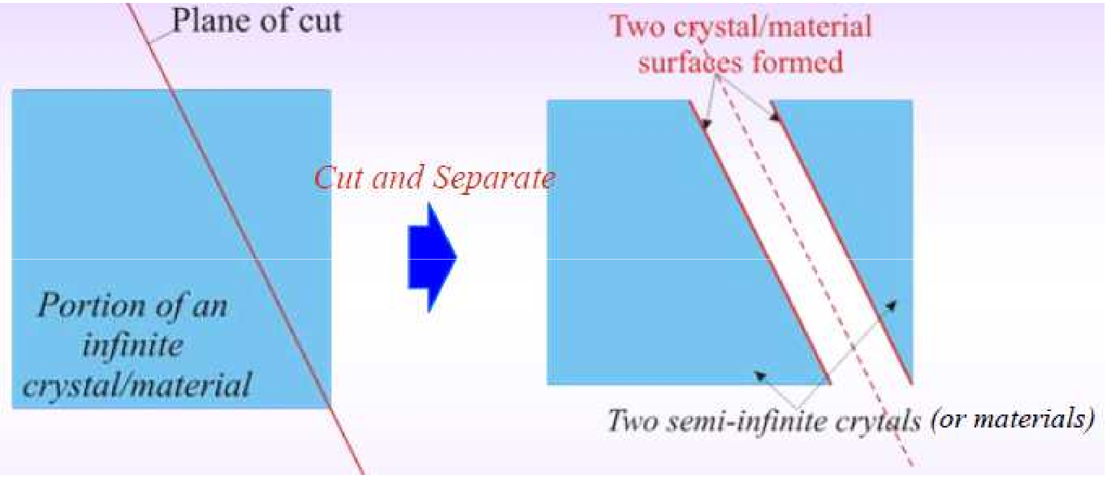
What is a surface and what is an interface?

- ❑ A cut through an infinite crystal creates two surfaces.
- ❑ The joining of two phases creates an interface.

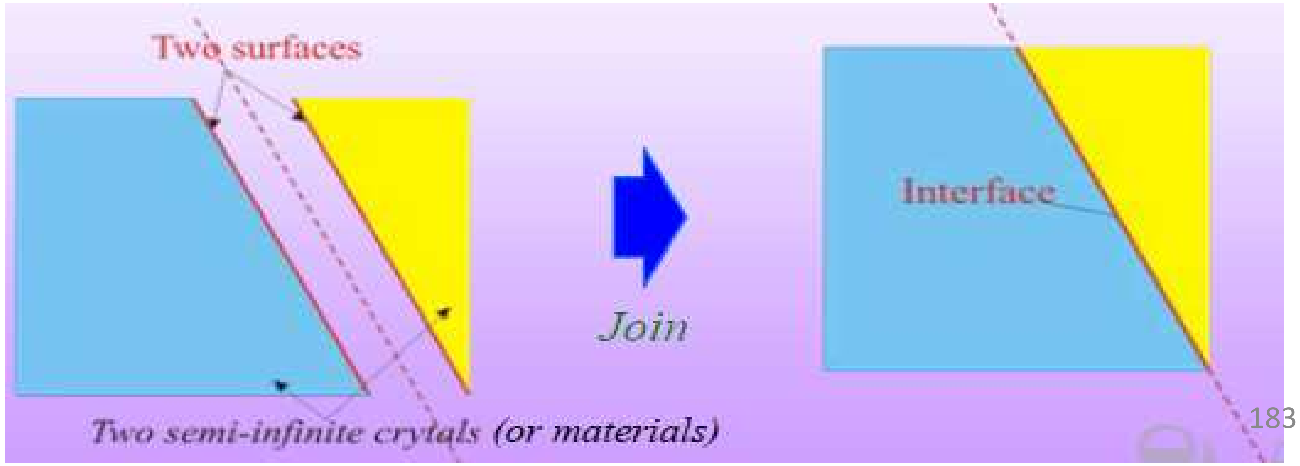
  (Two orientations of the same crystalline phase joined in different orientation also creates an interface called a grain boundary).

Creation of a surface





Creation of an interface



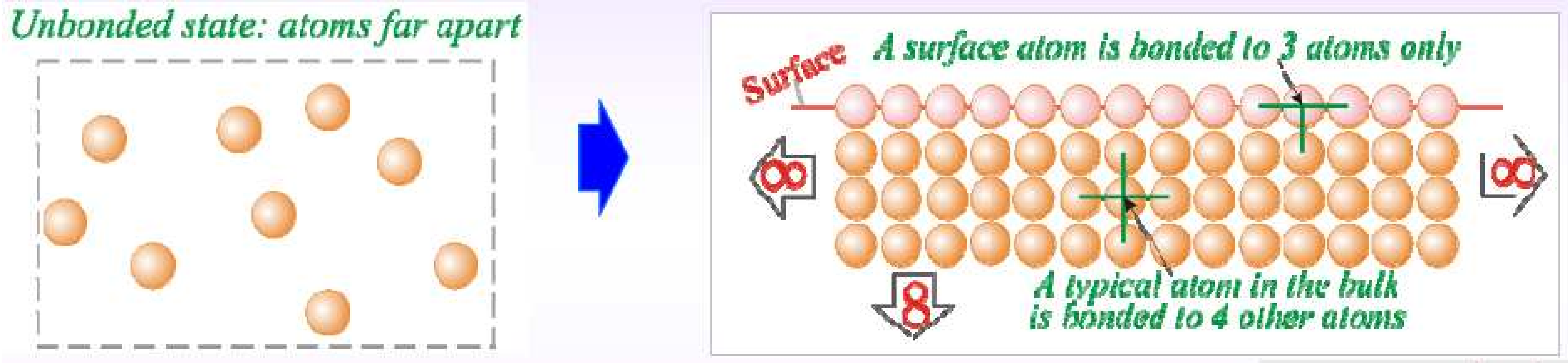
Surface energy

- To understand concept of surface energy let us do the following ideal thought experiment:
  - ✓ start with atoms far apart (upcoming figure)

    such that there is no ‘bonding’ (interactions) between them
  - ✓ bring the atoms close to form a ‘bonded state’ with a surface
- Let the energy of the ‘unbonded state’ be zero. Let the energy lowering on bond formation be E_b per bond.
- Each bulk atom is bonded to 4 atoms (as in the upcoming figure)

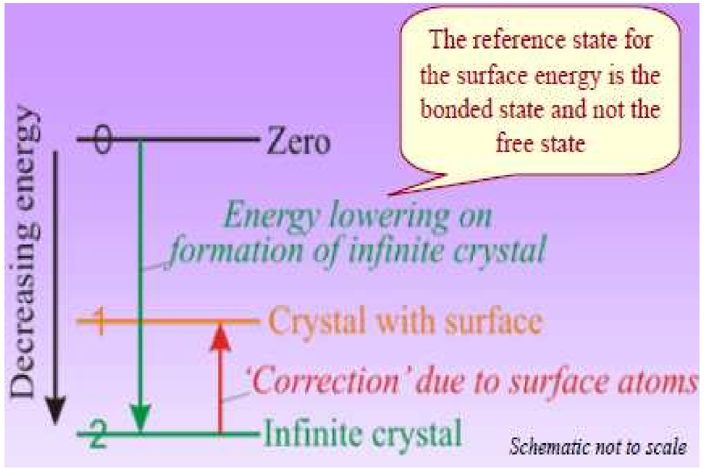
  Energy lowering of bulk atoms = $4E_b$ →this is negative energy w.r.t to the unbonded state
- Each surface atom is bonded to 3 other atoms only

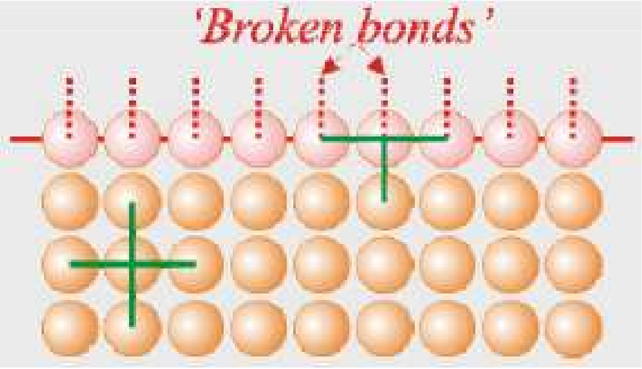
  Energy lowering of bulk atoms = $3E_b$ →this is also negative energy w.r.t to unbonded state!



Surface energy

- Energy lowering on the formation of infinite crystal/unit volume = [- (number of atoms) × $4E_b$]
- Energy of a crystal with a free surface/unit volume = [-(number of atoms)×$4E_b$] + [(number of surface atoms) × $1E_b$]
- *An alternate calculation without invoking surface energy*
- Energy of a crystal with a free surface/unit volume = [-(number of bulk atoms)×$4E_b$] - [(number of surface atoms) × $3E_b$]
- Hence, we have seen that surface energy is ‘not really an energy’ in the truest sense →it is a correction coming about because we had over counted the number of ‘fully bonded’ atoms. (Sir Richard Feynman may say that all forms of energy are accountant’s book keeping terms).
- However, the effects of surface energy is very real.



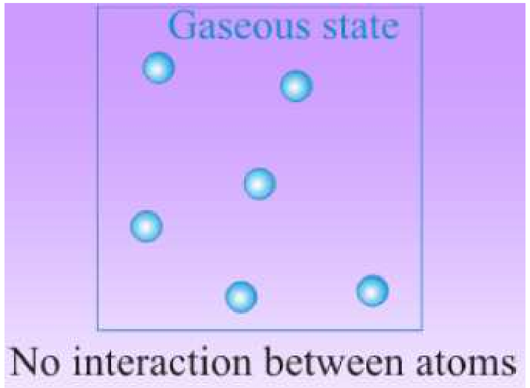


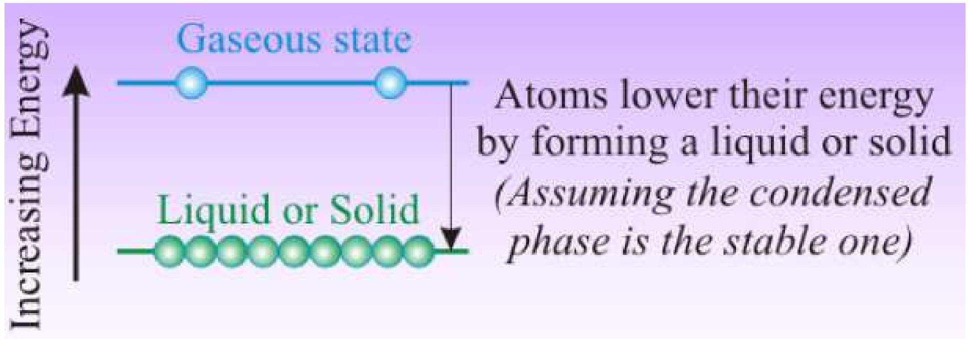
What is a broken bond?

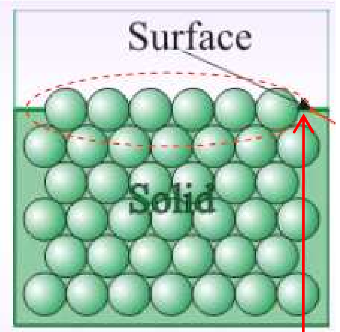
- ❑ The electron distribution in a material can be viewed in a simplified manner using the language of bonds. I.e. isolated atoms have a higher energy as compared to the atoms in a solid (we restrict ourselves to solids for now) and this lowering of energy can be visualized as a bond.
- ❑ The lowering of energy can be reported as bond energy/bond.
- ❑ The number and types of bonds an atom forms in the solid state depends on:
  - ✓ broadly speaking the electronic configuration of the constituent atoms
- ❑ Atoms on the surface have a lower coordination number as compared to atoms in the bulk of the solid. The missing ‘coordination’ can be viewed as a broken bond.
- ❑ The surface need not be a mere ‘termination of the bulk’ and may undergo relaxation or reconstruction to lower its energy.
- ❑ Also the surface may be considered a few atomic layers thick (i.e. it need not just be a monolayer of atoms).

Surface energy

- Surface Energy and Surface Tension are concepts associated with liquids and solids.
- If the Gibbs Free Energy (G) of the solid or liquid is lower than a given gaseous state under certain thermodynamic parameters (wherein the atoms are far apart without any interatomic forces), then the gas will condense (and form a solid or liquid).
- The lowering in the Gibbs Free Energy is due to the cohesive forces in the liquid or the bonding forces in the solid.
- The lowering in energy is calculated for an atom (or entity) fully bonded. The atoms on the surface are not fully bonded.
- The atoms on the surface have a higher energy than the bulk atoms (in the regime where the solid or the liquid have a lower energy than the gaseous state).
- Hence the reference state for the surface is the bulk and not the gaseous state.







Partly bonded surface atoms

Surface energy & Surface tension

- When the calculation of the lowering of the energy of the system on the formation of the condensed state was done all the atoms were taken into account (assumed to be bulk atoms) →i.e. an *over-counting was done*
- The ‘higher energy’ of the surface is with respect to the bulk and not with respect to the gaseous (non-interacting) state
- Hence the reference state for the surface is the bulk and not the gaseous state.
- Hence, it costs energy to put an atom on the surface as compared to the bulk → origin of Surface Energy (γ).
- The surface wants to minimize its area (wants to shrink) →origin of Surface Tension (σ)

$$\sigma = \frac{Force}{Length} = \frac{F}{L} \rightarrow \frac{[N]}{[m]}$$

$$\gamma = \frac{Energy}{Area} = \frac{E}{A} \rightarrow \frac{[J]}{[m^2]} = \frac{[Nm]}{[m^2]} = \frac{[N]}{[m]}$$

Dimensionally γ and σ are identical → Physically they are different type of quantities

γ is a scalar while σ is a second order tensor

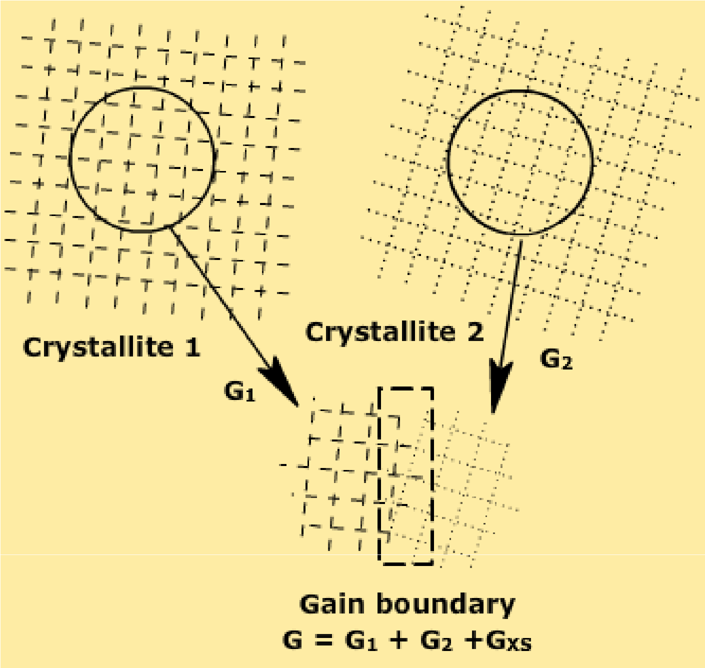
Solid → Surface energy ≈ Surface tension

Liquid → Surface energy ≠ Surface tension

\+ Surface energy is anisotropic

Interfacial free energy

- By interfacial energy we always mean the interfacial free energy. Interfacial free energy is the excess free energy associated with an interface. This excess free energy is the energy cost associated with the introduction of that interface.
- For example, consider two differently oriented crystallites as shown in Fig., let them be put together to form a grain boundary. Let G_1 be the bulk free energy (per unit volume) of the crystallite 1 and G_2 be the bulk free energy (per unit volume) of the crystallite 2.



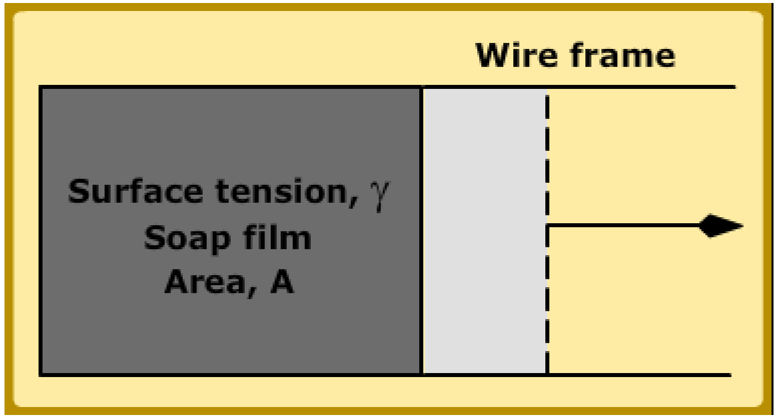
- When they are put together (a volume V_1 of the crystallite 1 and a volume V_2 of the crystallite 2), the resultant system with the grain boundary has an energy G which can be written as

$$G = G_1 V_1 + G_2 V_2 + G_{xs}$$

- G_{xs} is the excess free energy; it is always positive. Grain boundary energy is the excess free energy per unit area of the grain boundary; that is, $G_{xs} = \gamma_{gb} A_{gb}$. From this expression, it is also clear that the units of γ_{gb} is J/m^2

Solids : Interfacial free energy is not surface tension

- In a typical fluid-vapour interface, the interfacial excess free energy is the surface tension: the force that tries to minimize the surface area. If one of the phases across the interface is a solid, then, the surface tension and the interfacial free energy are not the same.
- In a typical fluid-vapour interface, the interfacial excess free energy is the surface tension: the force that tries to minimize the surface area. If one of the phases across the interface is a solid, then, the surface tension and the interfacial free energy are not the same.
- Consider a soap film in a wire frame as shown in Fig., let the surface tension of the film be γ J/m^2. Let ‘A’ be the area of the film. Suppose we increase the area of the film by ‘dA’ . The total work done in stretching the film by ‘dA’ is given by γ dA .
- Consider the free energy of a solid system with a free energy of ‘G’; there are two contributions to G; the first is the bulk free energy G_0; the second is the contribution from the interfaces, which is given by γ A, where γ is the interfacial energy per unit area and A is the area of the interface.



Surface tension in a liquid film

Solids : Interfacial free energy is not surface tension

- ❑ Now, there are two ways in which the interfacial free energy can be changed in this system. One is to keep γ a constant and change A; the other is to keep A constant but change γ itself. The second option is possible only in the case of solids since liquids and vapours cannot support any shear stresses. In other words,

$$G = G_0 + \gamma A$$

$$dG = \gamma dA + A d\gamma$$

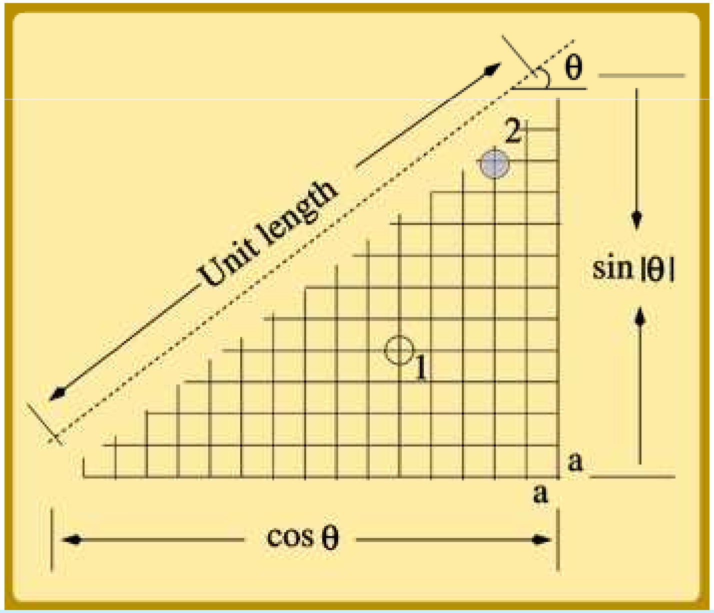
- ❑ Thus, we see that if dγ = 0, the change in free energy is equal to the work done in increasing the interface area; and, hence, the interfacial free energy is the same as surface tension. On the other hand, in general, in solids, the surface tension is not the same as the interfacial free energy.

Interfacial energy anisotropy in solids

- Interfacial energy is the interfacial excess free energy. Hence, it can be written in terms of enthalpy and entropy as follows: $\gamma = H_b - TS_b$
- where, H_b and S_b are the enthalpy and entropy associated with the boundary. Further, if one considers a solid-vapour interface in which a solid is in contact with its vapour, the enthalpy H_b can be replaced by internal energy associated with the boundary, E_b.
- Consider a temperature that is low enough that the entropy contribution to the excess free energy can be neglected. In such a solid-vapour interface, almost all the interfacial energy contribution comes from the internal energy of the boundary. One can estimate the internal energy contribution using a simple bond-breaking model in such a system as follows.
- Let us consider a crystalline solid. In the bulk, each atom has a certain number neighbor with which it bonds. For example, an atom in the bulk FCC structure bonds with 12 of its neighbors; an atom in the bulk BCC structure bonds with 8 of its neighbors; an atom in a simple cubic structure bonds with 6 of its neighbors and so on. However, if an atom is on the surface, certain number of its neighbors are missing; hence, the bonds are not satisfied; such dangling bonds are the ones which contribute to the internal energy of the system.
- In a crystalline solid, obviously, surface formed with different planes will have different energies because the number of broken bonds per unit areas are different on different planes. Hence, the interfacial energy is also anisotropic in crystalline solids. This anisotropy is more prominent at lower temperatures. As temperatures rise, the entropy contribution becomes dominant and makes the interfacial energy less anisotropic.

A bond-breaking model

- In this section, we develop a simple bond-breaking model to calculate the surface energy of a solid; we assume that the solid is in contact with its own vapour; we also assume that the temepratures are low enough that the primary contribution to the surface energy comes from the broken bonds.
- Consider a simple cubic lattice with a lattice parameter of ‘a’ . Let us consider a surface that makes an angle of θ with one of the principal axes of the crystal. The crystalline surface (of unit length) is shown schematically in Figure.



A cubic crystal of lattice parameter ‘a’ with a surface of unit length that makes an angle of with one of the principal axes of the crystal; we have assumed that the crystal is infinite in the third dimension (the axis perpendicular to the plane of the figure).

A bond-breaking model

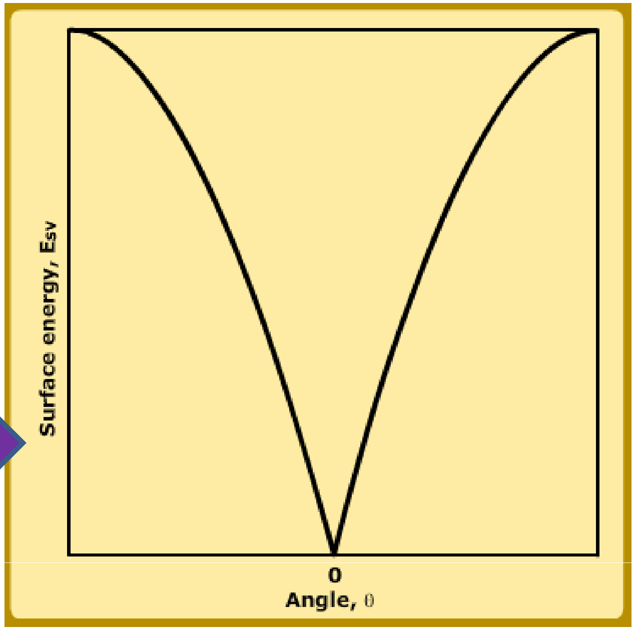
- The open circle marked 1 represents an atom in the bulk; it has formed four bonds in the plane of the figure; if we consider the crystal to be infinite in the direction perpendicular to the plane of the figure, it has also formed two bonds in the perpendicular direction: one above the plane and another below.
- The filled circle, which represents a surface atom has formed only two bonds out of the four that it can form in the plane of the figure. These dangling bonds are the ones that contribute to the enthalpy (in this case, internal energy) of the interfacial free energy.
- From the given geometry, it is clear that the number of broken bonds along the principal axes in the plane of the figure are $Cos(\theta)/a$ and $Sin(|\theta|)/a^2$.
- Accounting for the third dimension, the total number of broken bonds per unit area of such a surface is $[Cos(\theta)+Sin(|\theta|)]/a^2$
- If the bond strength is ε , since each bond is shared between two atoms, the internal energy due to the broken bonds per unit length of the surface plane (E_{sv}) is given by the expression

$$E_{sv}=\frac{\varepsilon}{2a^2}\left[\cos\theta+\sin|\theta|\right]$$

A bond-breaking model

- A schematic plot of the expression is shown in Figure. The key point to note is that the interfacial energy has a cusp at θ = 0; this means that any surface with any angle other than θ = 0; is energetically costlier for the system.

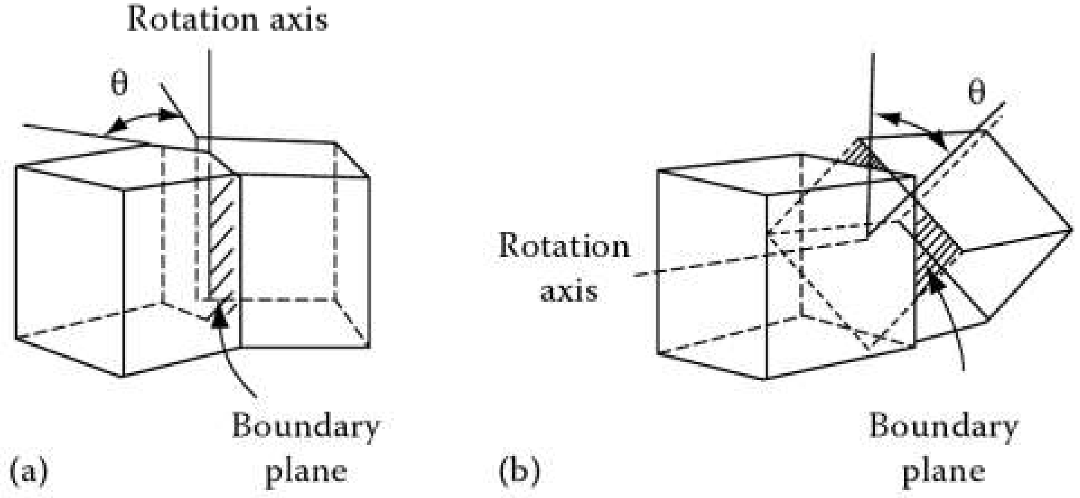
The plot of the expression 'E_{sv}' giving the interfacial energy as a function of , the angle of the surface plane.



- In a simple bond breaking model, we only consider the chemical part of the free energy. In a solid, at the free surface, the atoms can also have elastic relaxation. Such contributions to the free energy can be accounted for using molecular dynamics simulations.
- The grain boundary grooving is a phenomenon in which a grain boundary in contact with a vapor tends to develop a groove to achieve equilibrium of forces acting at the triple junction of vapour phase and the two grains.
- Using the groove angle, it is possible to determine the anisotropy in grain boundary energy. Further, as we show in the next section, the equilibrium shapes of crystals can be non-spherical and facetted. The relative surface areas of different facets in such crystals also indicate the relative surface energies (and hence help determine the anisotropy).

Boundaries in single phase solids

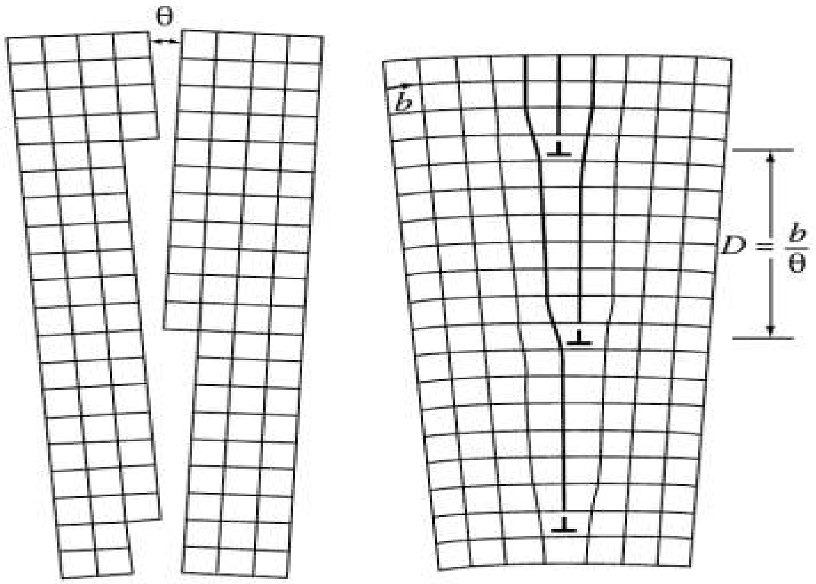
- The grains in a single-phase polycrystalline specimen are generally in many different orientations and many different types of grain boundary are therefore possible.
- The nature of any given boundary depends on the misorientation of the two adjoining grains and the orientation of the boundary plane relative to them.
- There are two type of boundaries called pure tilt boundaries and pure twist boundaries as shown in figure. A tilt boundary occurs when the axis of rotation is parallel to the plane of the boundary (Fig a), where as a twist boundary is formed when the rotation axis is perpendicular to the boundary (Fig. b)



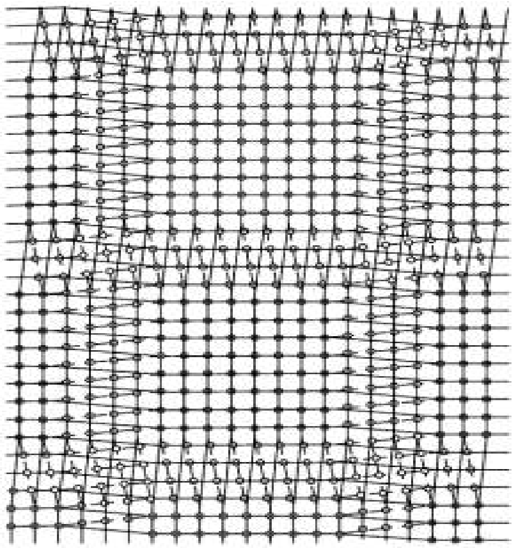
The relative orientations of the crystals and the boundary forming (a) a tilt boundary and a (b) twist boundary

Low-Angle boundaries

- It is simplest to first consider what happens when the misorientation between two grains is small.
- The misorientation angle (θ) is lessthan 10^0-15^0 is called **Low-Angle boundaries.** Two idealized boundaries are illustrated in below figure. These are symmetrical low-angle tilt and low-angle twist boundaries.
- The low-angle tilt boundaries is an array of parallel edge dislocations, whereas the twist boundary is a cross grid of two sets of screw dislocations. In each case the atoms in the regions between the dislocations fit almost perfectly into both adjoining crystals where as the dislocation cores are regions of poor fit in which the crystal structure is highly distorted.



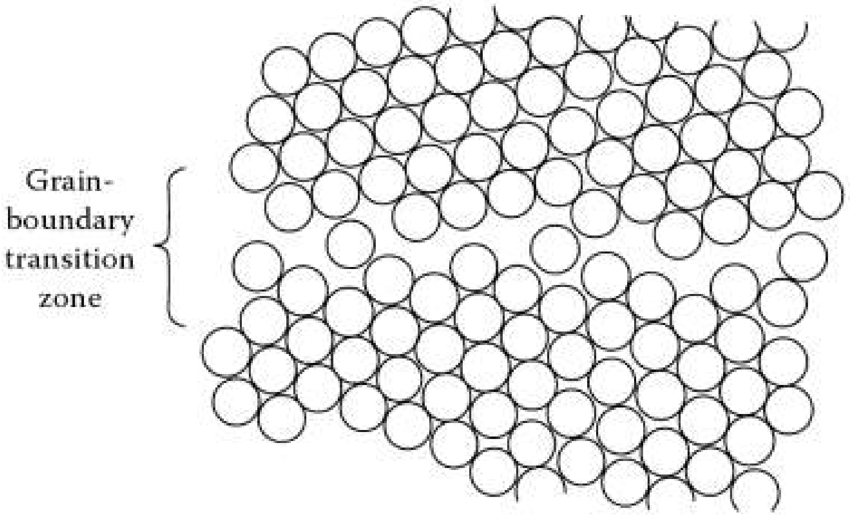
Low-Angle tilt boundary



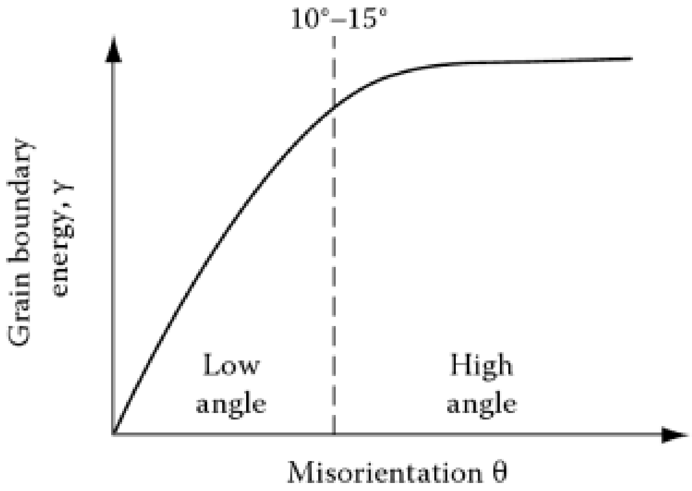
Low-Angle twist boundary

High-Angle boundaries

- When misorientation angle (θ) is greaterthan 10^0-15^0 is called **High-Angle boundaries.**
- High-angle boundaries contain large areas of poor fit and have a relatively open structure. The bonds between the atoms are broken or highly distorted and consequently the boundary is associated with a relatively high energy.
- In low-angle boundaries, however, most of the atoms fit very well into both lattices so that there is very little free volume and the inter atomic bonds are only slightly distorted.
- The regions of poor fit are restricted to the dislocation cores which are associated with a higher energy similar to that of the random high-angle boundary.



Disordered grain-boundary structure



Variation of grain-boundary energy with misorientation

Special High-Angle Grain Boundaries

- ❑ Not all high-angle boundaries have an open disordered structure. There are some special high-angle boundaries which have significantly lower energies than the random boundaries.
- ❑ These boundaries only occur at particular misorientations and boundary planes which allow the two adjoining lattices to fit together with relatively little distortion of the interatomic bonds.

- ❑ The simplest special high-angle grain boundary is the boundary between two grains. If the twin boundary is parallel to the twinning plane the atoms in the boundary fit perfectly into both grains. The resulted is a coherent twin boundary as shown in figure (a).
- ❑ In FCC metals this is { 1 1 1 } close-packed plane. Because the atoms in the boundary are essentially in undistorted positions the energy of a coherent twin boundary is extremely low in comparison to the energy of a random high-angle boundary.

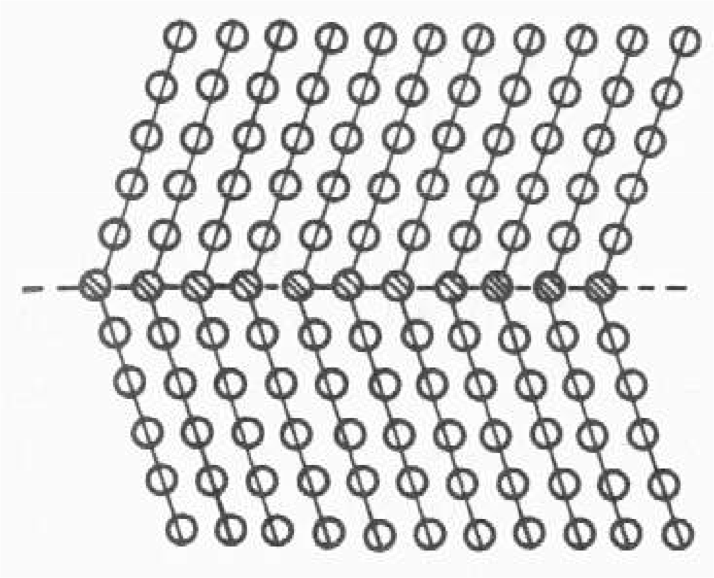


Fig. (a) : A coherent twin boundary

Structure of interfaces

- ❑ If the twin boundary does not lie exactly parallel to the twinning plane, Figure (b) the atoms do not fit perfectly into each grain and the boundary energy is much higher. This is known as an incoherent twin boundary .
- ❑ The energy of a twin boundary is therefore very sensitive to the orientation of the boundary plane.
- ❑ If γ is plotted as a function of the boundary orientation a sharp cusped minimum is obtained at the coherent boundary position is shown in figure (c).

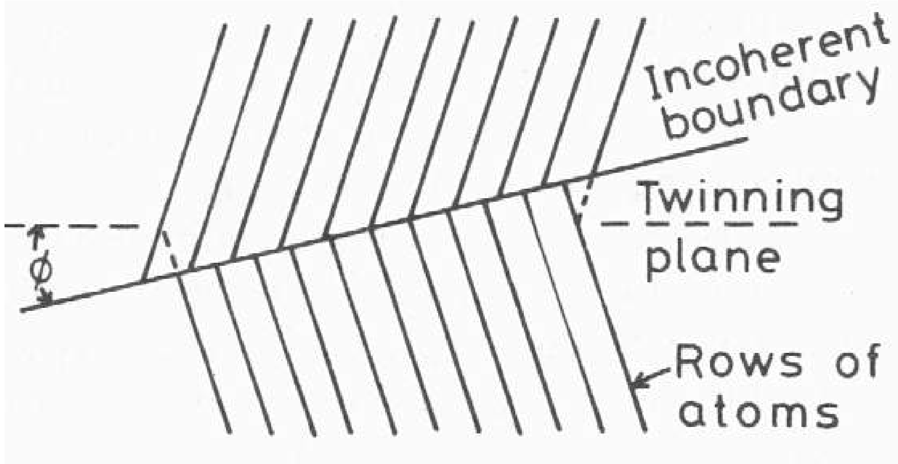


Fig. (b): An incoherent twin boundary

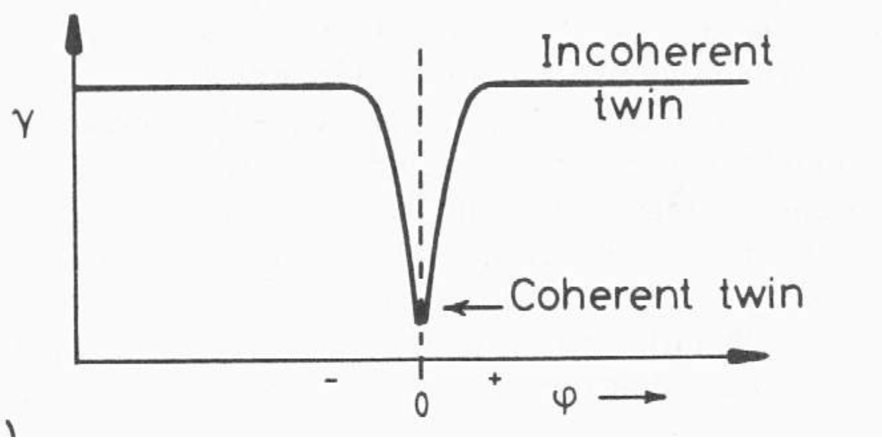


Fig. (b): Twin boundary energy as a function of the grain boundary orientation

Structure of interfaces

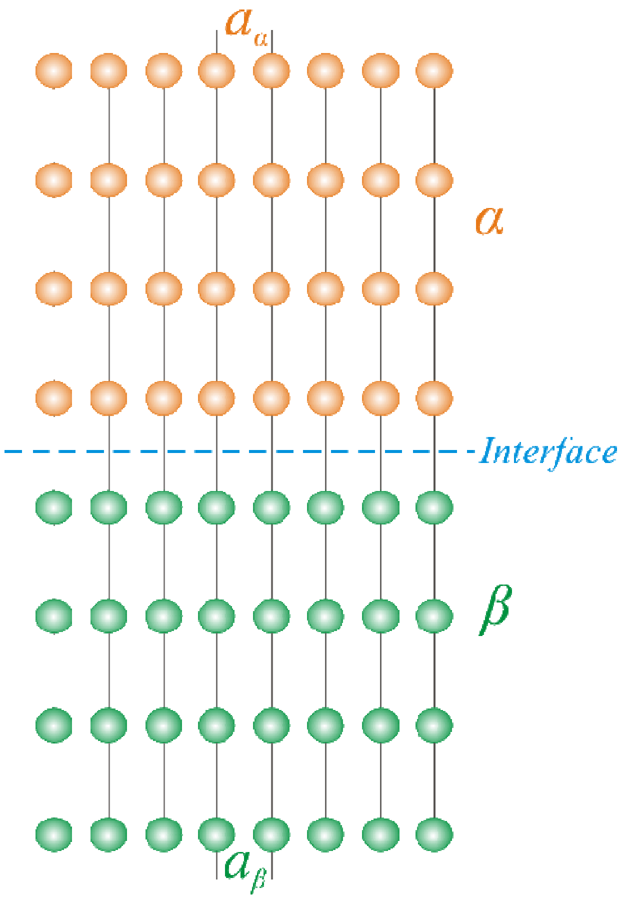
- ☐ we are concerned with crystalline solids and the three types of interfaces that they form, namely, solid-solid, solid-liquid and solid-vapour interfaces.
- ☐ The surface of a single crystal (of a pure element) is an example of a solid-vapour interface. The solidification front is an example of a solid-liquid interface. Any engineering material, if looked under the microscope, is teeming with solid-solid interfaces: grain boundaries, twin boundaries, precipitate-matrix interfaces and so on.
- ☐ Interfaces like the twin and grain boundaries separate the same phase (albeit with different crystal orientations). Hence, they are called homophase interfaces. In contrast, the solid-vapour or precipitate-matrix interface is called a heterophase interface.
- ☐ Many engineering properties of interest are decided by the structure of the solid-solid interfaces in the material. Hence, a classification of solid-solid interfaces in crystalline systems according to the structure of the interface itself is important.
- ☐ Based on the structure of the interface, a (crystalline) solid-solid interface can be classified into three broad categories. They are as follows:
- ☐ **Coherent interface :** An interface across which the lattice planes are continuous are called coherent interfaces.
- ☐ **Incoherent interface :** An interface across which there is no lattice plane continuity is called an incoherent interface.
- ☐ **Semi-coherent interface :** A typical interface in an engineering material is neither fully coherent nor completely incoherent. There are continuous lattice planes interspersed with regions of discontinuity. Such interfaces are called semi-coherent interfaces.

Structure of interfaces

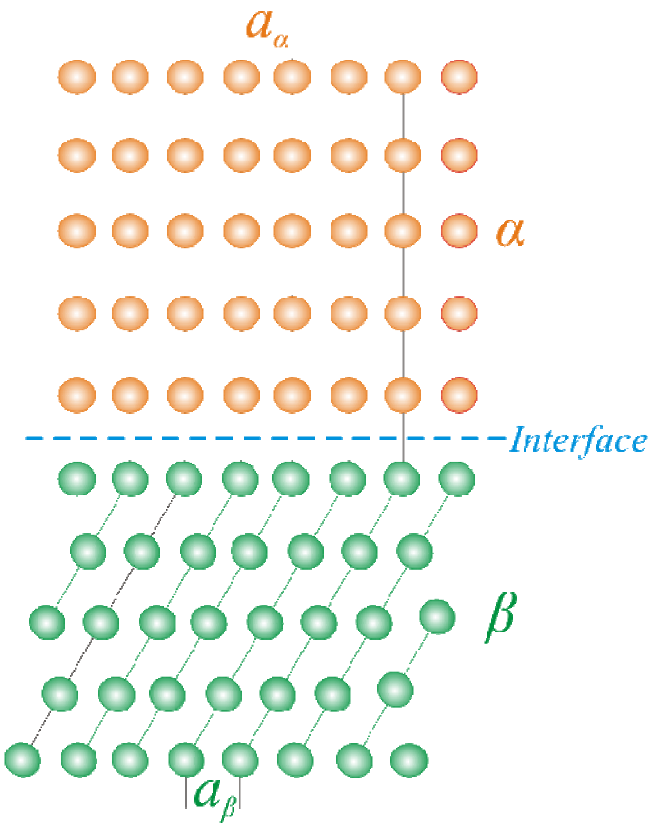
Coherent interface

- Coherent interfaces, as defined earlier, are interfaces across which the lattice planes are continuous. In some cases, the continuity can be maintained with- out any distortion of lattice planes;
- However, in most of the coherent interfaces, the lattice planes are elastically strained to maintain continuity; These elastic strains play a crucial role in determining the properties of the material containing such coherent interfaces.
- The Ni_3Al precipitates in Ni-base superalloys form coherent interfaces with the Ni-rich matrix. Al-Li and Al-Cu are some of the other systems in which coherent precipitates are seen.
- Certain twin boundaries can be coherent; they are known as coherent twin boundaries.
- The epitaxial growth of thin films on substrates also lead to coherent interfaces between the film and substrate.

Coherent without strain



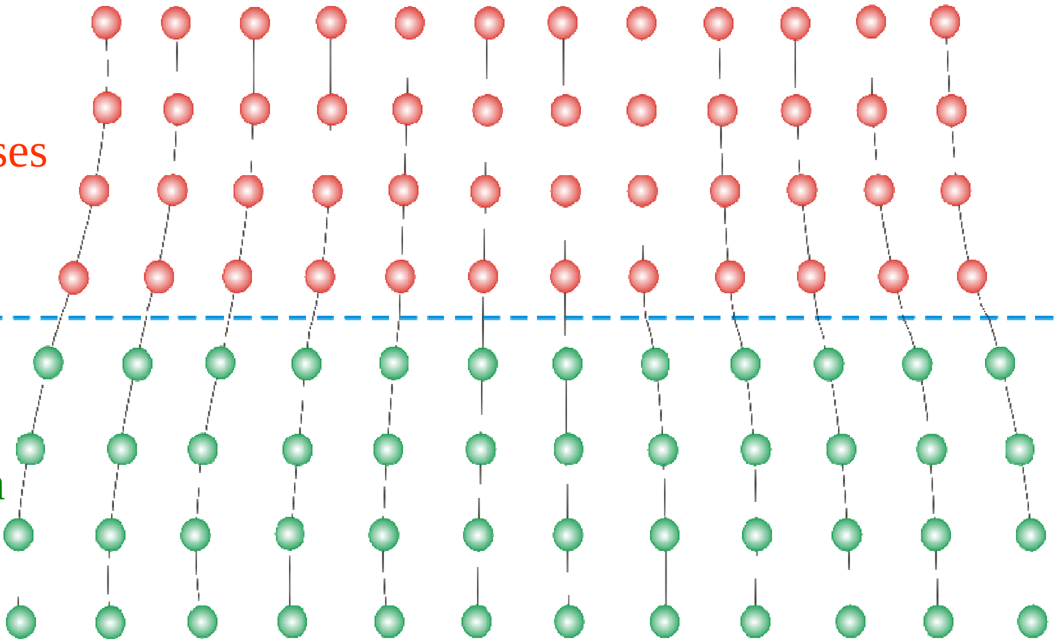
Same crystal structure (& lattice spacing) but different composition



Matching spacing but with different crystal structure

Schematics of strain free coherent interfaces

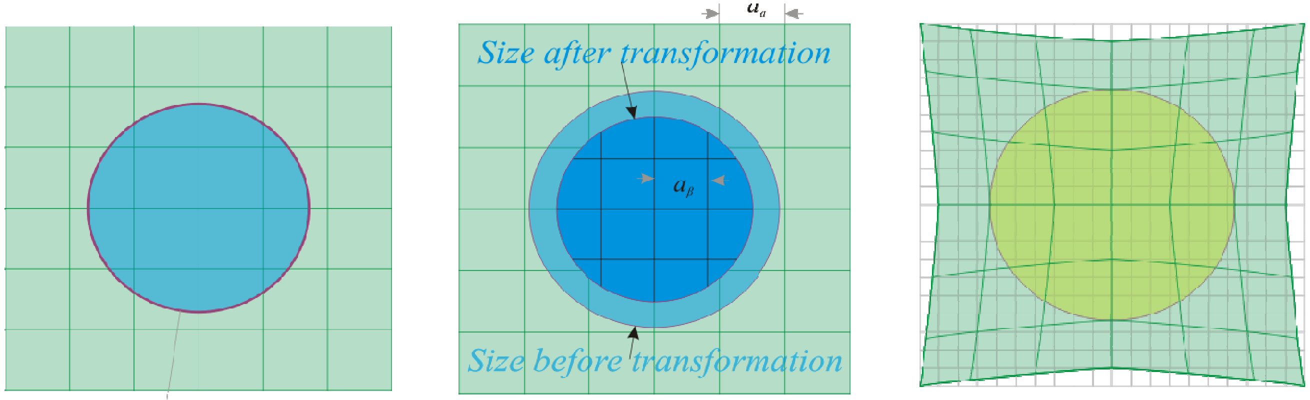
Coherent strained



Region with Tensile Stresses

Coherent interface with a small lattice mismatch
Coherency stresses develop in the adjoining crystals

Compressively stressed region



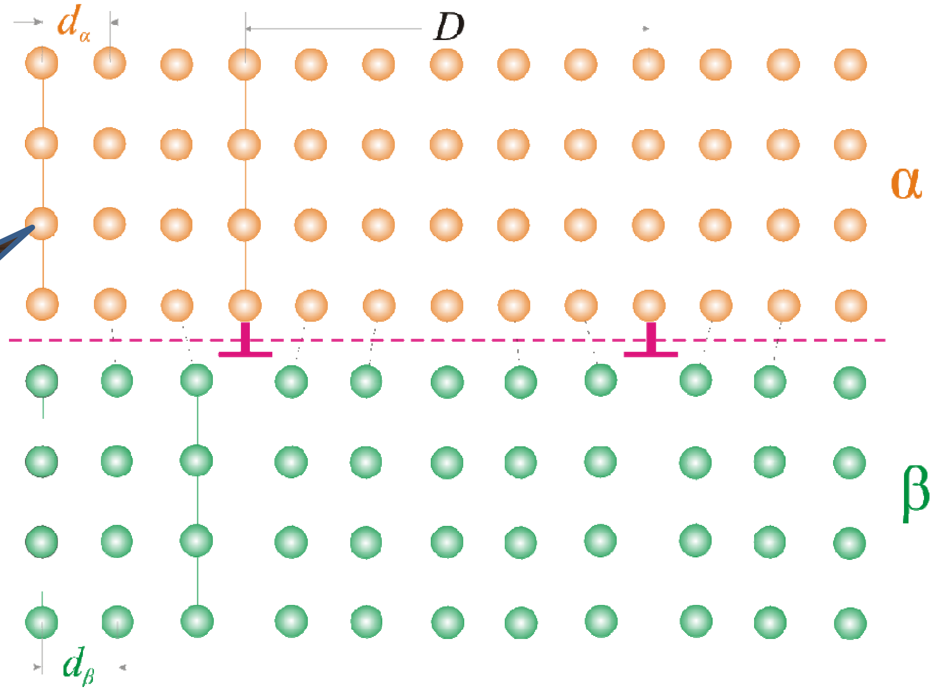
Region transforming to a precipitate of lower volume

Schematic showing a coherent precipitate and the origin of coherency strains

Structure of interfaces

Semi-coherent interface

- Interfaces across which some planes are continuous and some are not are known as semi-coherent interfaces.
- Semicoherent interfaces have an array of dislocations which partially relax the misfit strains arising from the lattice mismatch across the interface between the two materials
- The small angle grain boundaries which are made up of a wall of dislocations and CSL (conicident site lattice) grain boundaries are classic examples of semi-coherent boundaries.

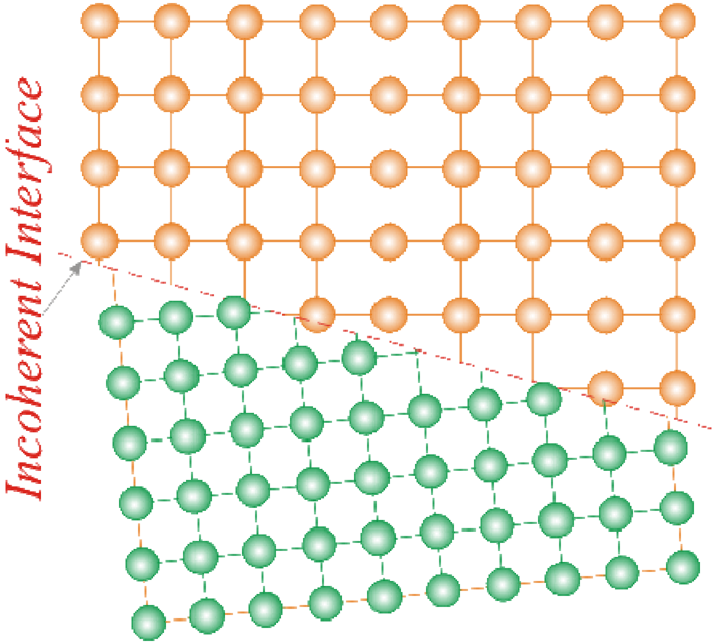


Schematic showing a Semi-coherent interface: A series of edge dislocations at a spacing of D partially relax the misfit strain at the interface

Structure of interfaces

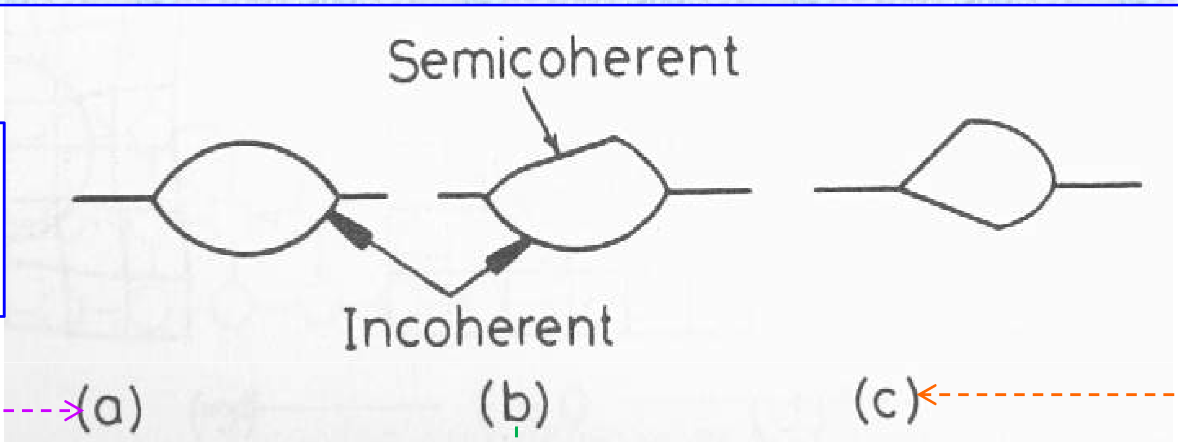
Incoherent interface

- ❑ Incoherent interfaces, as defined earlier, are interfaces across which there is no continuity of lattice planes.
- ❑ There is an elastic energy associated with incoherent boundaries, which is due to the difference in the volume of the particle without any constraints and the volume of the matrix available for the particle.
- ❑ Generic high angle grain boundaries are typically incoherent. Similarly, the inclusions in alloys (for example, MnS in steel) have incoherent interfaces.



Precipitates with mixed type interfaces

Rather special situations arise when a second-phase article is located on a grain boundary as it is necessary to consider the formation of interfaces with two differently oriented grains. Three possibilities are now arise…!

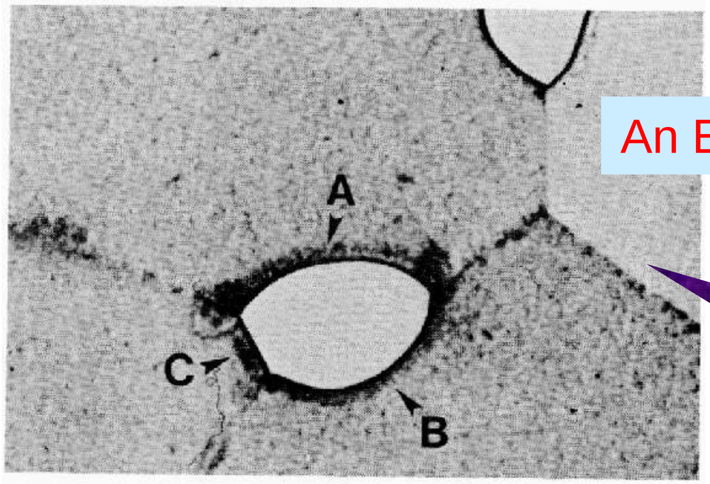


Incoherent interfaces with both grains

A coherent or semi coherent interface with one grain and an incoherent with other

It can have a coherent or semi coherent interface with both grains

An Example of grain boundary precipitate

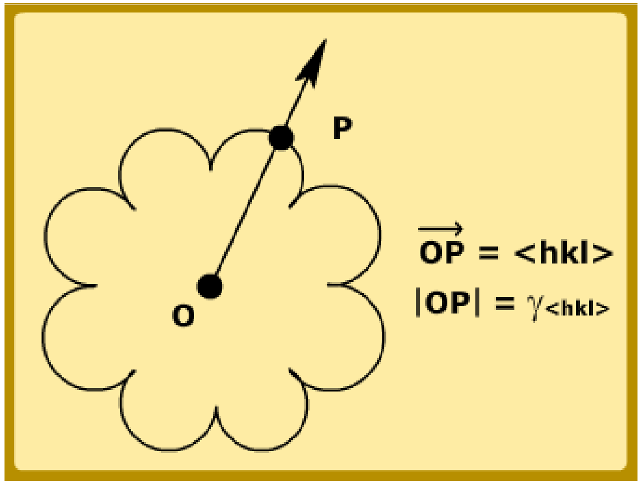


An α precipitate at a grain boundary triple point in an α-β Cu-In alloy. Interfaces A and B are incoherent, value C is semicoherent.

Equilibrium shapes of crystals

- ☐ Wulff plot is a nice way of representing the dependence of the interfacial energy on the surface plane orientation. In this method, we identify the lattice planes by their normals.
- ☐ Given a normal < h k l > and the surface energy γ_{hkl} associated with the surface plane with < h k l > as the normal, from an origin, we plot a point in the <h k l > direction at a distance which is equal to γ_{hkl} .
- ☐ The resultant plot is known as the Wulff plot. In the Figure below, we show a schematic of such a Wulff plot.

- ☐ Given a Wulff plot, it is possible to identify the equilibrium shape. The equilirium shape is that shape which minimises $\sum A_i \gamma_i$ where A_i is the area of the i^{th} plane with an interfacial energy of γ_i .
- ☐ From the Wulff plot, it is clear that planes whose energies lie at the cusps of the Wulff plot have lower energies; hence, if there be cusps in the Wulff plot, the equilibrium shape would consist of facets made up by such planes.

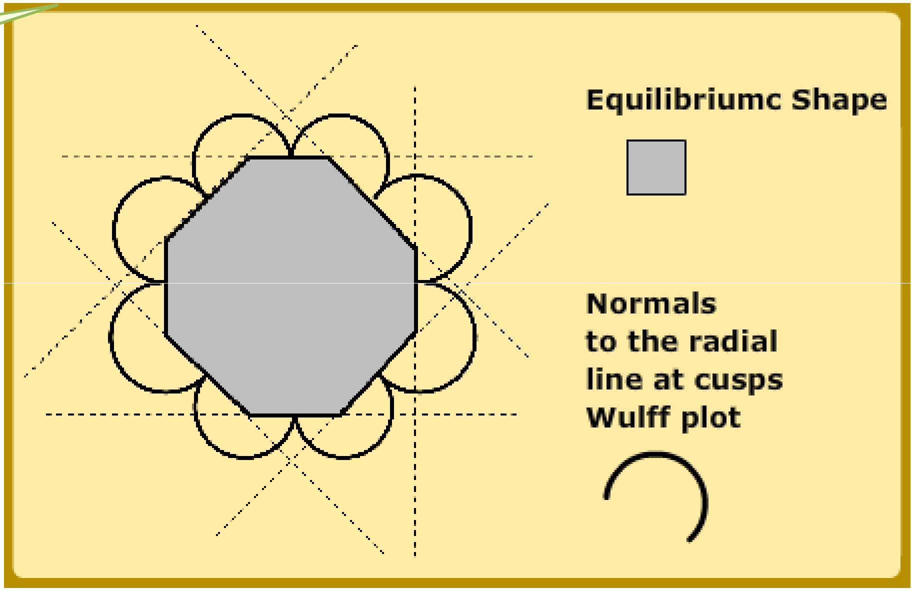


The Wul plot constructed by placing points in various directions corresponding to the surface energy for a plane with that direction as the normal.

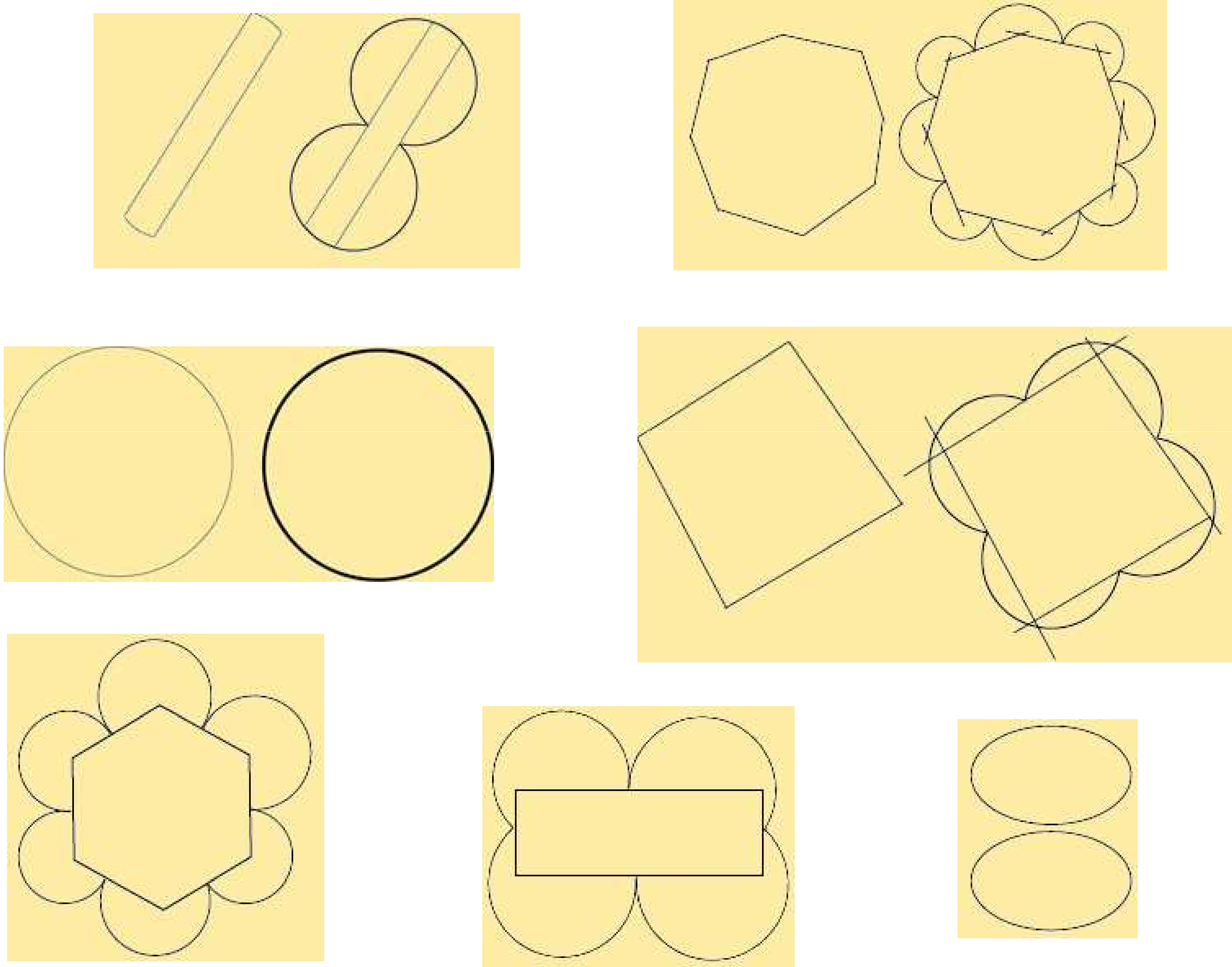
Equilibrium shapes of crystals

- The general procedure to obtain the equilibrium shape from the Wulff plot is shown in Figure; At every point on the Wulff plot, we draw a tangent (which is perpendicular to the radial line). The inner envelope of such tangents gives us the equilbrium shape. If there are cusps in the Wulff plot, this construction give facetted equilibrium shapes.

The Equilibrium shape identified from the Wul plot. We draw the normals to the radial direction at every point. The inner envelope of the normals forms the equilibrium shape. Note that when there are cusps, the normals at the cusps form facetted interfaces as shown.

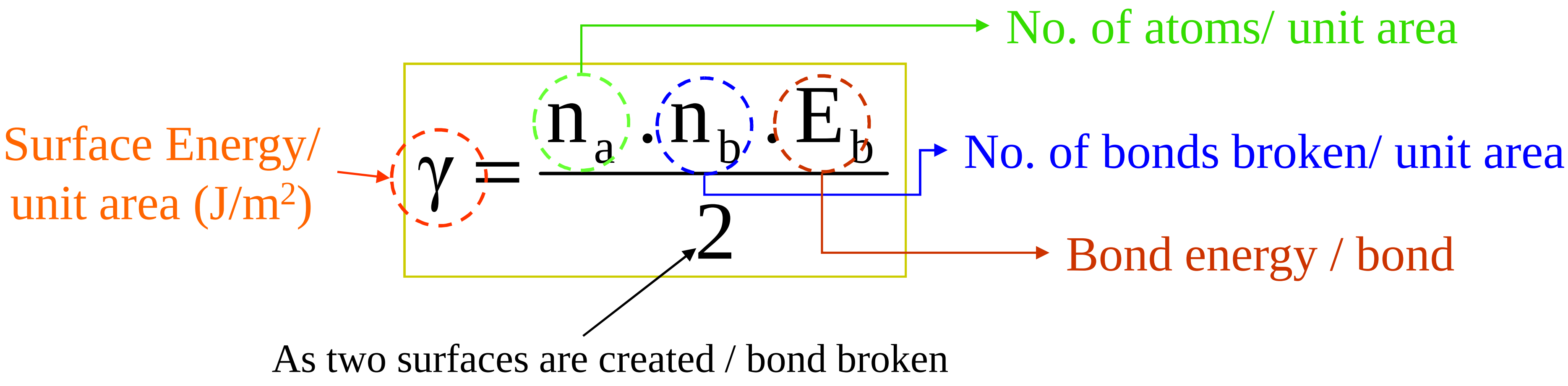


Equilibrium shapes of crystals



External Surface of the crystal

❑ External surfaces have energy related to the number of bonds broken at the surface



$$\gamma = \frac{n_a \cdot n_b \cdot E_b}{2}$$

No. of atoms/ unit area

Surface Energy/ unit area (J/m^2)

No. of bonds broken/ unit area

Bond energy / bond

As two surfaces are created / bond broken

Surface free energies of some crystals (J/m^2)								
NaCl	LiF	CaF$_2$	MgO	Si	Ag	Fe	Au	Cu
0.30	0.34	0.45	1.2	1.24	1.14	1.4	1.4	1.65

Comparison of Interfacial Energies of Various 2D Defects

Metal	Surface	Solid/ Liquid	Grain Boundary	Twin Boundary	Stacking Fault
	(J/m^2)				
Gold	1370	132	364	~10	55
Silver	1140	126	790	-	17
Platinum	1310	240	1000	196	~95
Nickel	1860	255	690	-	~400
Aluminium	1140	-	625	120	~200
Copper	1750	177	646	44	73
Iron	1950	204	780	190	-
Tin	680	54.5	-	-	-

Type of boundary	**Energy (J/m^2)**
Surface	~ 0.89
Grain boundary	~0.85
Twin Boundary	~ 0.63 0.498 (Cu)
Stacking Fault	0.08 (Cu) 0.2 (Al)

SOLIDIFICATION

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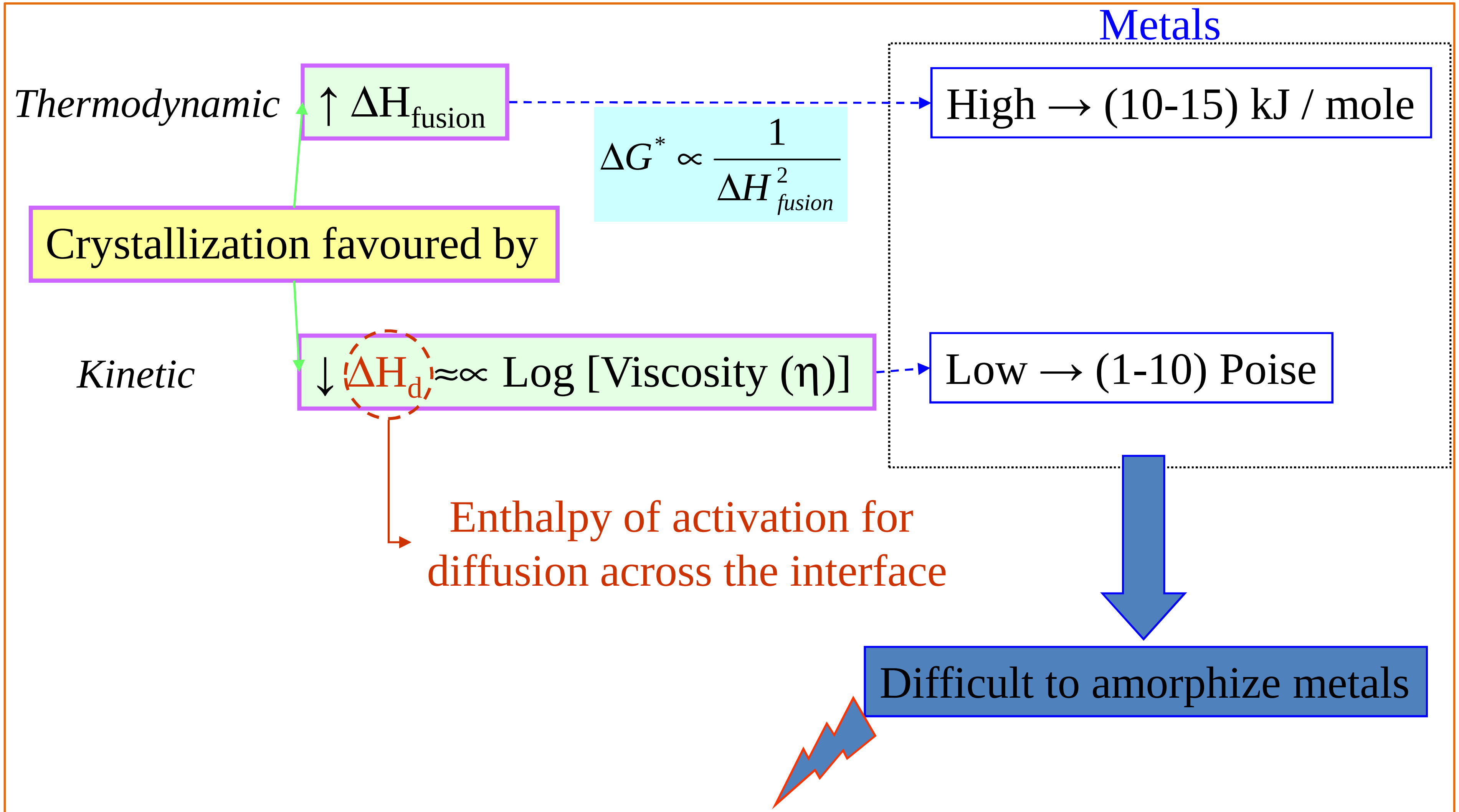
Introduction

- ❑ Let us start understanding phase transformations using the example of the solidification of a pure metal.
- ❑ 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.*

Mechanism of Crystallization



Metals

Thermodynamic ↑ ΔH_{fusion}

High ⟶ (10-15) kJ / mole

$$\Delta G^* \propto \frac{1}{\Delta H^2_{fusion}}$$

Crystallization favoured by

Kinetic ↓ $\Delta H_d \approx\propto$ Log [Viscosity (η)]

Low ⟶ (1-10) Poise

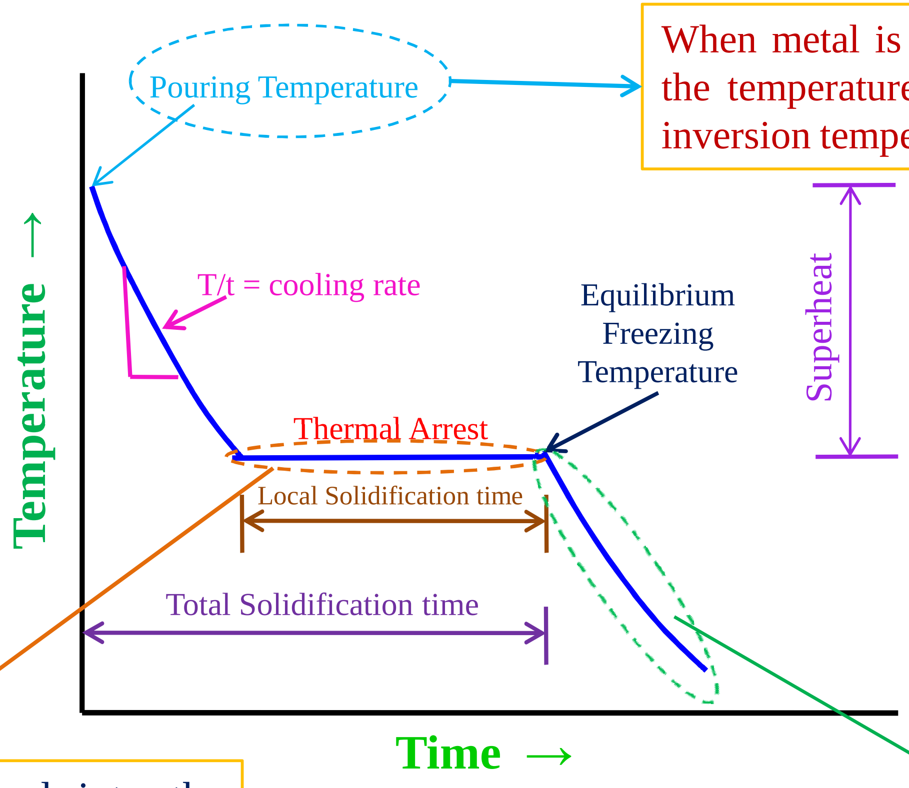
Enthalpy of activation for diffusion across the interface

Difficult to amorphize metals

Very fast cooling rates ~10^6 K/s are used for the amorphization of alloys

→ *splat cooling, melt-spinning.*

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

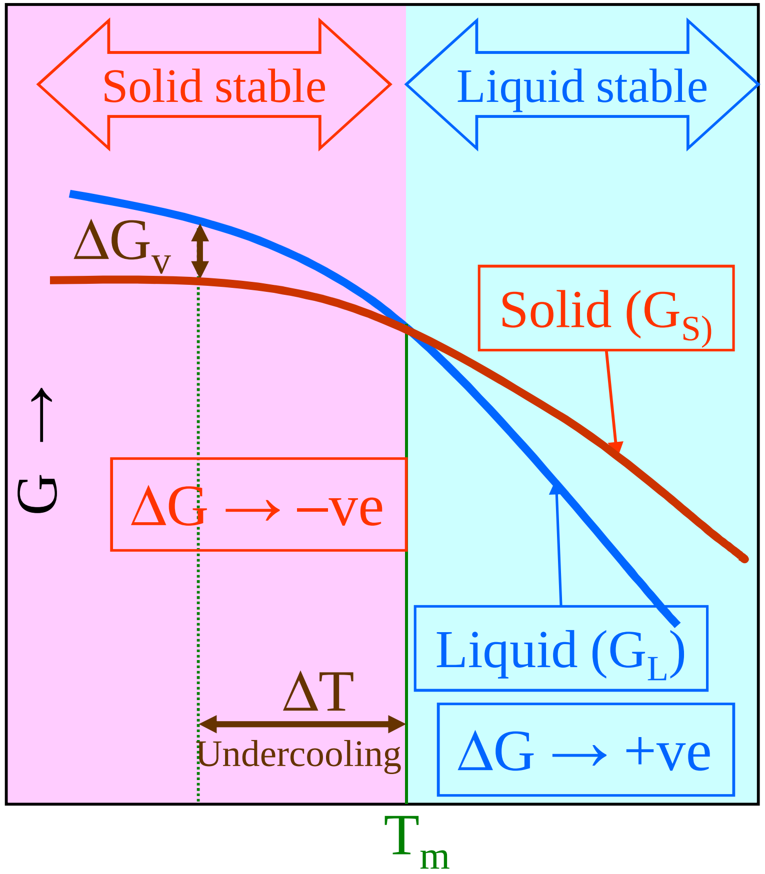
The solidified metal in the mould (called casting) gets cooled in the mould to the temperature of the surroundings

Driving force for solidification

- In dealing with phase transformations, we are often concerned with the difference in free energy between two phases at temperatures away from the equilibrium temperature.
- For example if a liquid metal is under cooled by ΔT below T_m before it solidifies, solidification will be accompanied by a decrease in free energy ΔG (J/mol) as shown in figure.
- This free energy decreases provides the driving force for solidification. The magnitude of this change can be obtained as follows.
- The free energies of the liquid and solid at a temperature T are given by

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$



Therefore, at a temperature T $\Delta G = \Delta H - T\Delta S$ →①

Where $\Delta H = H^L - H^S$ *and* $\Delta S = S^L - S^S$

Driving force for solidification

- At the equilibrium melting temperature T_m the free energies of solid and liquid are equal, i.e., $\Delta G = 0$. Consequently

$$\Delta G = \Delta H - T_m \Delta S = 0$$

- And therefore at T_m

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

→②

- This is known as the entropy of fusion. It is observed experimentally that the entropy of fusion is a constant ≈ R (8.3 J/mol . K) for most metals (Richard's rule).
- For small undercoolings (ΔT) the difference in the specific heats of the liquid and solid (C_p^L - C_p^S) can be ignored.
- Combining equations 1 and 2 thus gives

$$\boxed{\Delta G \cong L - T\frac{L}{T_m}}$$

- i.e., for small ΔT

$$\boxed{\Delta G \cong \frac{L\Delta T}{T_m}}$$

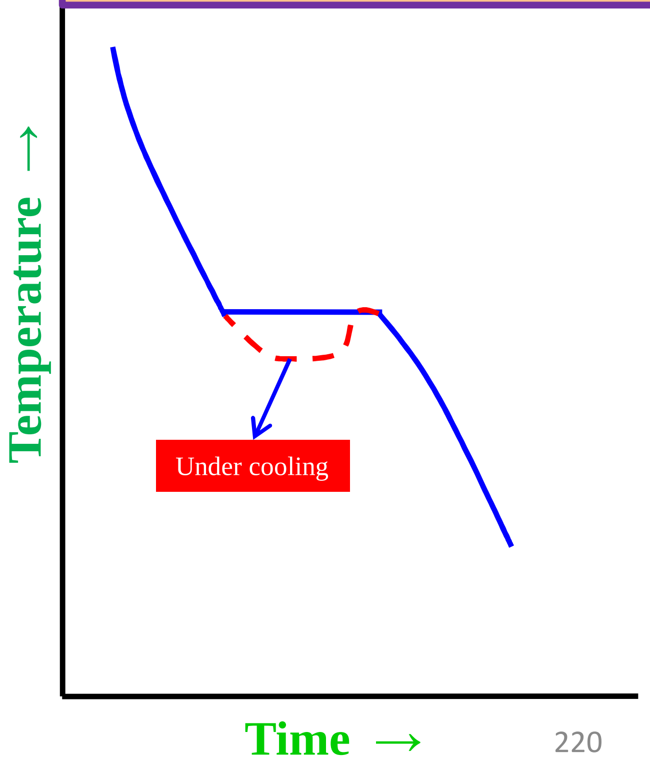
This is called Turnbull's approximation

Solidification of pure metal : Supercooling

- 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

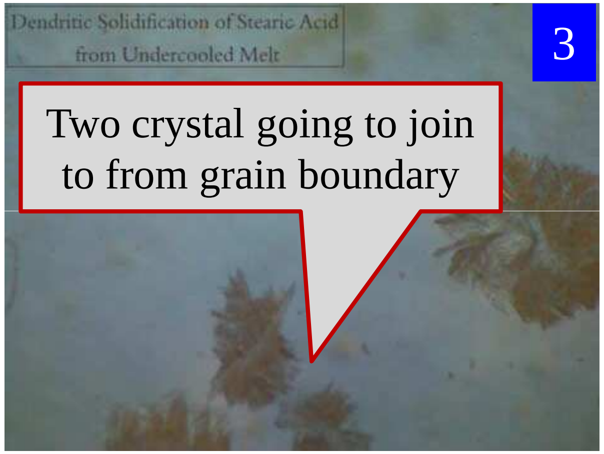
1

Solid

2

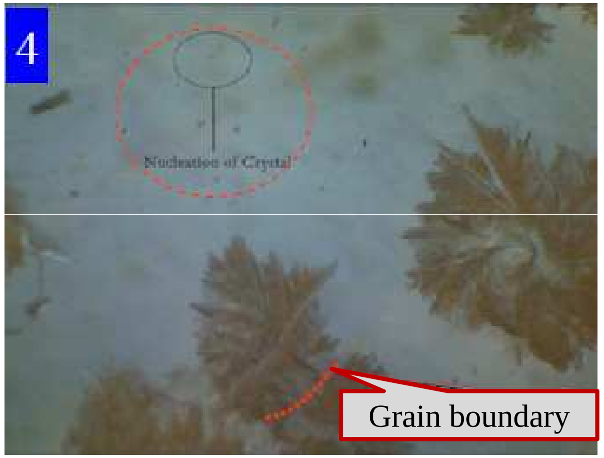
Growth of crystal

3



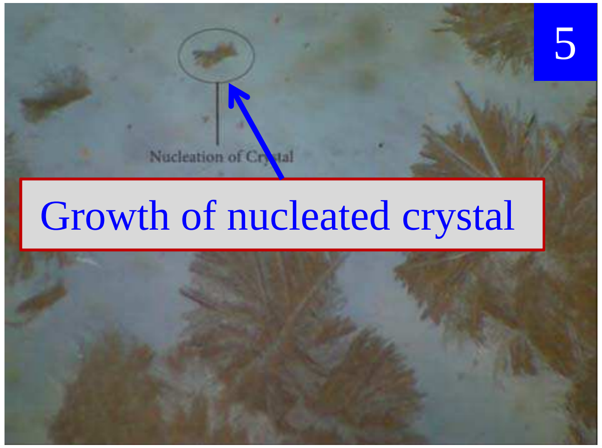
Two crystal going to join to from grain boundary

4



Grain boundary

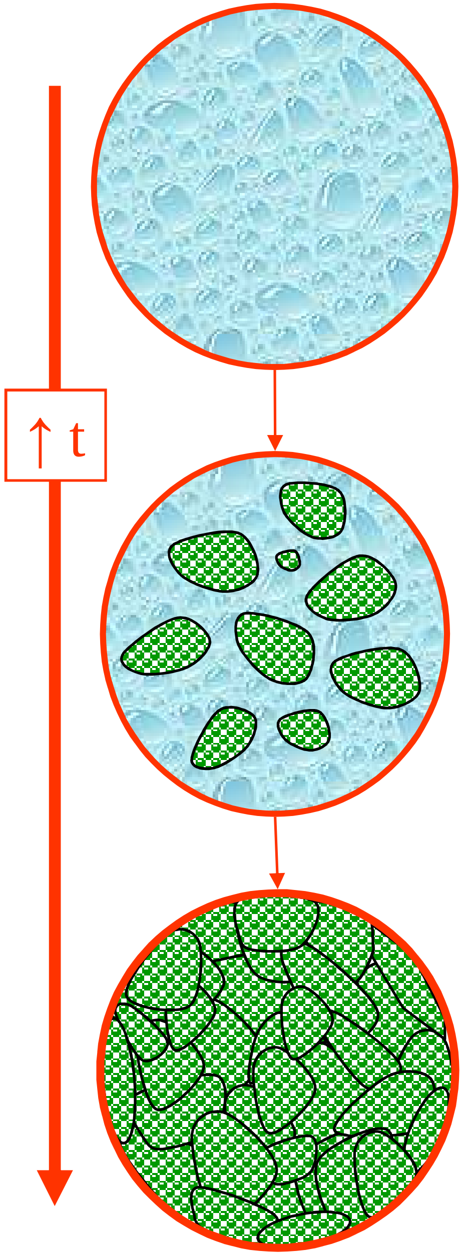
5



Growth of nucleated crystal

6

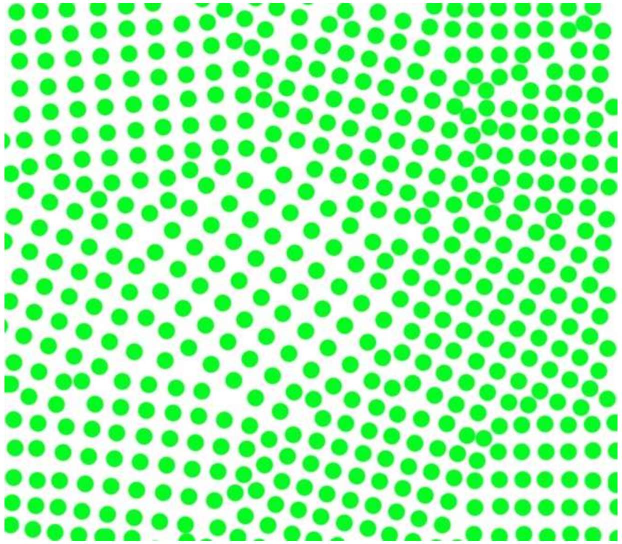
Solidification Complete

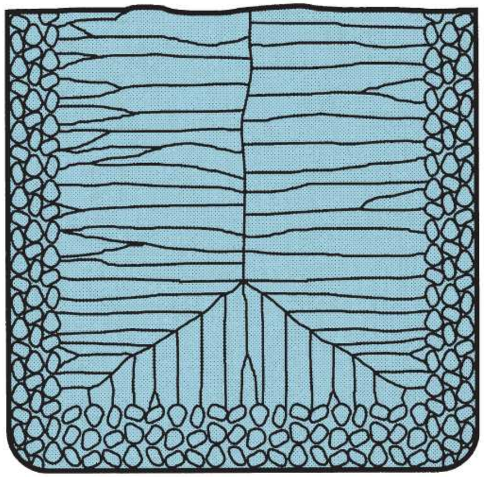


"For sufficient Undercooling"

Solidification of pure metal

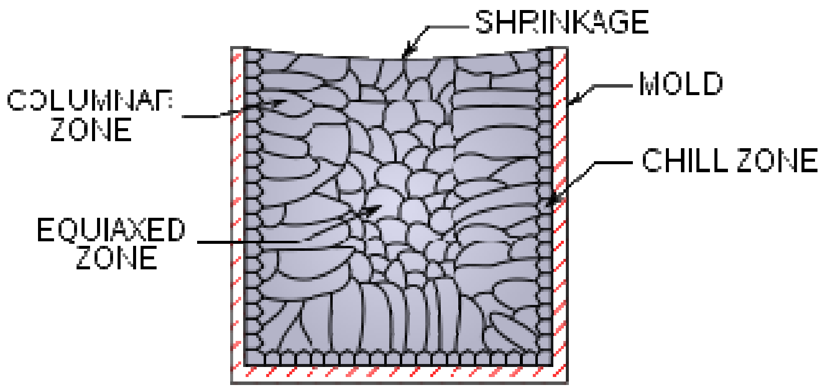
- This mismatch leads to a noncrystalline (amorphous) structure at the grain boundary with the atoms irregularly spaced.
- Since the last liquid to solidify is generally along the grain boundaries, there tends to be higher concentration of impurity atoms in that area. Figure (previous page) shows schematically 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.

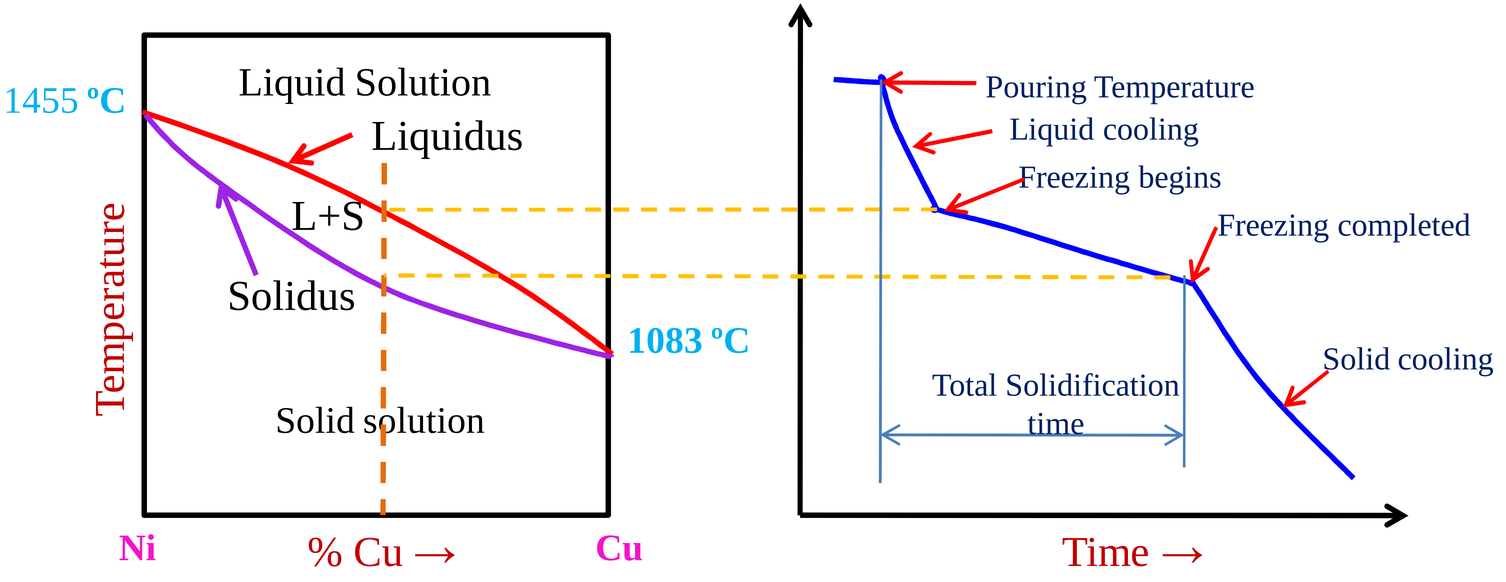




Solidification of Alloys

- 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.

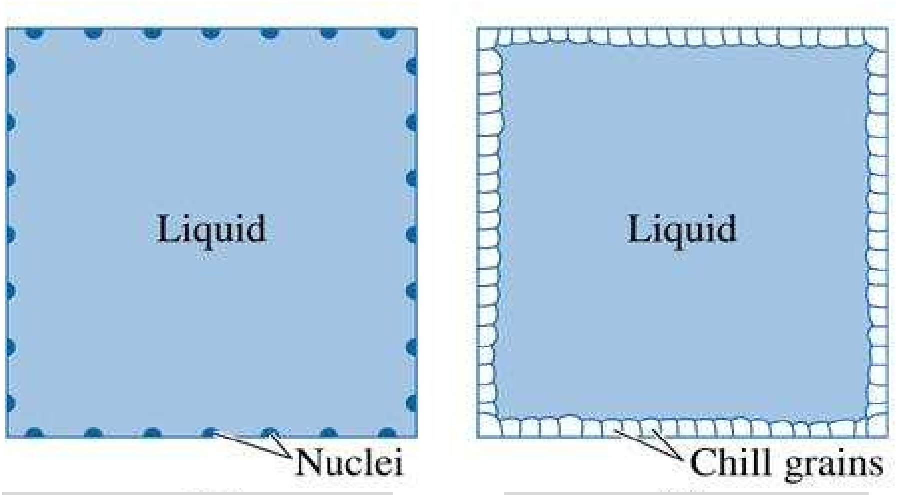




Cast Structure

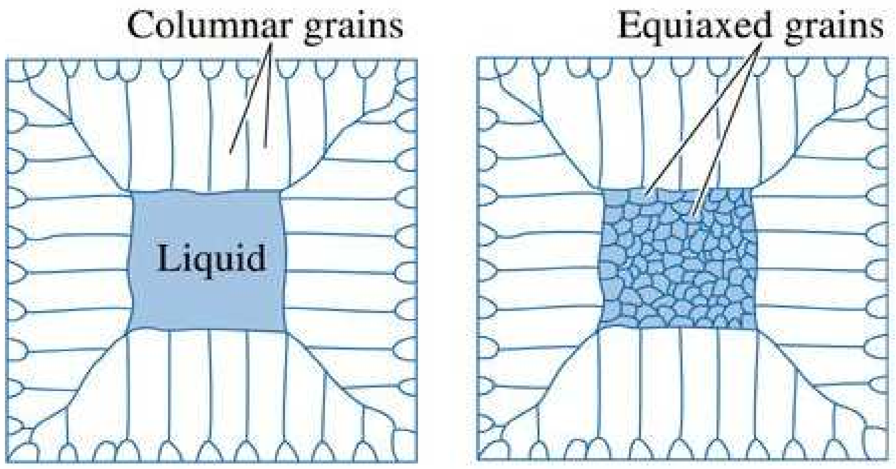
- ❑ **Chill Zone:** A region of small, randomly oriented grains that forms at the surface of a casting as a result of heterogeneous nucleation.
- ❑ **Columnar Zone:** A region of elongated grains having a preferred orientation that forms as a result of competitive growth during the solidification of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

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



Nucleation begins

Chill zone forms

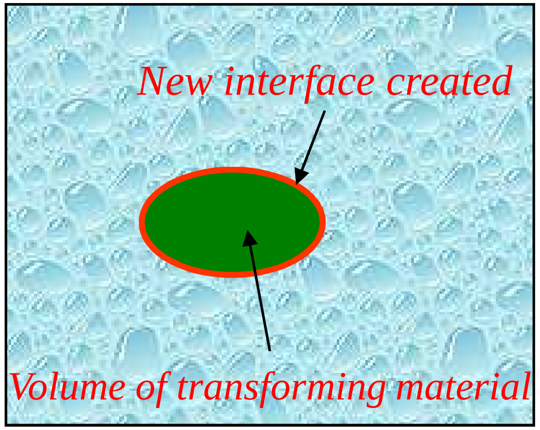


preferred growth produces the columnar zone

additional nucleation creates the equiaxed zone

Remember….!

- We have seen phase transformations using the example of the solidification of a pure metal.
- 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 $G_{Liquid} < G_{Solid}$). 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.



Energies involved

- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- Strain energy ↑

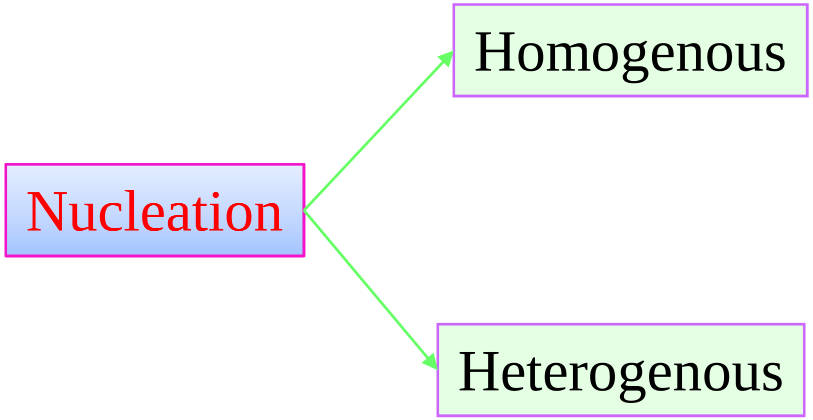
Solid-solid transformation

Nucleation

Solidification = Nucleation + Growth

- Nucleation: localized formation of a distinct thermodynamic phase.
- Nucleation an 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 semi conductor industry.
- Most nucleation processes are physical, rather than chemical.
- There are two types of nucleation : homogeneous and heterogeneous. This distinction between them 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, where as for the heterogeneous type, nuclei form preferentially at structural inhomogeneities such as container surfaces insoluble impurities grain boundaries, dislocations and so on

Nucleation



Nucleation

Homogenous

Heterogenous

- *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

Homogeneous Nucleation

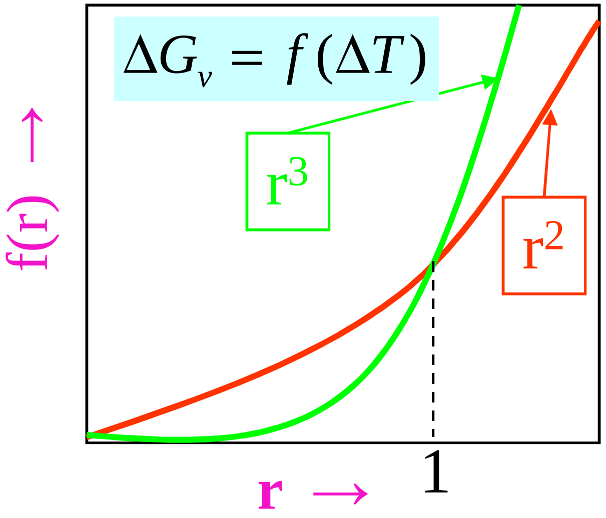
- ❑ Let us consider L→S transformation taking place by homogenous nucleation. Let the system be undercooled to a fixed temperature ΔT. Let us consider the formation of a spherical crystal of radius ‘r’ from the melt. We can neglect the strain energy contribution.
- ❑ Let the change in ‘G’ during the process be ΔG. This is equal to the decrease in bulk free energy + the increase in surface free energy. This can be computed for a spherical nucleus as below.

Neglected in L → S transformations

Free energy change on nucleation =

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

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



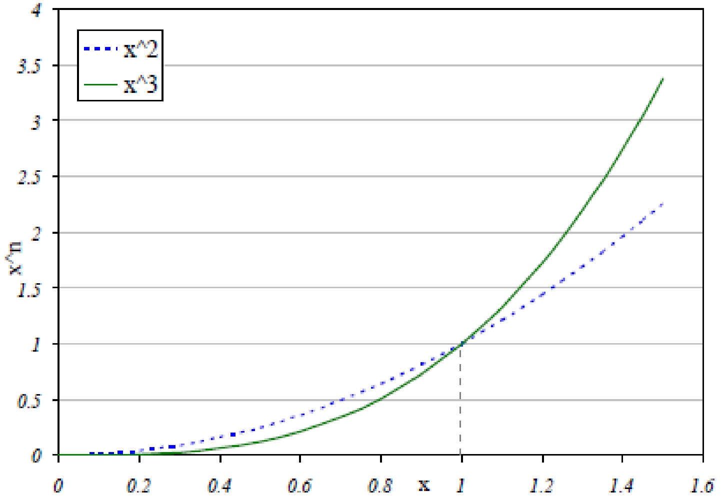
$$\Delta G = \left(\frac{4}{3}\pi r^3\right).(\Delta G_v) + \left(4\pi r^2\right).(\gamma)$$

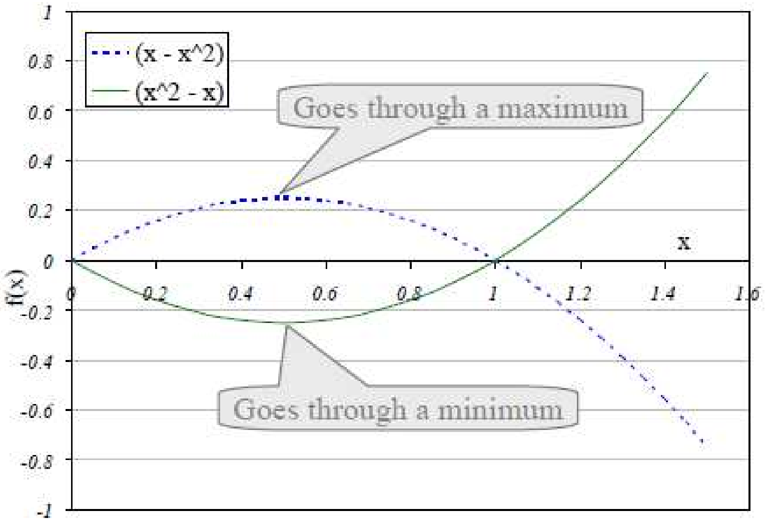
✓*Note that below a value of ‘1’ the lower power of ‘r’ dominates; while above ‘1’ the higher power of ‘r’ dominates.*
✓*In the above equation these powers are weighed with other ‘factors/parameters’, but the essential logic remains.*

Homogeneous Nucleation

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

- In the above equation, the r^3 term is +ve and the r^2 term is -ve. Such kinds of equations are often encountered in materials science, where one term is opposing the process and the other is supporting it. Example of such processes are crack growth (where surface energy opposes the process and the strain energy stored in the material supports crack growth).
- In the current case it is the higher power is supporting the phase transformation. Since the higher power dominates above '1', the function will go through a maximum as in fig. below. This implies the ΔG function will go through a maximum. I.e. if the process just even starts it will lead to an increase in ΔG!
- On the other hand the function with -ve contribution from the lower power (to ΔG) will go through a minimum (fig. below) and such a process will take place down-hill in G and stop.





Homogeneous Nucleation

- As we have noted previously ΔG vs r plot will go through a maximum (implying that as a small crystal forms 'G' will increase and hence it will tend to dissolve). The maximum of ΔG vs r plot is obtained by, by setting dΔG/dr = 0. The maximum value of ΔG corresponds to a value of 'r' called the critical radius (denoted by superscript *).
- If by some 'accident' (technically a 'statistical random fluctuation') a crystal (of 'preferred' crystal structure) size > r* (called supercritical nuclei) forms then it can grow down-hill in 'G'. Crystals smaller than r* (called embryos) will tend to shrink to reduce 'G'. The critical value of ΔG at r* is called ΔG*. Reduction in G (below the liquid state) is obtained only after r_0 is obtained (which can be obtained by setting ΔG = 0).

$$\frac{d\Delta G}{dr} = 0 \Rightarrow \begin{cases} r_1^* = 0 \\ r_2^* = -\dfrac{2\gamma}{\Delta G_v} \end{cases}$$

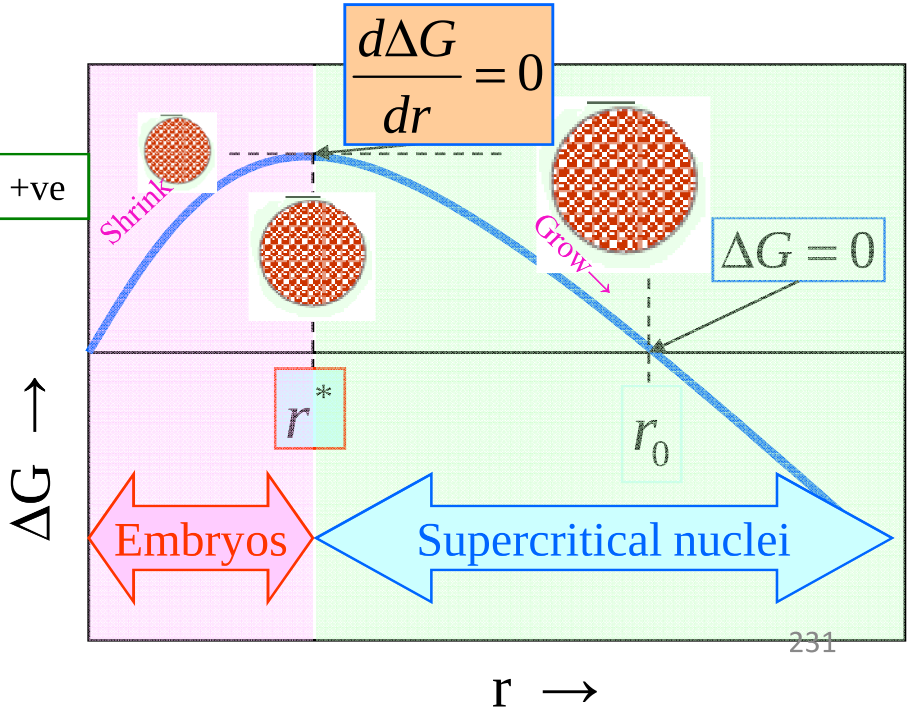
Trivial

As ΔG_v is –ve, r^* is +ve

$$\boxed{r^* = -\frac{2\gamma}{\Delta G_v}}$$

$$\boxed{\Delta G^* = \frac{16}{3}\pi \frac{\gamma^3}{\Delta G_v^2}}$$

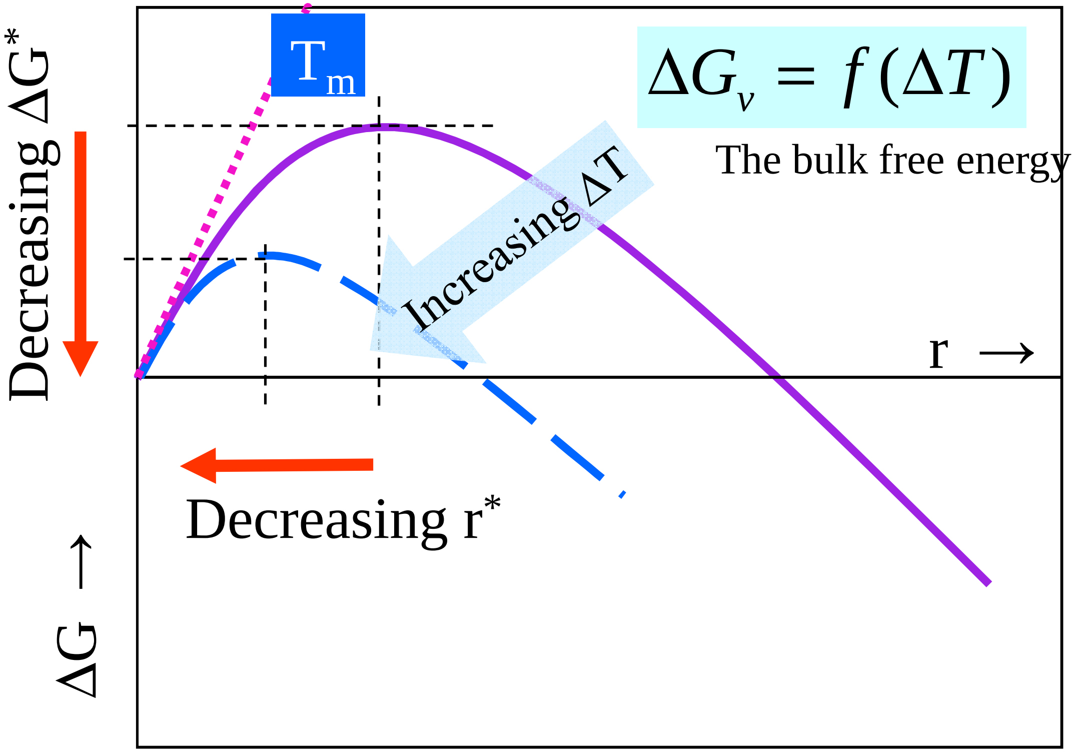
$$\Delta G = 0 \Rightarrow r_0 = -\frac{3\gamma}{\Delta G_v}$$



Homogeneous Nucleation

What is the effect of undercooling (ΔT) on r* and ΔG*?

- ❑ We have noted that ΔG_V is a function of undercooling (ΔT). At larger undercooling ΔG_V increases and hence r* and ΔG* decrease. This is evident from the equations for r* and ΔG* as below
- ❑ At T_m , ΔG_V is zero and r* is infinity! → That the melting point is not the same as the freezing point!! This energy (G) barrier to nucleation is called the ‘*nucleation barrier*’.



$$\Delta G_v = f(\Delta T)$$

The bulk free energy reduction is a function of undercooling

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

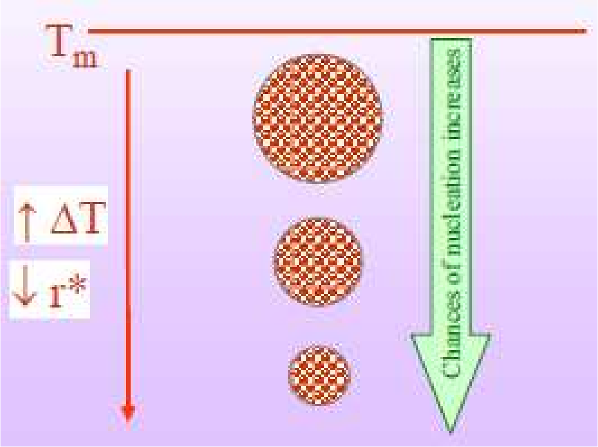
$$\Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{\Delta G_v^2}$$

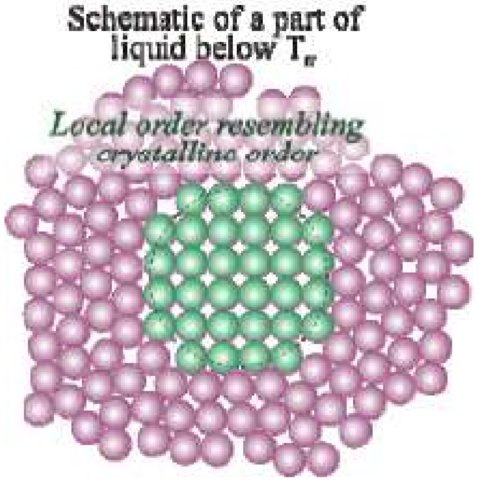
Using the Turnbull approximation (linearizing the G-T curve close to T_m), we can get the value of ΔG interms of the enthalpy of solidification.

$$\Delta G^* = \frac{16}{3}\pi\gamma^3\frac{T_m^2}{\Delta T^2\ \Delta H^2}$$

How are atoms assembled to form a nucleus of r* →“Statistical Random Fluctuation”

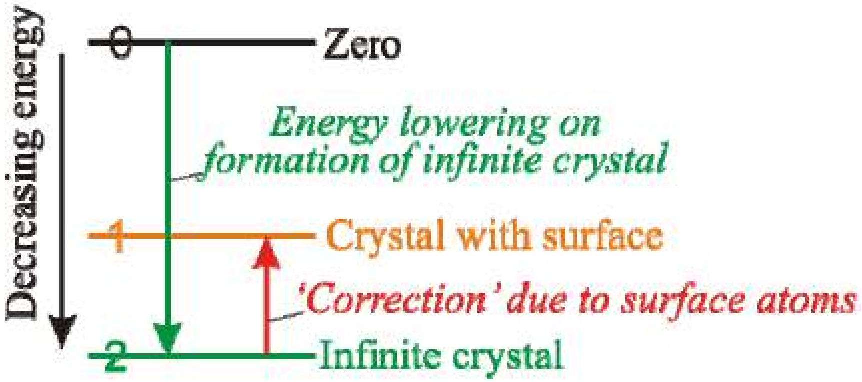
- To cause nucleation (or even to form an embryo) atoms of the liquid (which are randomly moving about) have to come together in a order, which resembles the crystalline order, at a given instant of time. Typically, this crystalline order is very different from the order (local order), which exists in the liquid.
- This ‘coming together’ is a random process, which is statistical in nature →i.e. the liquid is exploring ‘locally’ many different possible configurations and randomly (by chance), in some location in the liquid, this order may resemble the preferred crystalline order.
- Since this process is random (& statistical) in nature, the probability that a larger sized crystalline order is assembled is lower than that to assemble a smaller sized ‘crystal’.
- Hence, at smaller undercoolings (where the value of r* is large) the chance of the formation of a supercritical nucleus is smaller and so is the probability of solidification (as at least one nucleus is needed → which can grow to cause solidification). At larger undercoolings, where r* value is relatively smaller, the chance of solidification is higher.

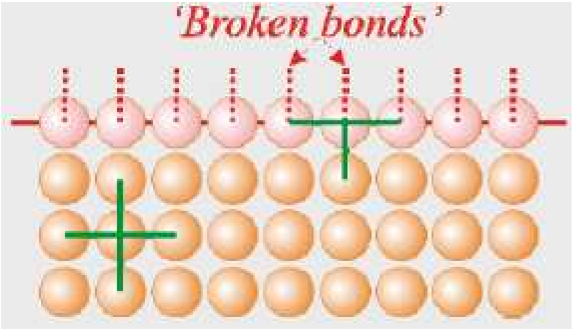




What is meant by the ‘Nucleation Barrier’ →an alternate perspective

- Here we try to understand: “What exactly is meant by the nucleation barrier?”.
- It is sometime difficult to fathom out as to the surface energy can make freezing of a small ‘embryo’ energetically ‘infeasible’ *(as we have already noted that unless the crystallite size is > r_0 the energy of the system is higher)*. Agreed that for the surface the energy lowering is not as much as that for the bulk*, but even the surface (with some ‘unsaturated bonds’) is expected to have a lower energy than the liquid state (where the crystal is energetically favored). I.e. the specific concern being: “can state-1 in figure below be above the zero level (now considered for the liquid state)?” →“Is the surface so bad that it even negates the effect of the bulk lowering?”
- We will approach this mystery from a different angle - by first asking the question: “what is meant by melting point?” & “what is meant by undercooling?”.

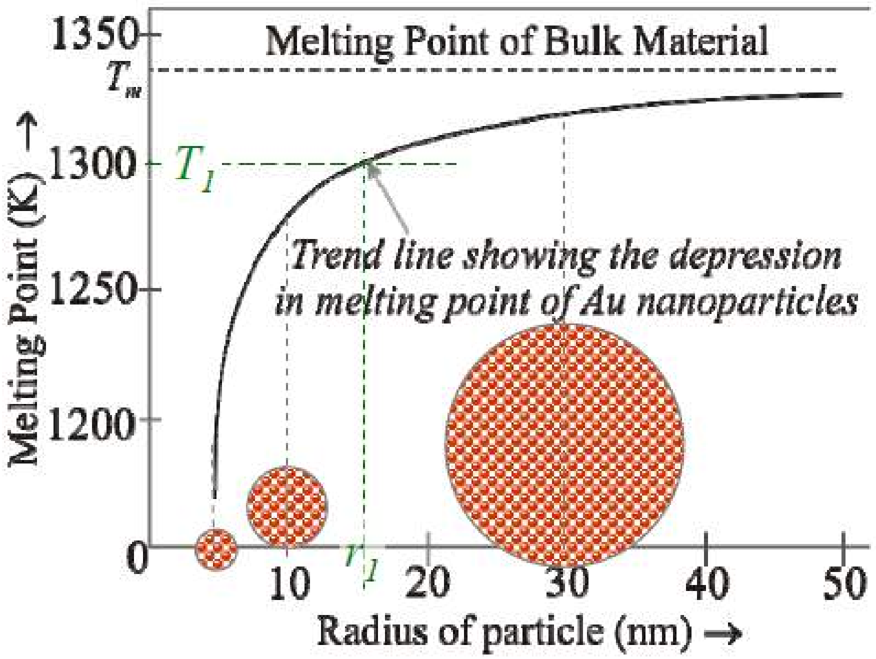




Melting point, undercooling, freezing point

- The plot below shows melting point of Au nanoparticles, plotted as a function of the particle radius. It is to be noted that the melting point of nanoparticles decreases below the 'bulk melting point' (a 5nm particle melts more than 100 ^{0}C below T_m^{Bulk}). This is due to surface effects (surface is expected to have a lower melting point than bulk!?*) →actually, the current understanding is that the whole nanoparticle melts simultaneously (not surface layer by layer).

- Let us continue to use the example of Au. Suppose we are below T_m^{Bulk} (1337K=1064 ^{0}C, i.e. system is undercooled w.r.t the bulk melting point) at T_1 (=1300K →ΔT = 37K) and suppose a small crystal of r_2 = 5nm forms in the liquid. Now the melting point of this crystal is ~1200K →this crystal will 'melt-away'. Now we have to assemble a crystal of size of about 15nm (= r_1) for it 'not to melt'. This needless to say is much less probable (and it is better to undercool even further so that the value of r* decreases). Thus the mystery of 'nucleation barrier' vanishes and we can 'think of' melting point ≡ freezing point (for a given size of particle)!



Other materials like Pb, Cu, Bi, Si show similar trend lines

- T_m is in heating for the bulk material and in cooling if we take into account the size dependence of melting point everything 'sort-of' falls into place .

Homogenous Nucleation Rate

- ☐ The process of nucleation (of a crystal from a liquid melt, below T_m^{Bulk}) we have described so far is a dynamic one. Various atomic configurations are being explored in the liquid state - some of which resemble the stable crystalline order. Some of these 'crystallites' are of a critical size $r^*_{\Delta T}$ for a given undercooling (ΔT). These crystallites can grow to transform the melt to a solid→by becoming supercritical. Crystallites smaller than r* (embryos) tend to 'dissolve'.
- ☐ As the whole process is dynamic, we need to describe the process in terms of 'rate' →the nucleation rate [dN/dt ≡ number of nucleation events/time].
- ☐ Also, true nucleation is the rate at which crystallites become supercritical. To find the nucleation rate we have to find the number of critical sized crystallites (N*) and multiply it by the frequency/rate at which they become supercritical.
- ☐ If the total number of particles (which can act like potential nucleation sites - in homogenous nucleation for now) is N_t , then the number of critical sized particles given by an Arrhenius type function with a activation barrier of ΔG^*.

$$N^* = N_t \, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

- The number of potential atoms, which can jump to make the critical nucleus supercritical are the atoms which are ‘adjacent’ to the liquid→let this number be s*.
- If the lattice vibration frequency is ν and the activation barrier for an atom facing the nucleus (i.e. atom belonging to s*) to jump into the nucleus (to make in supercritical) is ΔH_d, the frequency with which nuclei become supercritical due atomic jumps into the nucleus is given by: $\nu' = S^* \nu e^{\left(-\frac{\Delta H_d}{kT}\right)}$

Rate of nucleation = No. of critical sized particles x Frequency with which they become supercritical

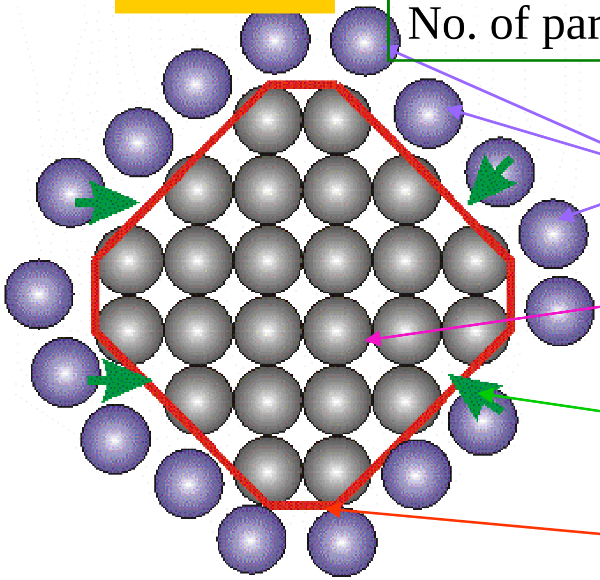
$$I = \frac{dN}{dt}$$

$$N^* = N_t \, e^{\left(-\frac{\Delta G^*}{kT}\right)}$$

No. of particles/volume in L

$$\nu' = s^* \nu \, e^{\left(-\frac{\Delta H_d}{kT}\right)}$$

ν → lattice vibration frequency (~10^{13} /s)



s^* atoms of the liquid facing the nucleus

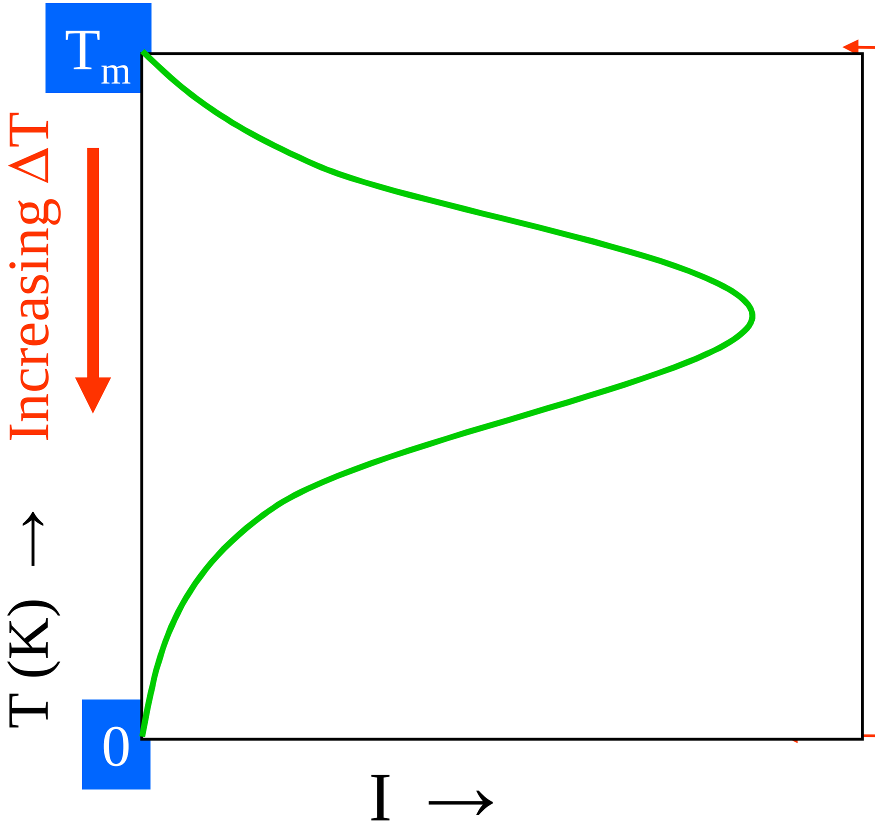
Critical sized nucleus

Jump taking particle to supercriticality
→ nucleated *(enthalpy of activation = ΔH_d)*

Critical sized nucleus

Homogenous Nucleation Rate

- ❑ The nucleation rate (I = dN/dt) can be written as a product of the two terms as in the equation below.
- ❑ How does the plot of this function look with temperature?
- ❑ At T_m , ΔG^* is ∞→I = 0 (as expected if there is no undercooling there is no nucleation).
- ❑ At T = 0K again I = 0
- ❑ This implies that the function should reach a maximum between $T = T_m$ and T = 0.
- ❑ A schematic plot of I(T) (or I(ΔT)) is given in the figure below. An important point to note is that the nucleation rate is not a monotonic function of undercooling.



$T = T_m \rightarrow \Delta G^* = \infty \rightarrow I = 0$

$$I = N_t\, s^*\, \nu\, e^{-\left(\frac{\Delta G^* + \Delta H_d}{kT}\right)}$$

Note: ΔG^* is a function of T

- ▪ $\Delta G^* \uparrow \;\Rightarrow I \downarrow$
- ▪ $T \uparrow \;\Rightarrow I \uparrow$

$T = 0 \rightarrow I = 0$

Heterogenous Nucleation

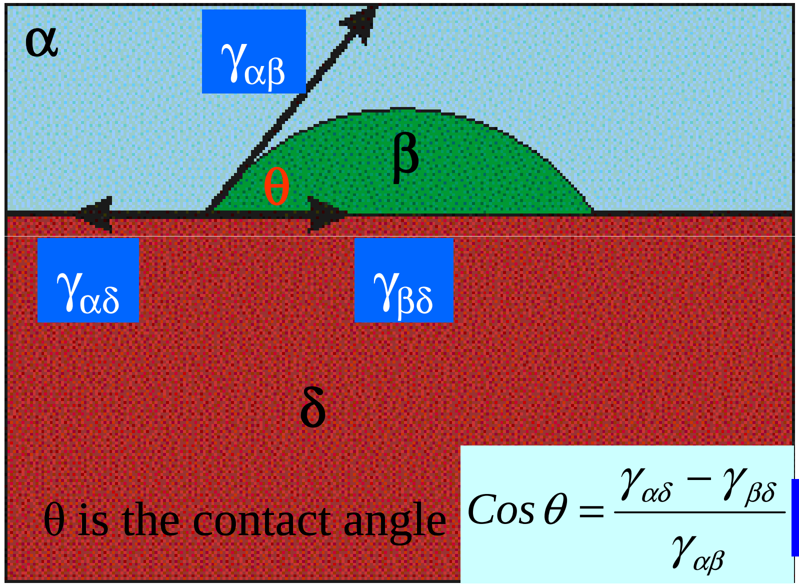
- We have already talked about the ‘nucleation barrier’ and the difficulty in the nucleation process. This is all the more so for fully solid state phase transformations, where the strain energy term is also involved (which opposes the transformation).
- The nucleation process is often made ‘easier’ by the presence of ‘defects’ in the system.
- In the solidification of a liquid this could be the mold walls.
- For solid state transformation suitable nucleation sites are: non-equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults, inclusions and surfaces.
- One way to visualize the ease of heterogeneous nucleation → heterogeneous nucleation at a defect will lead to destruction/modification of the defect (make it less “‘defective’”). This will lead to some free energy ΔG_d being released →thus reducing the activation barrier.

$$\Delta G_{\text{hetro, defect}} = (\mathrm{V})\left(\Delta G_v - \Delta G_s\right) + \mathrm{A}\gamma - (\Delta G_d)$$

- Increasing ΔG_d (i.e. increasing ΔG^*)
    - Homogenous sites
    - Vacancies
    - Dislocations
    - Stacking Faults
    - Grain boundaries (triple junction…), Interphase boundaries
    - Free Surface

Heterogenous Nucleation

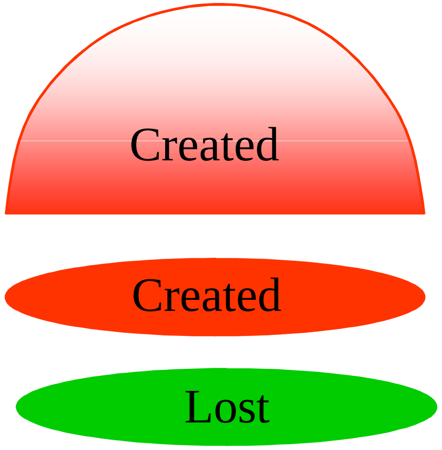
- ☐ Consider the nucleation of β from α on a planar surface of inclusion δ. The nucleus will have the shape of a lens *(as in the figure below).*
- ☐ Surface tension force balance equation can be written as in equation (1) below. The contact angle can be calculated from this equation *(as in equation (3)).*
- ☐ Keeping in view the interface areas created and lost we can write the ΔG equation as below (2).



θ is the contact angle

$$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \quad \to 3$$

Interfacial Energies



$A_{lens}\ \gamma_{\alpha\beta}$

$A_{circle}\ \gamma_{\beta\delta}$

$A_{circle}\ \gamma_{\alpha\delta}$

Surface tension force balance ⟶ $\gamma_{\alpha\beta} Cos\,\theta + \gamma_{\beta\delta} = \gamma_{\alpha\delta}$ →1

$$\Delta G = (V_{lens})\Delta G_v + (A_{lens})\gamma_{\alpha\beta} + (A_{circle})\,\gamma_{\beta\delta} - (A_{circle})\,\gamma_{\alpha\delta} \quad \to 2$$

$V_{lens} = \pi h^2(3r-h)/3$

$A_{lens} = 2\pi rh$

$h = (1-Cos\theta)r$

$r_{circle} = r\ Sin\theta$

Heterogenous Nucleation

- Using the procedure as before (for the case of the homogenous nucleation) we can find r* for heterogeneous nucleation. Using the surface tension balance equation we can write the formulae for r*and ΔG* using a single interfacial energy $\gamma_{\alpha\beta}$ (and contact angle θ).
- Further we can write down ΔG^*_{hetero} in terms of ΔG^*_{homo} and contact angle θ.

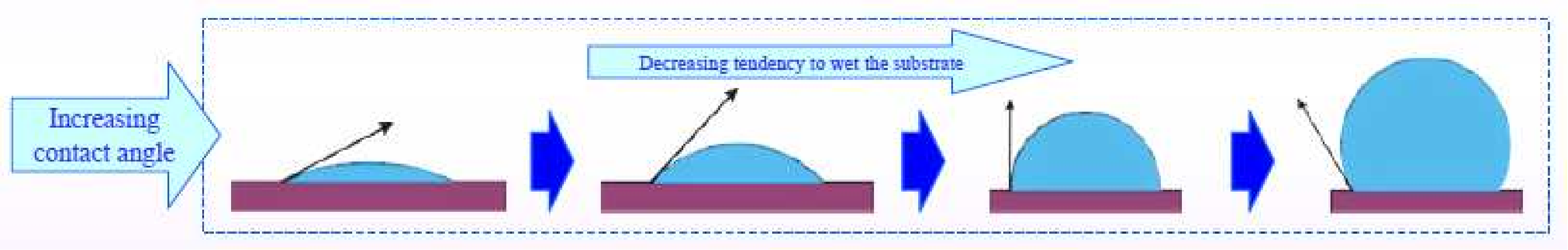
$$\frac{d\Delta G}{dr}=0 \;\Rightarrow\; r^*_{hetero} = -\frac{2\gamma_{\alpha\beta}}{\Delta G_V}$$

$$\Delta G^*_{hetero} = \frac{4}{3}\pi\frac{\gamma^3_{\alpha\beta}}{\Delta G_V^2}\left(2-3Cos\theta+Cos^3\theta\right)$$

$$\Delta G^*_{hetero} = \frac{1}{4}G^*_{homo}\left(2-3Cos\theta+Cos^3\theta\right)$$

$$\frac{\Delta G^*_{hetero}}{G^*_{homo}} = \frac{1}{4}\left(2-3Cos\theta+Cos^3\theta\right)$$

Just a function of θ → The contact angle

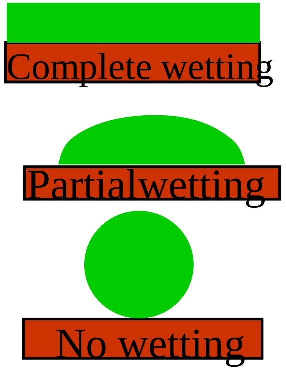


$$\frac{\Delta G^*_{hetero}}{G^*_{homo}} = \frac{1}{4}\left(2-3Cos\theta+Cos^3\theta\right)= f(\theta)$$

$\theta = 0^0 \rightarrow f(\theta) = 0$

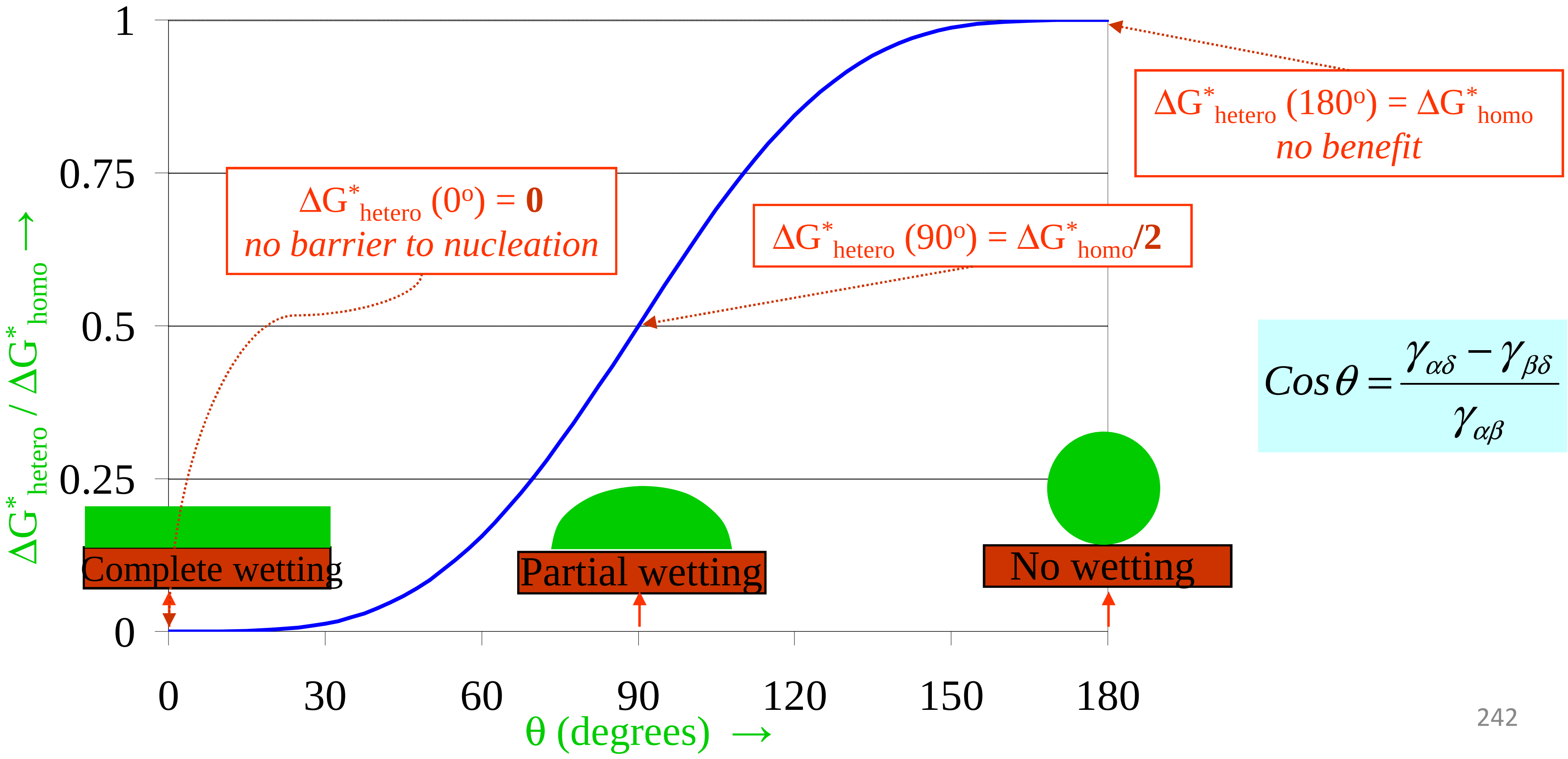
$\theta = 90^0 \rightarrow f(\theta) = 1/2$

$\theta = 180^0 \rightarrow f(\theta) = 1$



The plot of $\Delta G^*_{hetero} / \Delta G^*_{homo}$ is shown in the next page

- Plot of ΔG^*_{hetero} /ΔG^*_{homo} is shown below. This brings out the benefit of heterogeneous nucleation vs homogenous nucleation
- If the β phase nucleus (lens shaped) completely wets the substrate/inclusion (δ-phase) (i.e. θ = 0°) →then $\Delta G^*_{hetero} = 0$ →there is no barrier to nucleation.
- On the other extreme if β-phase does not we the substrate (i.e. θ = 180°) → $\Delta G^*_{hetero} = \Delta G^*_{homo}$ → there is no benefit of the substrate. In reality the wetting angle θ is somewhere between 0°-180°.
- Hence, we have to chose a heterogeneous nucleating agent with a minimum 'θ' value



$\Delta G^*_{hetero}(0^o) = \mathbf{0}$
no barrier to nucleation

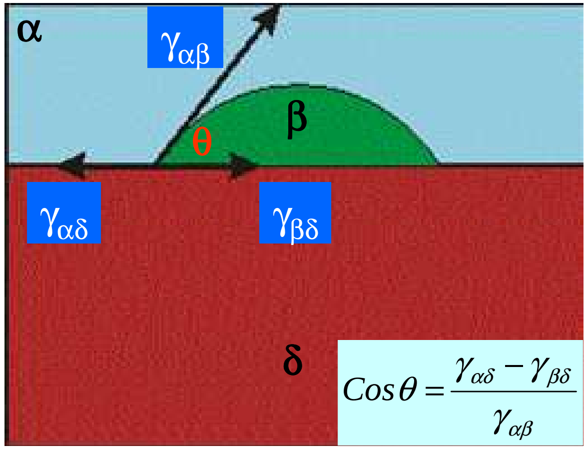
$\Delta G^*_{hetero}(90^o) = \Delta G^*_{homo}/\mathbf{2}$

$\Delta G^*_{hetero}(180^o) = \Delta G^*_{homo}$
no benefit

$$Cos\,\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}}$$

Choice of heterogeneous nucleating agent

- Heterogeneous nucleation has many practical applications.
- During the solidification of a melt if only a few nuclei form and these nuclei grow, we will have a coarse grained material *(which will have a lower strength as compared to a fine grained material- due to Hall-Petch effect).*
- Hence, nucleating agents are added to the melt (e.g. Ti for Al alloys, Zr for Mg alloys) for grain refinement.



How to get a small value of θ? (so that 'easy' heterogeneous nucleation).

- Choosing a nucleating agent with a low value of $\gamma_{\beta\delta}$ (low energy βδ interface)
- (Actually the value of $(\gamma_{\alpha\delta} - \gamma_{\beta\delta})$ will determine the effectiveness of the heterogeneous nucleating agent → high $\gamma_{\alpha\delta}$ or low $\gamma_{\beta\delta}$)

How to get a low value of $\gamma_{\beta\delta}$

- We can get a low value of $\gamma_{\beta\delta}$
  - Crystal structure of β and δ are similar
  - lattice parameters are as close as possible
- Examples of such choices are
  - ✓ Seeding rain-bearing clouds → AgI or NaCl → nucleation of ice crystals
  - ✓ Ni (FCC, a = 3.52 Å) is used a heterogeneous nucleating agent in the production of artificial diamonds (FCC, a = 3.57 Å) from graphite

Why does heterogeneous nucleation rate dominate?

- ☐ To understand the above questions, let us write the nucleation rate for both cases as a pre-exponential term and an exponential term. The pre-exponential term is a function of the number of nucleation sites.
- ☐ However, the term that dominates is the exponential term and due to a lower ΔG* the heterogeneous nucleation rate is typically higher.

$$I_{\text{homo}} \propto I^{0}_{\text{homo}} \; e^{-\left(\frac{\Delta G^{*}_{\text{homo}}}{kT}\right)}$$

$$I_{\text{hetero}} \propto I^{0}_{\text{hetero}} \; e^{-\left(\frac{\Delta G^{*}_{\text{hetero}}}{kT}\right)}$$

= f(number of nucleation sites)

$\sim 10^{42}$

= f(number of nucleation sites)

$\sim 10^{26}$

BUT

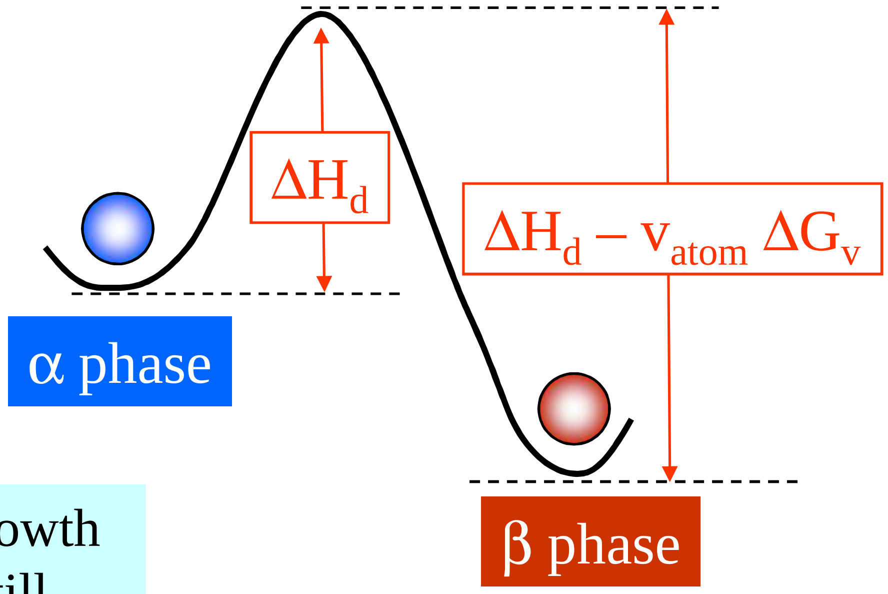
the exponential term dominates

$$\mathbf{I_{hetero} > I_{homo}}$$

Growth of a Pure solid

- At transformation temperature the probability of jump of atom from α → β (across the interface) is same as the reverse jump
- Growth proceeds below the transformation temperature, wherein the activation barrier for the reverse jump is higher.
- There are basically two different types of solid/liquid interface: an atomically rough or diffuse interface associated with metallic systems, and an atomically flat or sharply defined interface often associated with nonmetals.

- Because of the differences in atomic structure these two types of interface migrate in quite different ways . Rough interface migrate by a **continuous growth** processes while flat interface migrate by **lateral growth (Spiral growth and surface nucleation)** process involving ledges.



Trasformation α → β = Nucleation of β phase + Growth till α is exhausted

Summary

- 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 -42ºC rather than at its freezing temperature 0ºC.

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.

Diffusional Transformations

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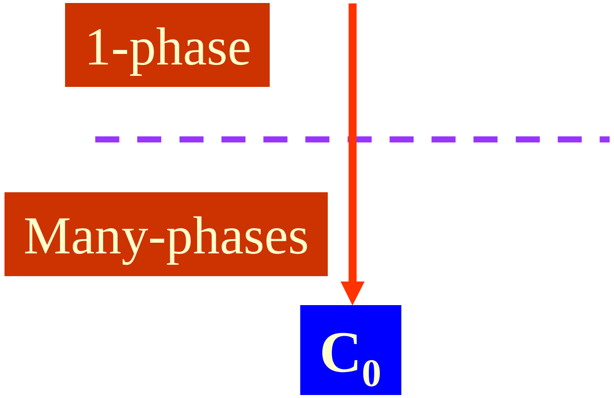
Introduction

- The majority of phase transformations that occur in the solid state takes place by thermally activated atomic movements.
- The transformations that will be dealt with in this chapter are those that are induced by a change of temperature of an alloy that has a fixed composition.



1-phase

Many-phases

C_0

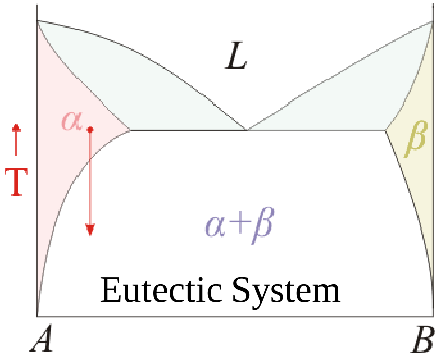
- Usually we will be concerned with the transformations caused by a temperature change from a single phase region of a (binary) phase diagram to a region where one or moreother phases are stable.
- The different types of phase transformations that are possible can be roughly divided in to several groups (*see in next slide).*

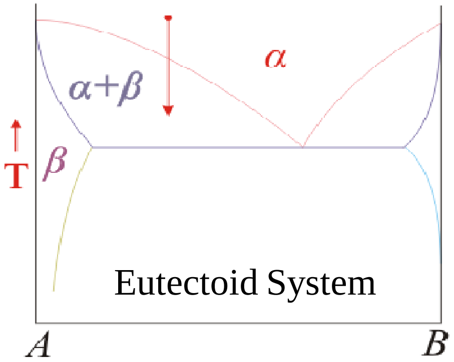
Classification of Diffusional transformations

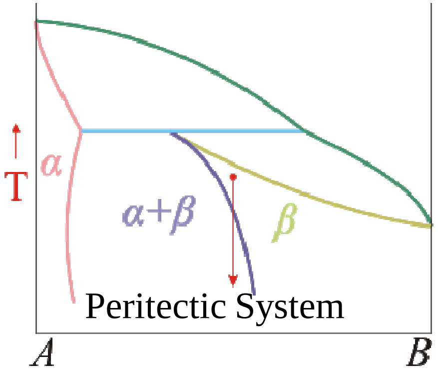
Diffusional Transformations

- Precipitation $\alpha' \rightarrow \alpha + \beta$
  - $\alpha' \rightarrow$ metastable supersaturated solid solution
- Eutectoid $\gamma \rightarrow \alpha + \beta$
- Ordering $\alpha(disordered) \rightarrow \alpha'(ordered)$
- Massive $\beta \rightarrow \alpha$
  - *Original phase decomposes to one or more new phases which have the same composition as the parent phase but different crystal structures*
- Polymorphic $\beta_{crystal-1} \rightarrow \alpha_{crystal-2}$

Classification of Diffusional transformations



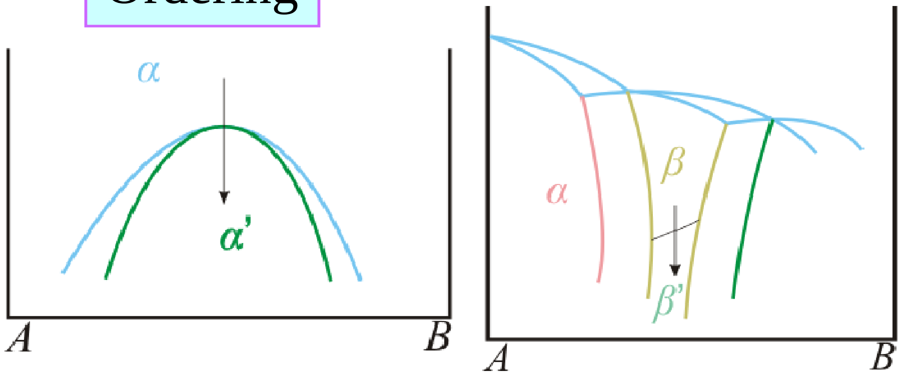




Precipitation

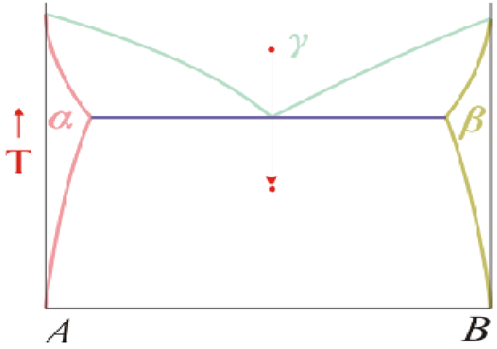
$$\alpha' \rightarrow \alpha + \beta$$

Ordering



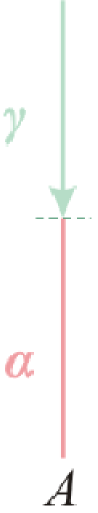
$$\alpha\,(disordered) \rightarrow \alpha'(ordered)$$

Eutectoid

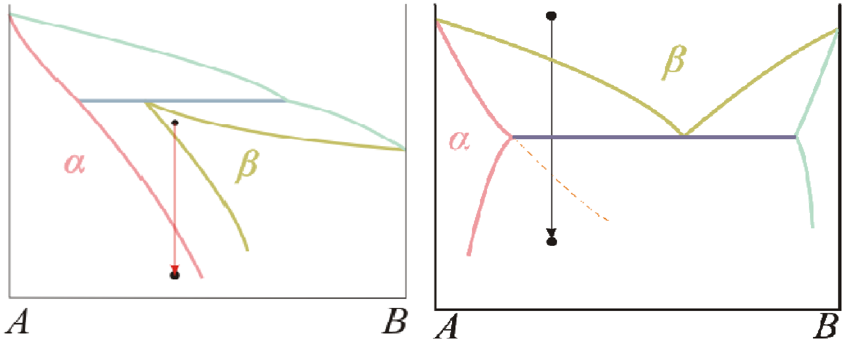


$$\gamma \rightarrow \alpha + \beta$$

Polymorphic



$$\beta_{crystal-1} \rightarrow \alpha_{crystal-2}$$



Massive

$$\beta \rightarrow \alpha$$

Introduction

- ❑ Diffusional transformations involve nucleation and growth. Nucleation involves the formation of a different phase from a parent phase (e.g. crystal from melt). Growth involves attachment of atoms belonging to the matrix to the new phase (e.g. atoms ‘belonging’ to the liquid phase attach to the crystal phase).
- ❑ Nucleation we have noted is ‘uphill’ in ‘G’ process, while growth is ‘downhill’ in G.
- ❑ Growth can proceed till all the ‘prescribed’ product phase forms (by consuming the parent phase).

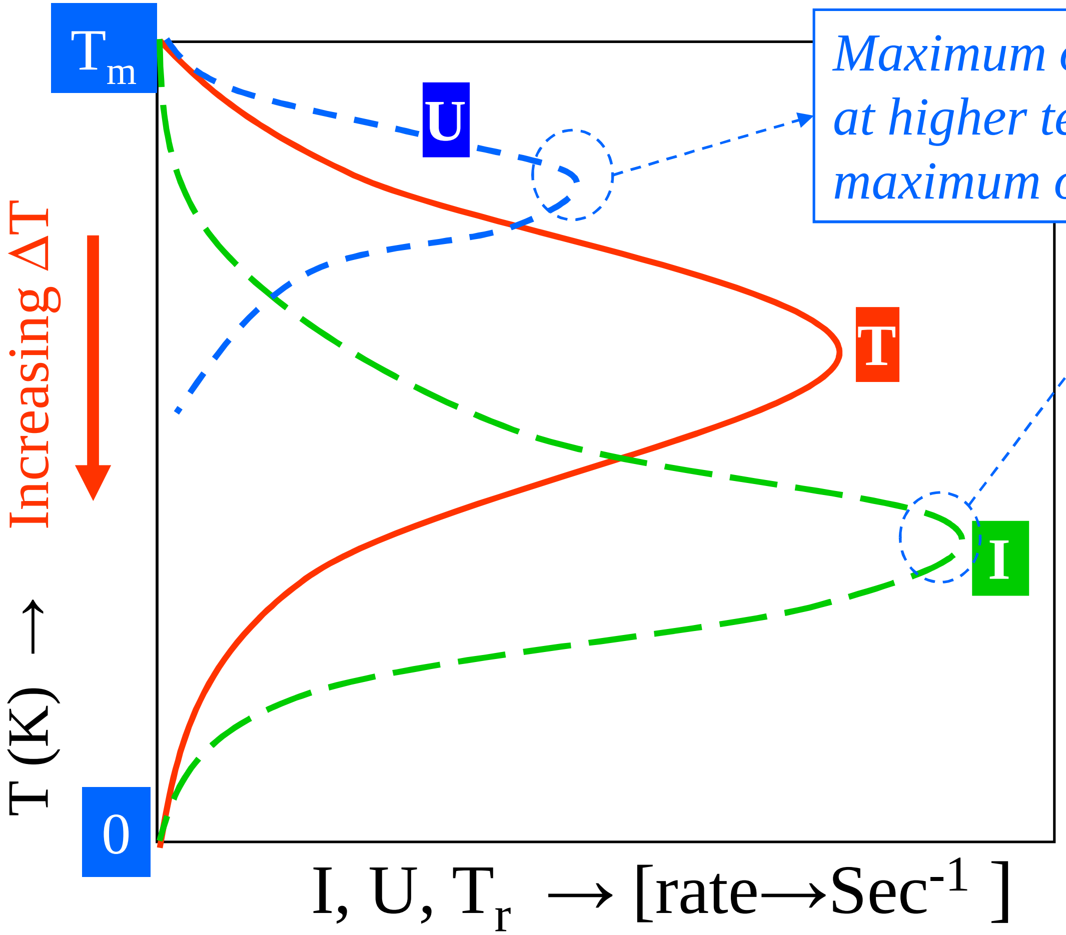
Transformation rate

- ❑ As expected transformation rate (T_r) is a function of nucleation rate (I) and growth rate (U).
- ❑ In a $\alpha \rightarrow \beta$ transformation, if X_β is the fraction of β-phase formed, then dX_β/dt is the transformation rate.
- ❑ The derivation of T_r as a function of I & U is carried using some assumptions (e.g. *Johnson-Mehl and Avarami models*).
- ❑ We have already seen the curve for the nucleation rate (I) as a function of the undercooling.
- ❑ The growth rate (U) curve as a function of undercooling looks similar. The key difference being that the maximum of U-ΔT curve is typically above the I-ΔT curve.
- ❑ This fact that $T(U_{max}) > T(I_{max})$ give us an important ‘handle’ on the scale of the transformed phases forming.

Transformation Rate

Transformation rate = f(Nucleation rate, Growth rate)

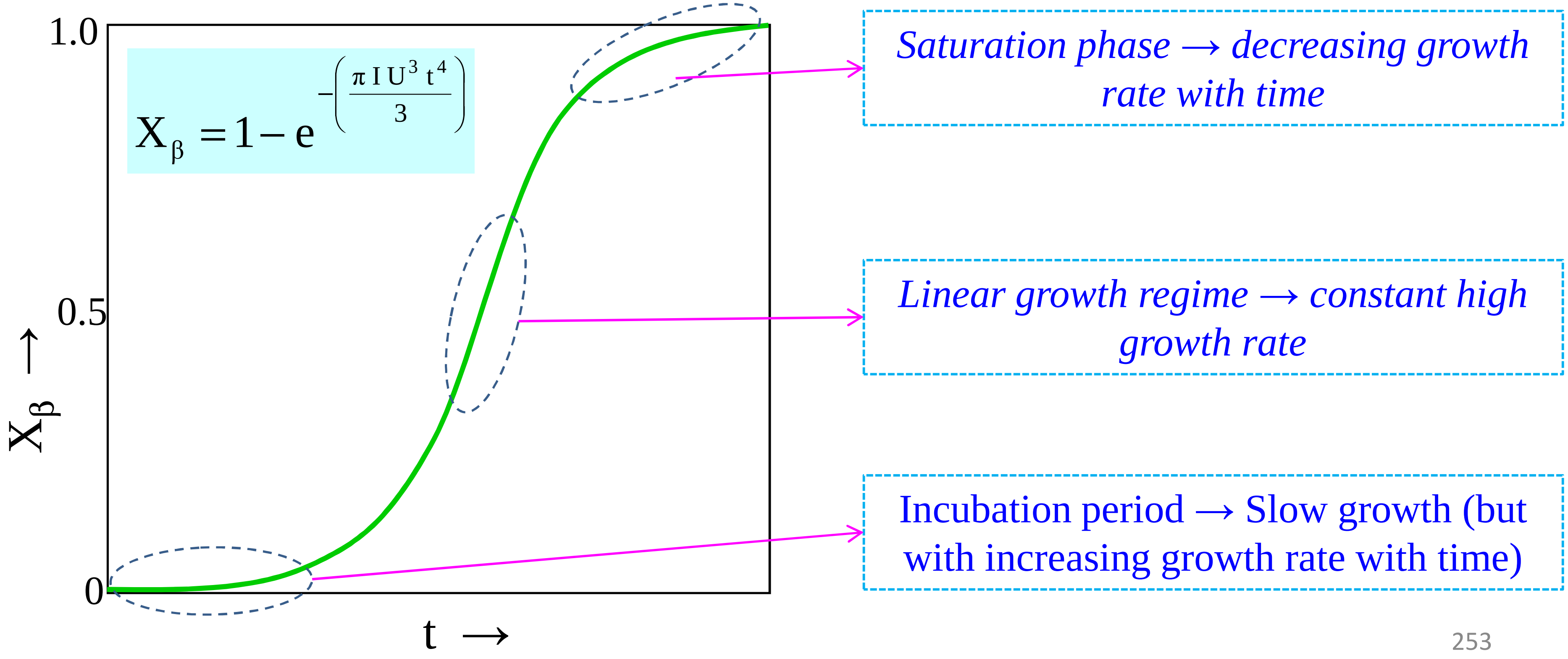
$$\boxed{T} = \frac{dX_\beta}{dt} = f(\boxed{I}, \boxed{U})$$



Maximum of growth rate usually at higher temperature than maximum of nucleation rate

Transformation Rate

- ❑ Fraction of the product (β) phase forming with time →the sigmoidal growth curve
- ❑ Many processes in nature (etc.), e.g. growth of bacteria in a culture (number of bacteria with time), marks obtained versus study time(!), etc. tend to follow a universal curve the sigmoidal growth curve.
- ❑ In the context of phase transformation, the fraction of the product phase (X_β) forming with time follows a sigmoidal curve (function and curve as below).



$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

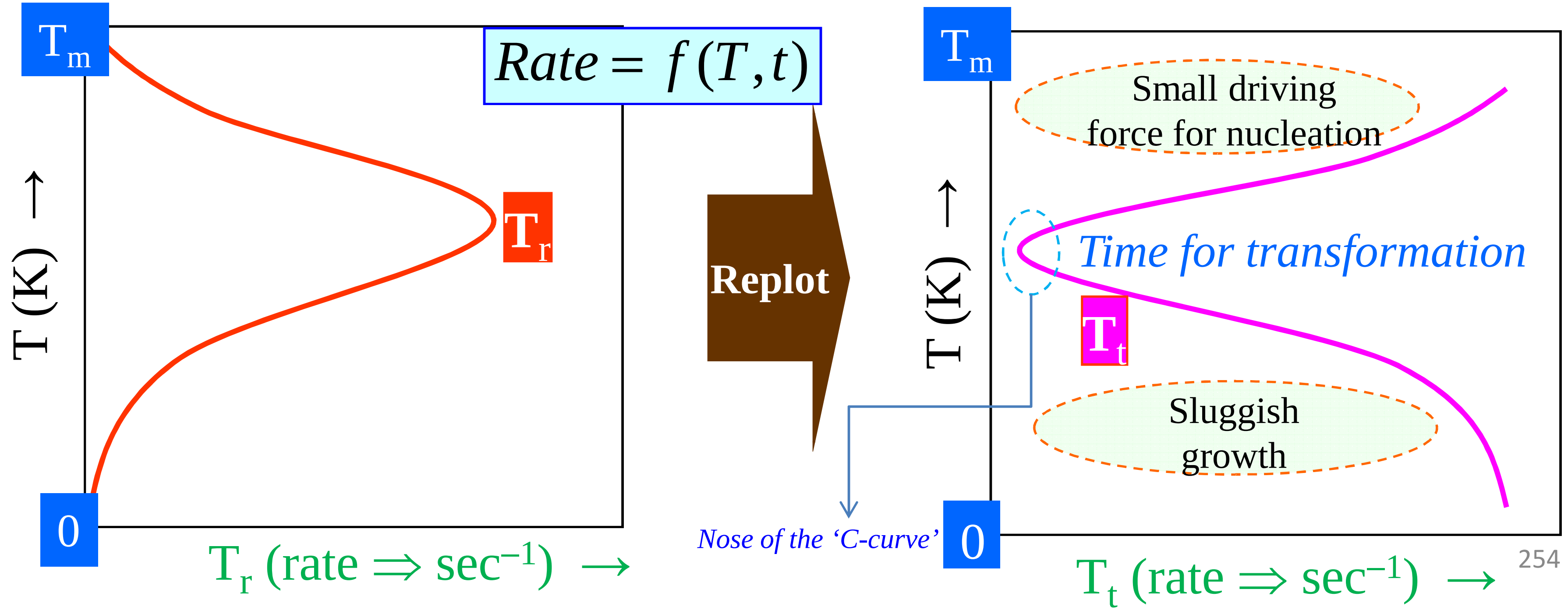
Saturation phase → decreasing growth rate with time

Linear growth regime → constant high growth rate

Incubation period → Slow growth (but with increasing growth rate with time)

From ‘Rate’ to ‘time’ : The Origin of TTT diagrams

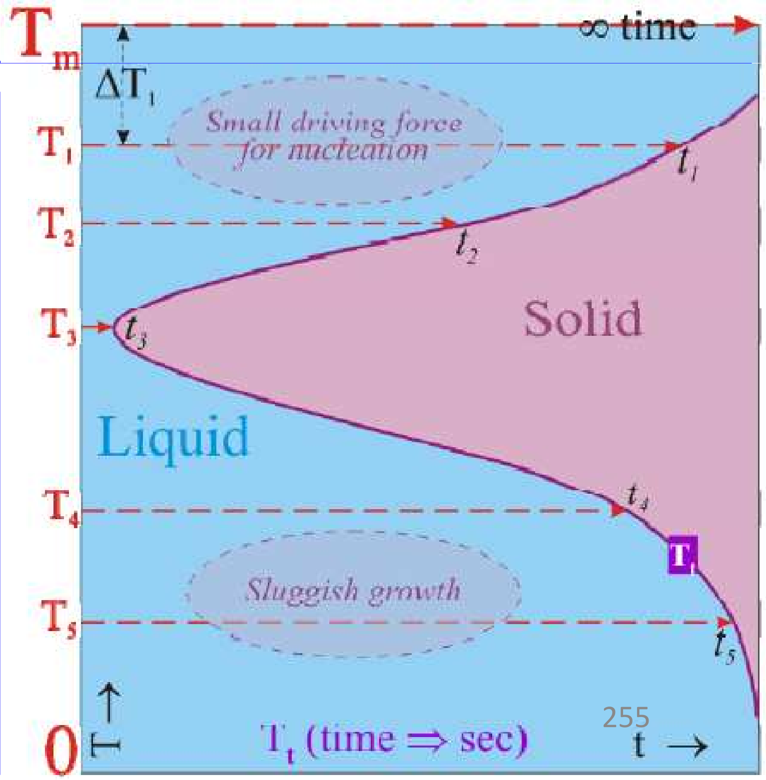
- The transformation rate curve (T_r -T plot) has hidden in it the I-T and U-T curves.
- An alternate way of plotting the Transformation rate (T_r) curve is to plot Transformation time (T_t) [i.e. go from frequency domain to time domain]. Such a plot is called the Time-Temperature-Transformation diagram (TTT diagram).
- High rates correspond to short times and vice-versa. *Zero rate implies ∞ time (no transformation).*
- This T_t -T plot looks like the ‘C’ alphabet and is often called the ‘C-curve. The minimum time part is called the nose of the curve.



Understanding the TTT diagram

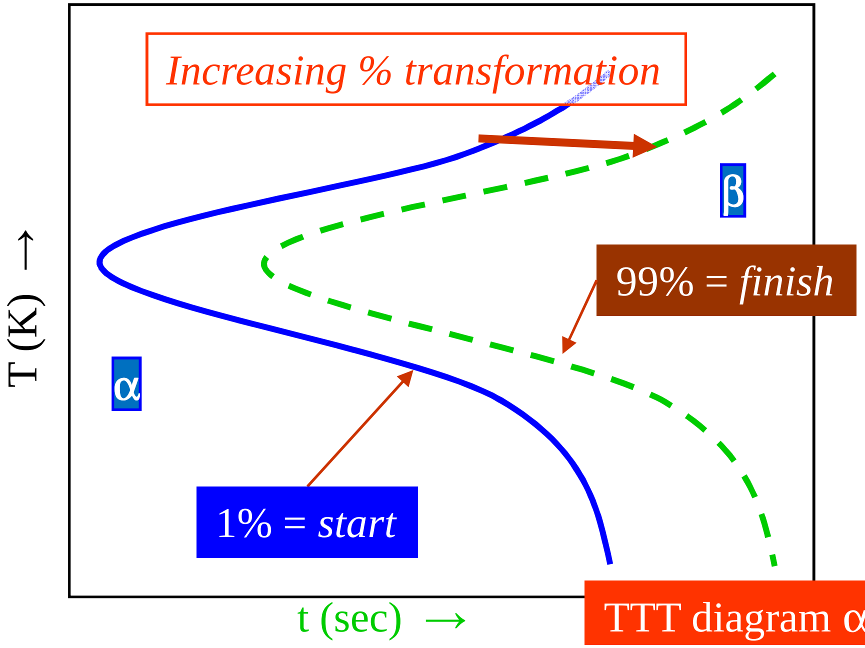
- ❑ Though we are labeling the transformation temperature T_m , it represents other transformations, in addition to melting.
- ❑ Clearly the T_t function is not monotonic in undercooling. At T_m it takes infinite time for transformation.
    - ✓ Till T_3 the time for transformation decreases (with undercooling) [i.e. $T_3 < T_2 < T_1$] →due to small driving force for nucleation.
    - ✓ After T_3 (the minimum) the time for transformation increases [i.e. $T_3 < T_4 < T_5$]→due to sluggish growth.

- ➢ The diagram is called the TTT diagram because it plots the time required for transformation if we hold the sample at fixed temperature (say T_1) or fixed undercooling (ΔT_1). The time taken at T_1 is t_1.
- ➢ To plot these diagrams we have to isothermally hold at various undercoolings and note the transformation time. I.e. instantaneous quench followed by isothermal hold.
- ➢ Hence, these diagrams are also called Isothermal Transformation Diagrams. Similar curves can be drawn for α→β *(solid state) transformation.*



Transformation Rate

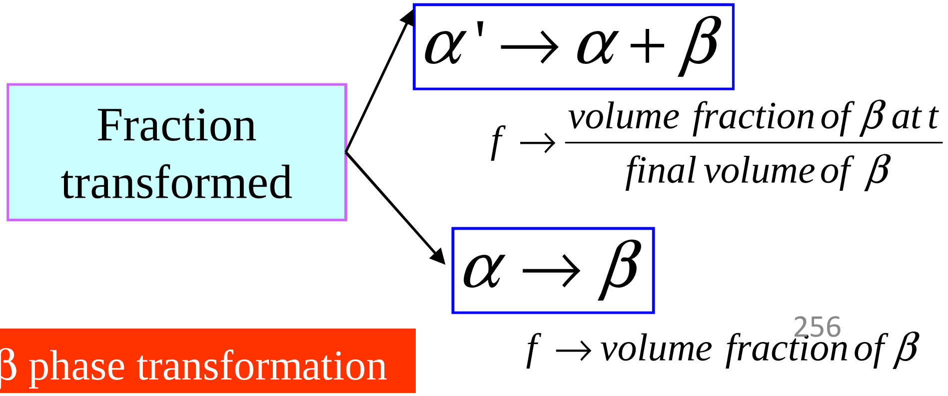
- ❑ This is a phase diagram where the blue region is the Liquid (parent) phase field and purplish region is the transformed product (crystalline solid).
- ❑ Clearly the picture of TTT diagram presented before is incomplete → transformations may start at a particular time, but will take time to be completed *(i.e. between the Liquid phase field and solid phase field there must be a two phase region L+S).*
- ❑ This implies that we need two 'C' curves → one for start of transformation and one for completion. A practical problem in this regard is related to the issue of how to define start and finish *(is start the first nucleus which forms? Does finish correspond to 100%?)* . Since practically it is difficult to find 'β%' and '100%', we use practical measures of start and finish, which can be measured experimentally. Typically this is done using optical metallography and a reliable 'resolution of the technique is about 1% for start and 99% for finish.



TTT diagram α → β phase transformation

- ❑ Another obvious point: as x-axis is time any 'transformation paths' have to be drawn such that it is from left to right (i.e. in increasing time).

How do we define the fractions transformed?



$$\alpha' \rightarrow \alpha + \beta$$

$$f \rightarrow \frac{\text{volume fraction of } \beta \text{ at } t}{\text{final volume of } \beta}$$

$$\alpha \rightarrow \beta$$

$$f \rightarrow \text{volume fraction of } \beta$$

Overall Transformation Kinetics

- ❑ The ‘C’ curve depends on various factors as listed in diagram below.

f(t,T) determined by

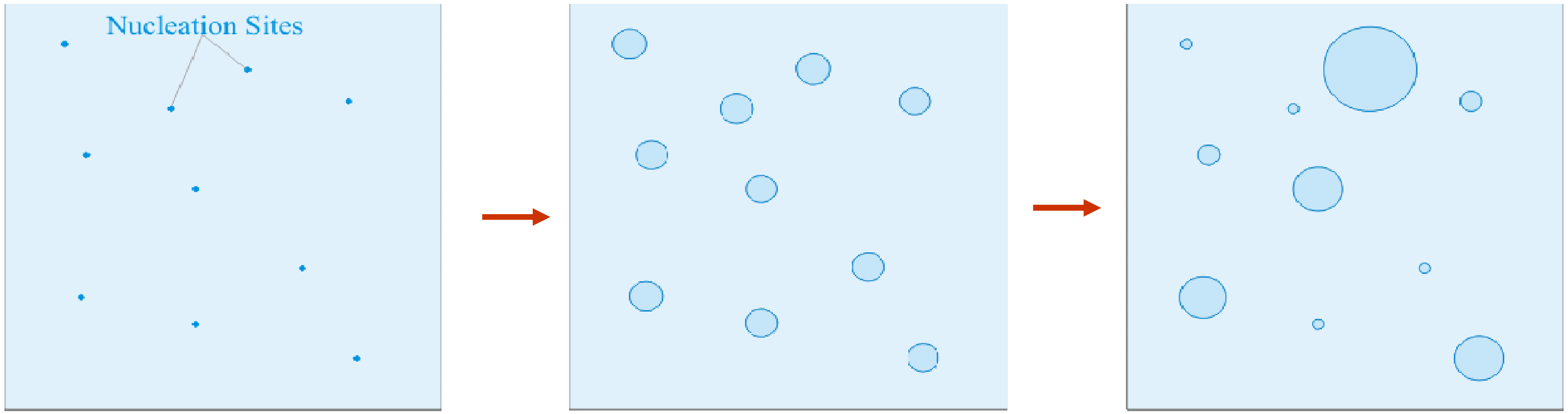
- Nucleation rate
- Growth rate
- Density and distribution of nucleation sites
- Overlap of diffusion fields from adjacent transformed volumes
- Impingement of transformed volumes

- ❑ Some common assumptions used in the derivation are
  - ➢ constant number of nuclei
  - ➢ constant nucleation rate
  - ➢ constant growth rate.

Overall Transformation Kinetics

Constant number of nuclei

- Generally constant number of nuclei will form at the beginning of the transformation.
- One assumption to simplify the derivation is to assume that the number of nucleation sites remain constant and these form at the beginning of the transformation.
- This situation may be approximately valid for example if a nucleating agent (inoculant) is added to a melt (the number of inoculant particles remain constant).
- In this case the transformation rate is a function of the number of nucleation sites (fixed) and the growth rate (U). Growth rate is expected to decrease with time.
- In Avrami model the growth rate is assumed to be constant (till impingement).



$$f = F(number\ of\ nucleation\ sites, growth\ rate)$$

$growth\ rate \downarrow with\ time$

Overall Transformation Kinetics

Constant growth rate

- ❑ Generally in cellular transformations constant growth rate is observed.

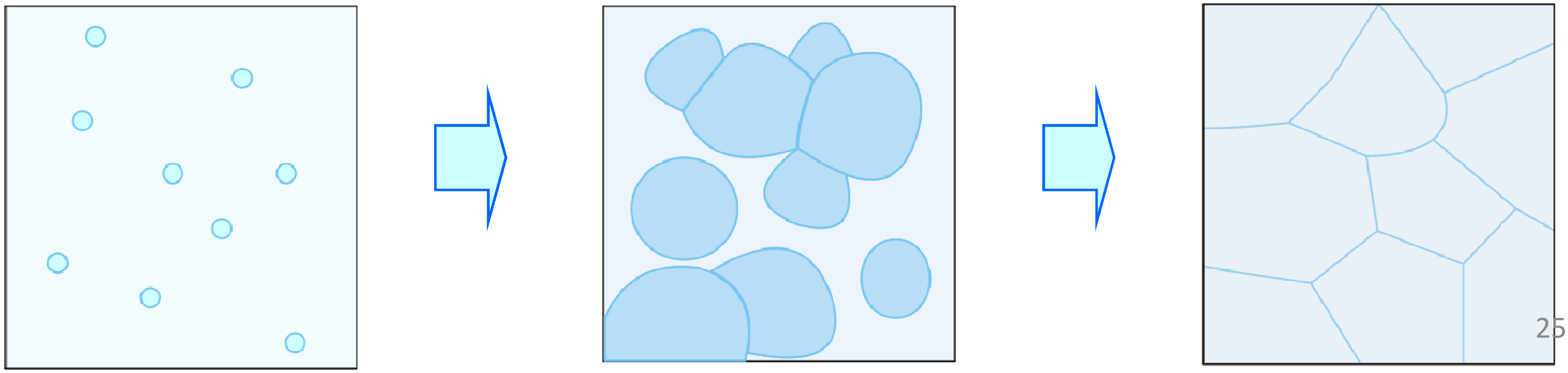
Cellular Transformations → Constant growth rate

- Pearlitic transformation
- Cellular Precipitation
- Massive Transformation
- Recrystallization

All of the parent phase is consumed by the product phase

$\boxed{\alpha \rightarrow \beta + \gamma}$ $\boxed{\alpha \rightarrow \beta}$

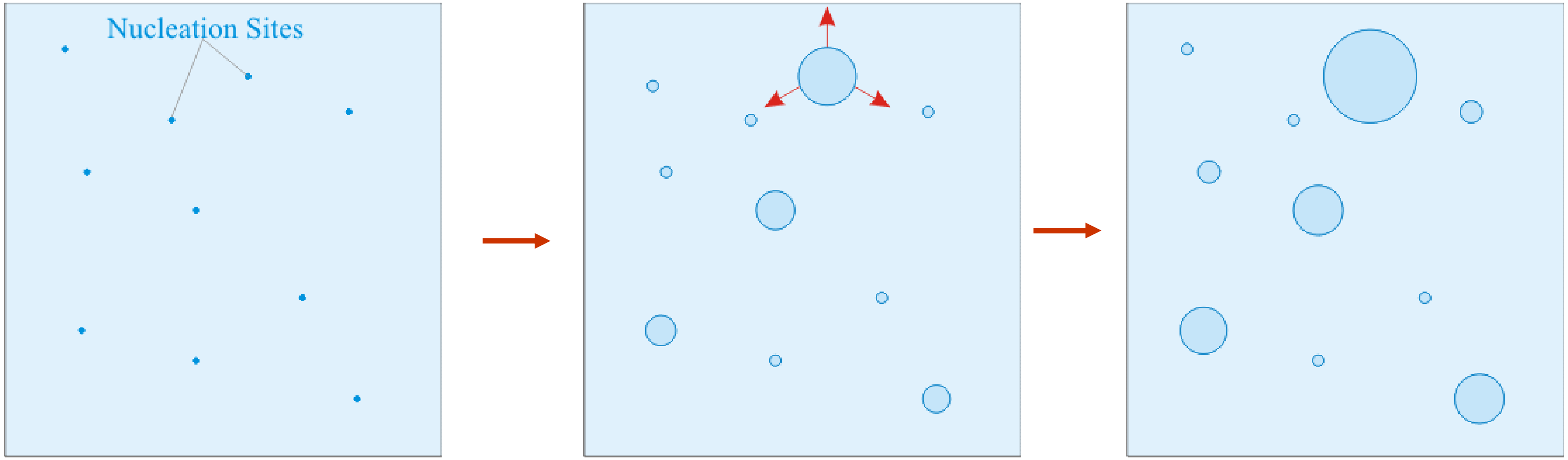
- ❑ Termination of transformation does not occur by a gradual reduction in the growth rate but by the impingement of the adjacent cells growing with a constant velocity.



Overall Transformation Kinetics

Constant nucleation rate

- Another common assumption is that the nucleation rate (I) is constant.
- In this case the transformation rate is a function of both the nucleation rate (fixed) and the growth rate (U).
- Growth rate decreases with time.
- If we further assume that the growth rate is constant (till impingement), then we get the Johnson-Mehl model.



$$f = F(number\ of\ nucleation\ sites, growth\ rate)$$

$$growth\ rate \downarrow with\ time$$

Derivation of f(T,t) : Avrami Model

- Parent phase has a fixed number of nucleation sites N_n per unit volume (and these sites are exhausted in a very short period of time
- Growth rate ($U = dr/dt$) constant and isotropic (as spherical particles) till particles impinge on one another.
- At time t the particle that nucleated at $t = 0$ will have a radius $r = Ut$
- Between time $t = t$ and $t = t + dt$ the radius increases by $dr = Udt$
- The corresponding volume increase $dV = 4\pi r^2\, dr$
- Without impingement, the transformed volume fraction (f) *(the extended transformed volume fraction)* of particles that nucleated between $t = t$ and $t = t + dt$ is:

$$\boxed{f = N_n\, 4\pi r^2 \left(dr\right) = N_n\, 4\pi \left[Ut\right]^2 \left(Udt\right) = N_n\, 4\pi U^3 t^2 dt}$$

- This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = N_n\, 4\pi U^3 t^2 dt} \Rightarrow \boxed{\int_0^X \frac{dX}{1-X} = \int_{t=0}^{t=t} N_n\, 4\pi U^3 t^2 dt}$$

$$X_\beta = 1 - e^{-\left(\frac{4\pi\, N_n U^3\, t^3}{3}\right)}$$

- *Based on the assumptions note that the growth rate is not part of the equation →it is only the number of nuclei.*

Derivation of f(T,t): Johnson-Mehl Model

- ❑ Parent phase completely transforms to product phase (α → β)
- ❑ Homogenous Nucleation rate of β in untransformed volume is constant (I)
- ❑ Growth rate (U = dr/dt) constant and isotropic (as spherical particles) till particles impinge on one another

- ❑ At time t the particle that nucleated at t = 0 will have a radius $r = Ut$
- ❑ The particle which nucleated at t = τ will have a radius $r = U(t - \tau)$
- ❑ Number of nuclei formed between time t = τ and t = τ + dτ → $Id\tau$
- ❑ Without impingement, the transformed volume fraction (f) *(called the extended transformed volume fraction)* of particles that nucleated between t = τ and t = τ + dτ is:

$$\boxed{f = \frac{4}{3}\pi r^3 \left(Id\tau\right) = \frac{4}{3}\pi \left[U(t-\tau)\right]^3 \left(Id\tau\right)}$$

- ❑ This fraction (f) has to be corrected for impingement. The corrected transformed volume fraction (X) is lower than f by a factor (1–X) as contribution to transformed volume fraction comes from untransformed regions only:

$$\boxed{f = \frac{dX}{1-X}} \Rightarrow \boxed{\frac{dX}{1-X} = \frac{4}{3}\pi r^3 \left(Id\tau\right) = \frac{4}{3}\pi \left[U(t-\tau)\right]^3 \left(Id\tau\right)}$$

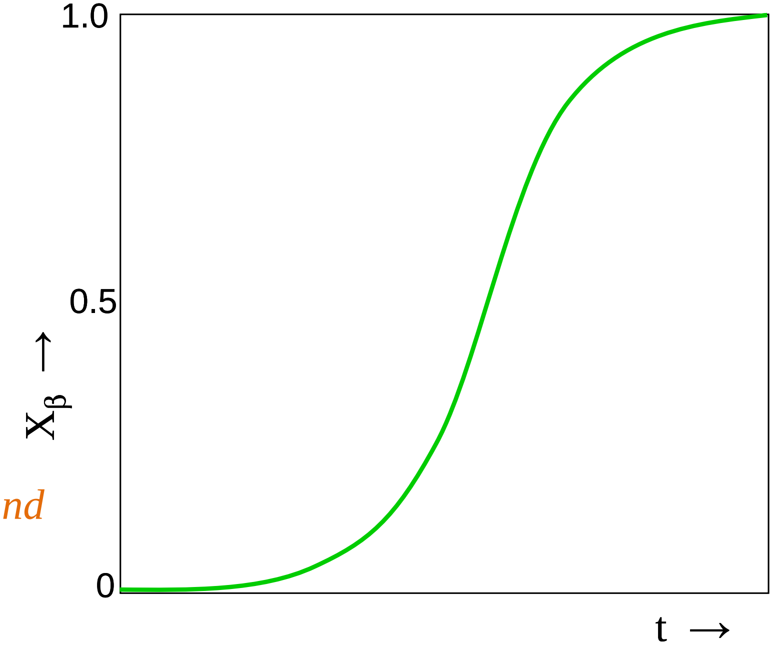
Derivation of f(T,t): Johnson-Mehl Model

$$\int_0^X \frac{dX}{1-X} = \int_{\tau=0}^{\tau=t} \frac{4}{3}\pi\left[U(t-\tau)\right]^3 \left(I d\tau\right)$$

$$X_\beta = 1 - e^{-\left(\frac{\pi I U^3 t^4}{3}\right)}$$

Note that X_β is both a function of I and U. I & U are assumed constant

For a isothermal transformation

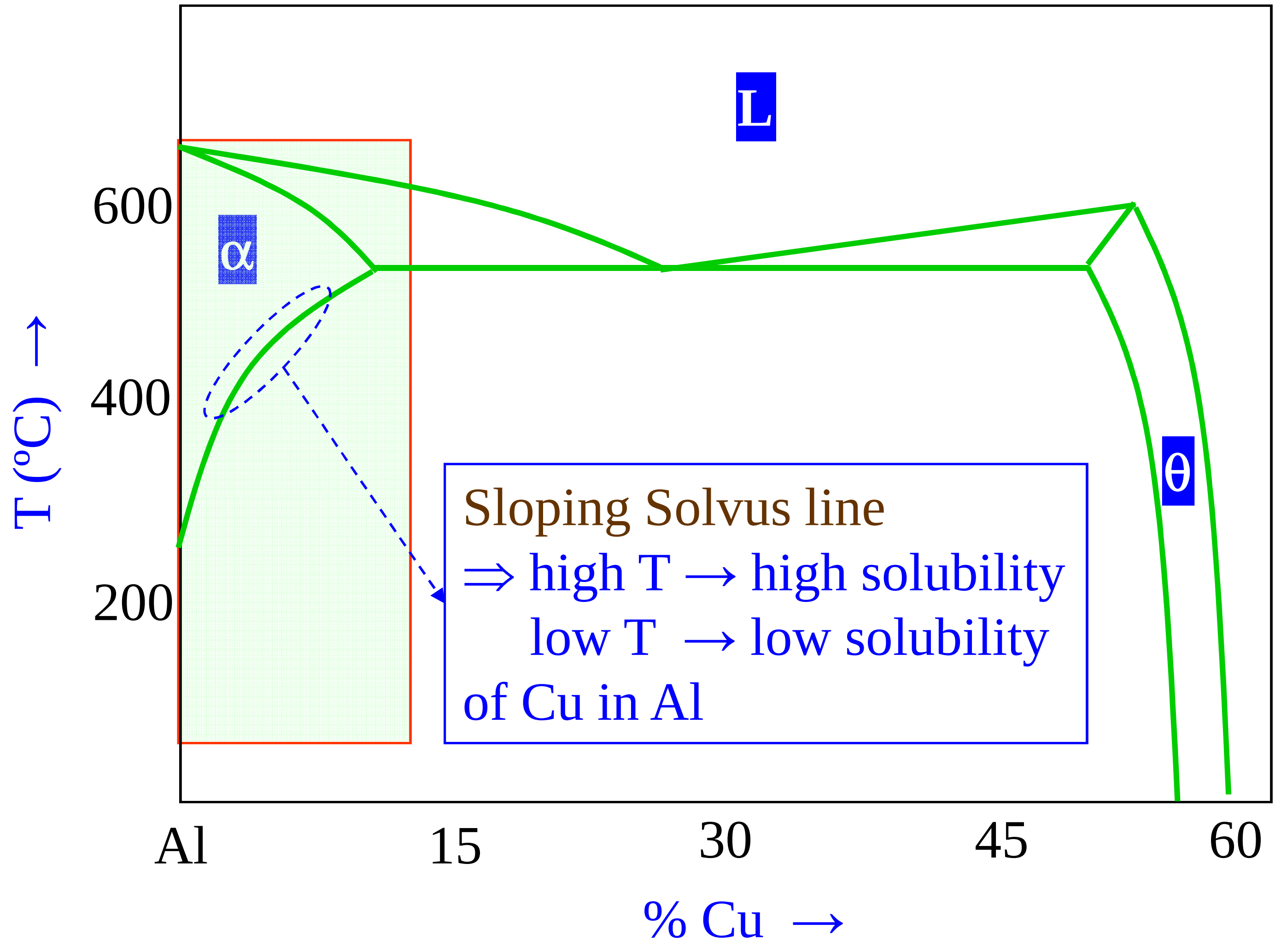


$\left(\frac{\pi I U^3}{3}\right)$ → is a constant during isothermal transformation

Precipitation Hardening

- ❑ The most important heat treating process for non ferrous alloys is *age hardening*, or *precipitation hardening*.
- ❑ In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature.
- ❑ The purpose of precipitation hardening treatment is to improve strength of the materials. It can explained by with respect to dislocations.
- ❑ The presence of dislocation weakens the crystal → easy plastic deformation
- ❑ Putting hindrance to dislocation motion increases the strength of the crystal
- ❑ Fine precipitates dispersed in the matrix provide such an impediment.
- ❑ For example: Strength of Al → 100 MPa
  Strength of Duralumin (Al + 4% Cu + other alloying elements) → 500 Mpa
- ❑ Two stages are generally required in heat treatment to produce age hardening:
  - ✓ Solution treatment
  - ✓ Aging

Precipitation Hardening



Sloping Solvus line

⇒ high T → high solubility

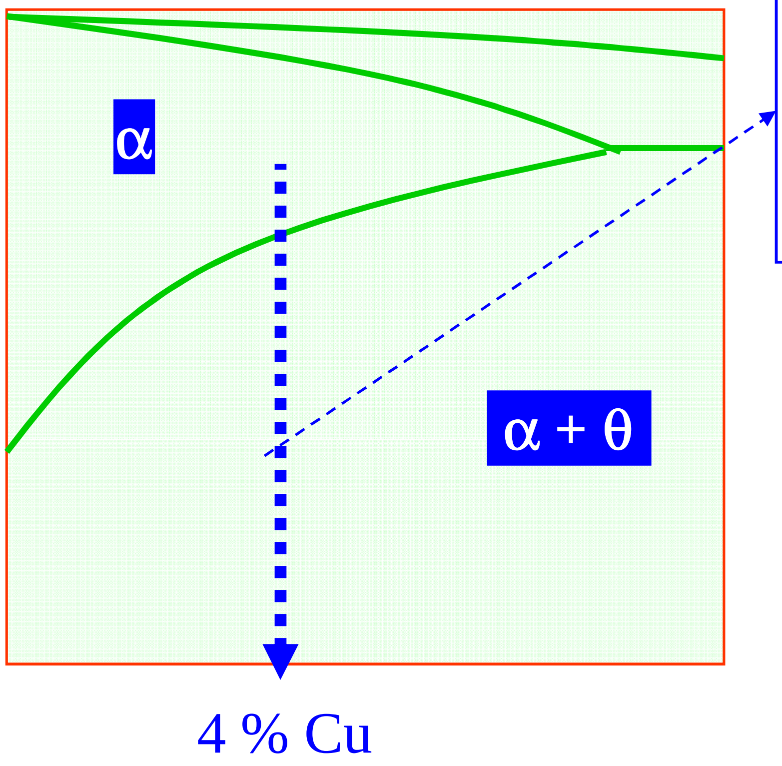
low T → low solubility

of Cu in Al

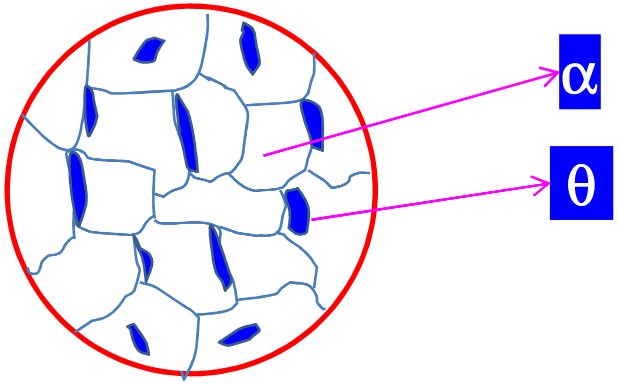
Al rich end of the Al-Cu phase diagram

Precipitation Hardening

On Equilibrium cooling



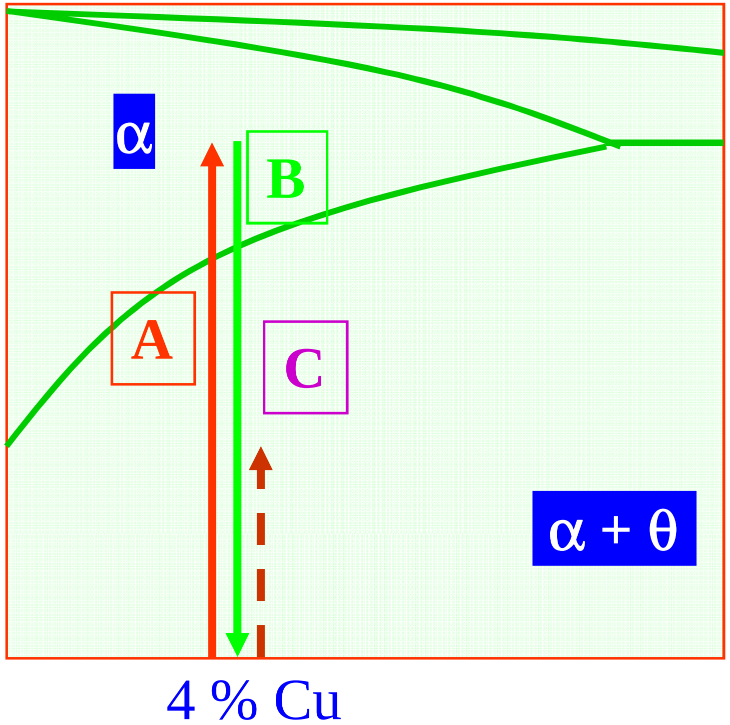
- $\alpha \rightarrow \alpha + \theta$
- Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*



$$\begin{pmatrix}\alpha\,(FCC)\\ 4\,\%\,Cu\\ 550^{o}\,C\end{pmatrix} \xrightarrow{slow\ cool} \begin{pmatrix}\alpha\,(FCC)\\ 0.5\,\%\,Cu\\ RT\end{pmatrix} + \begin{pmatrix}\theta\ CuAl_2\,(Tetragonal)\\ 52\,\%\,Cu\\ RT\end{pmatrix}$$

Precipitation Hardening

To obtain a fine distribution of precipitates the cycle A → B → C is used



Solution treating at high temperature, then quenching (second phase is in solid solution) →Cycle A and B

A Heat (to 550°C) → solid solution α

B Quench (to RT) → supersaturated solution

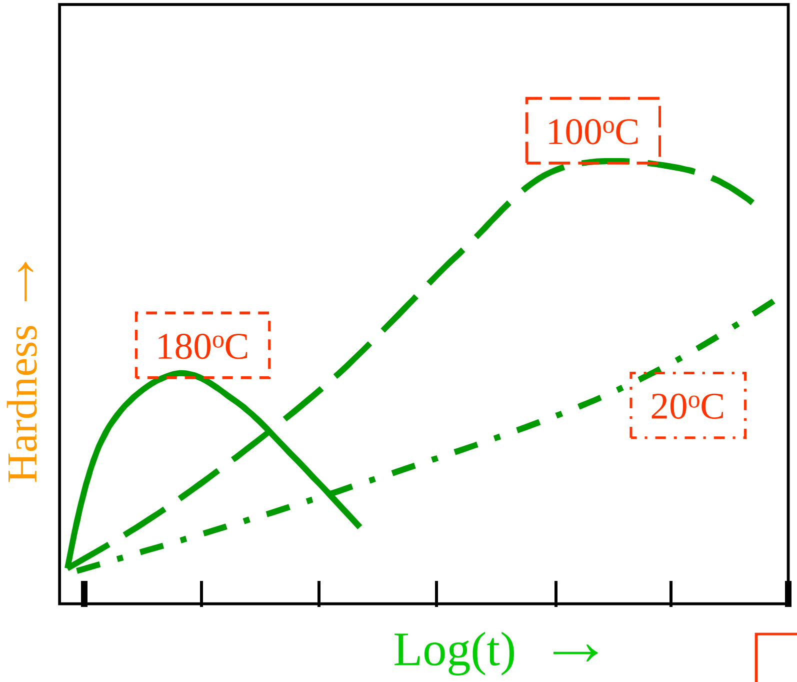
Increased vacancy concentration

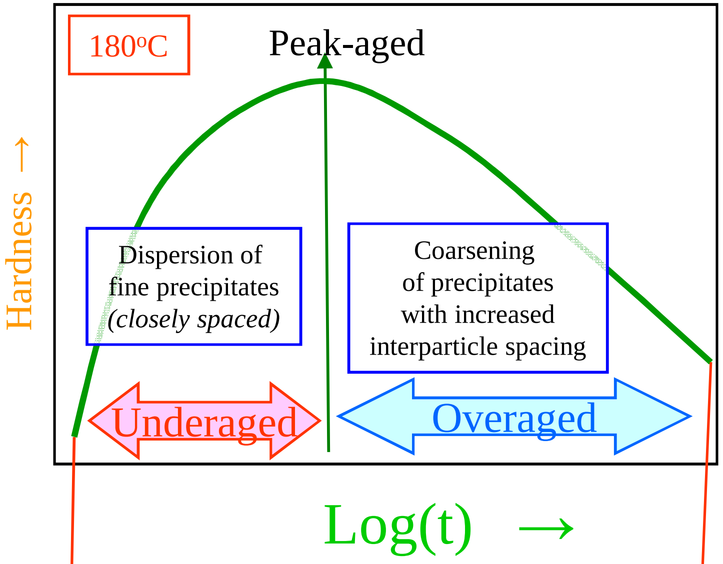
Ageing at room temperature or slightly higher temperature (Precipitation of second phase, giving strengthening effect) →Cycle C

C Age (*reheat* to 200°C) → fine precipitates

Note: Treatments A, B, C are for the same composition

Precipitation Hardening





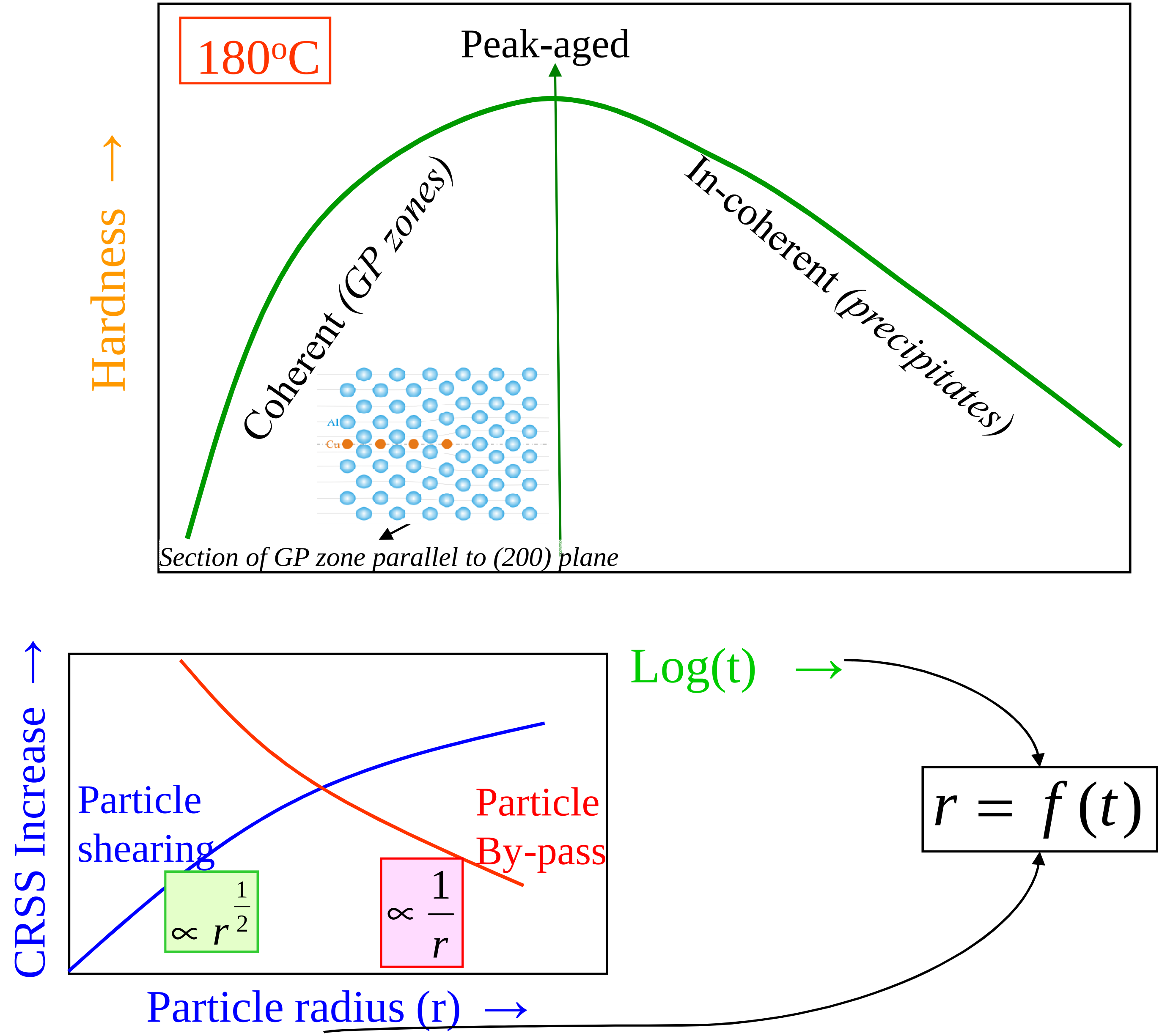
Region of solid solution strengthening *(no precipitation hardening)*

Region of precipitation hardening *(but little/some solid solution strengthening)*

- ❑ Higher temperature ⇒ less time of aging to obtain peak hardness
- ❑ Lower temperature ⇒ increased peak hardness

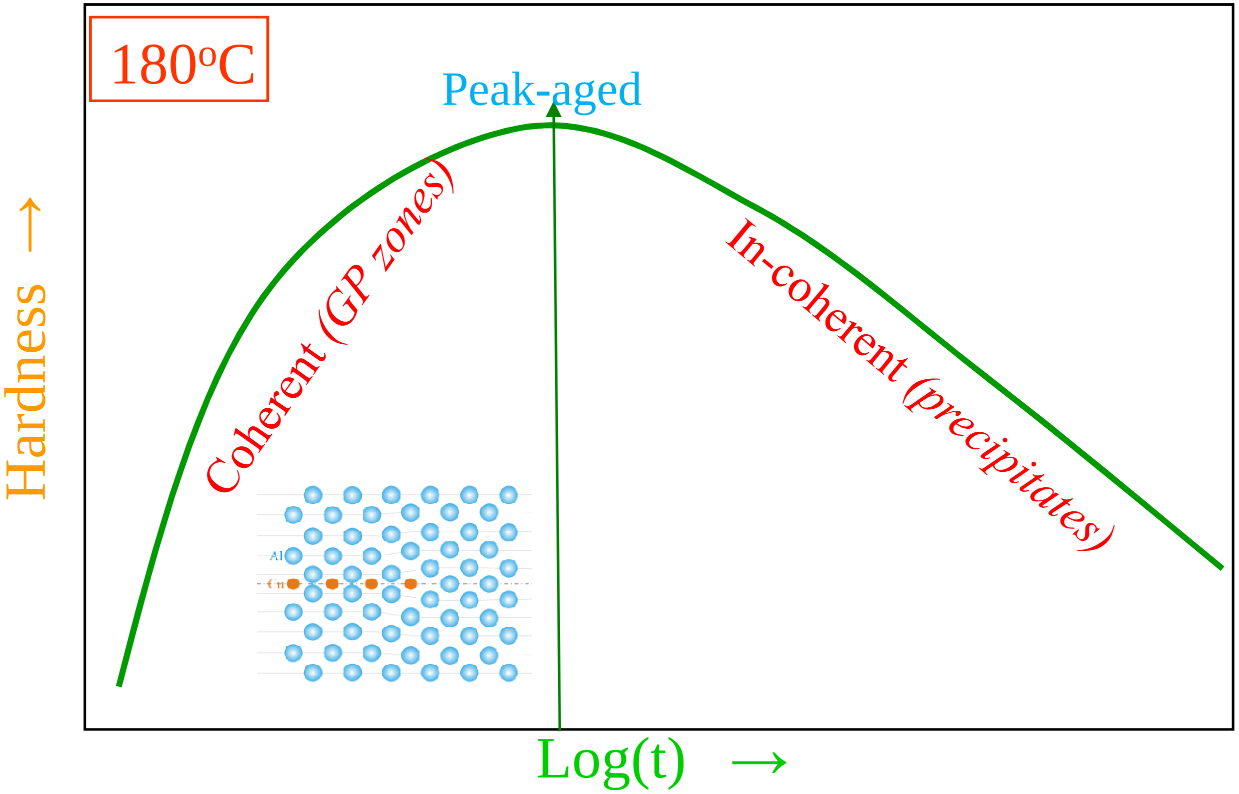
⇒ optimization between time and hardness required

Precipitation Hardening



Precipitation Hardening

A complex set of events are happening parallely/sequentially during the aging process → These are shown schematically in the figure ⇒



Increasing size of precipitates with increasing interparticle (inter-precipitate) spacing

Interface goes from coherent to semi-coherent to incoherent

Precipitate goes from GP zone → θ'' → θ' → θ

Precipitation Hardening

GP Zones

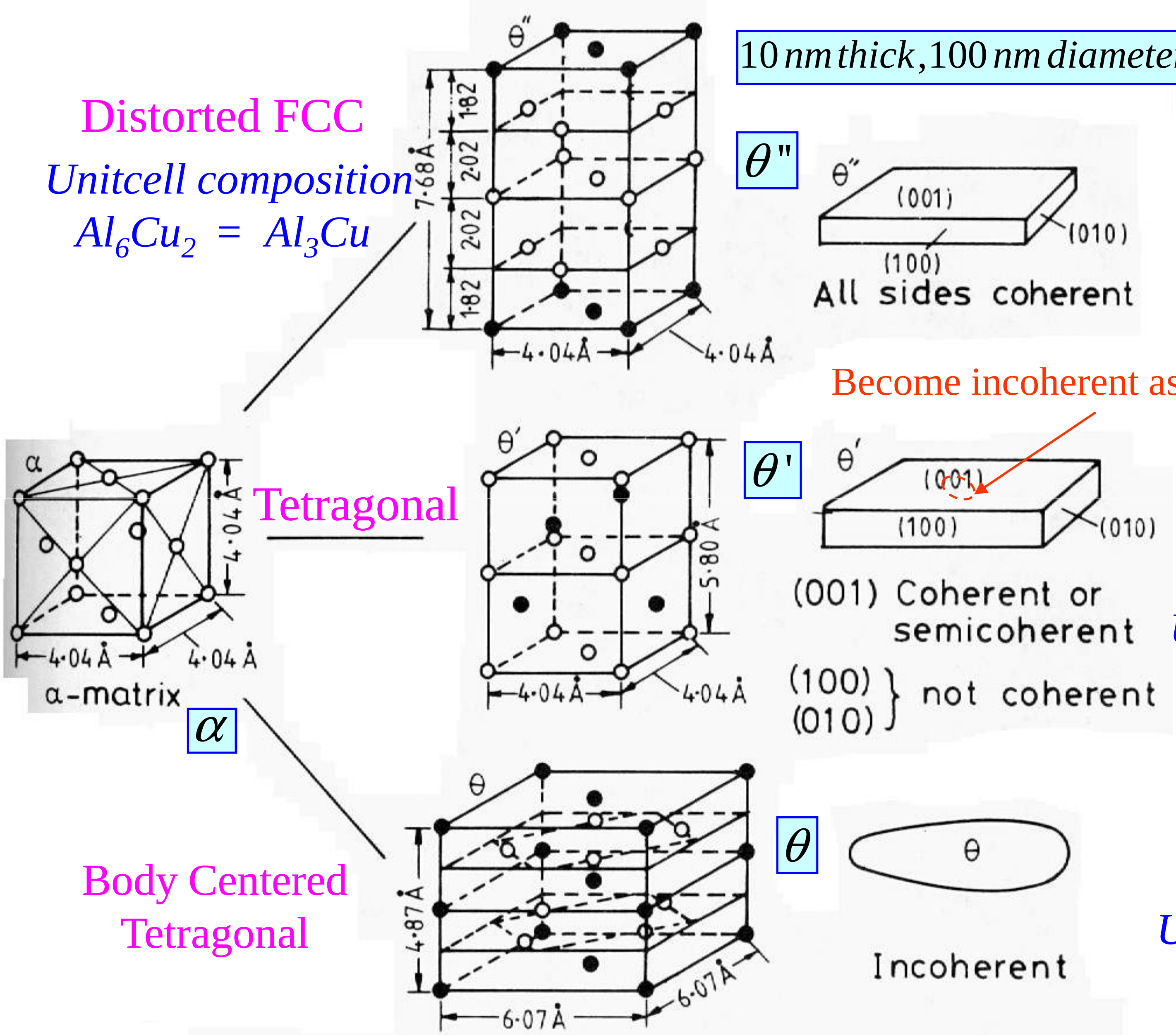
- ☐ Cu rich zones fully coherent with the matrix → low interfacial energy
- ☐ (Equilibrium θ phase has a complex tetragonal crystal structure which has incoherent interfaces)
- ☐ Zones minimize their strain energy by choosing disc-shape ⊥ to the elastically soft <100> directions in the FCC matrix
- ☐ The driving force ($\Delta G_v - \Delta G_s$) is less but the barrier to nucleation is much less (ΔG^*)
- ☐ 2 atomic layers thick, 10nm in diameter with a spacing of ~10nm
- ☐ The zones seem to be homogenously nucleated (excess vacancies seem to play an important role in their nucleation)
- ☐ Due to large surface to volume ratio the fine precipitates have a tendency to coarsen → small precipitates dissolve and large precipitates grow
- ☐ Coarsening

  ⇒ ↓ in number of precipitate

  ⇒ ↑ in interparticle (inter-precipitate) spacing

  ⇒ reduced hindrance to dislocation motion ($\tau_{max} = Gb/L$)

Precipitation Hardening



Structure and morphology of θ″, θ′ and θ in Al–Cu (○ Al, ● Cu).

Distorted FCC

Unitcell composition

$Al_6Cu_2 = Al_3Cu$

$10\,nm\,thick, 100\,nm\,diameter$

θ''

$(001)_{\theta''} \| (001)_{\alpha}$

$[100]_{\theta''} \| [100]_{\alpha}$

Become incoherent as ppt. grows

α

Tetragonal

θ'

$(001)_{\theta'} \| (001)_{\alpha}$

$[100]_{\theta'} \| [100]_{\alpha}$

Unitcell composition

$Al_4Cu_2 = Al_2Cu$

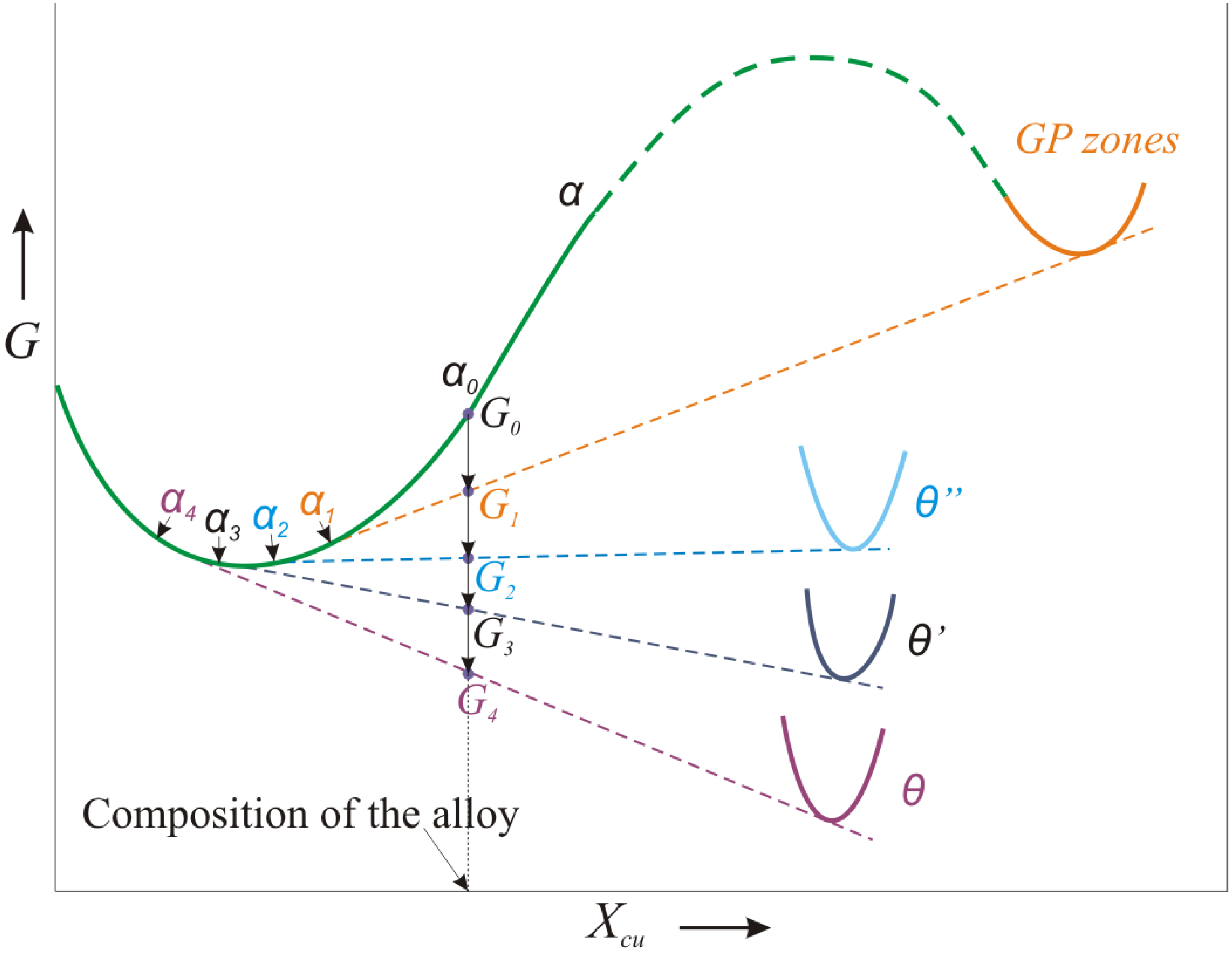
Body Centered Tetragonal

θ

Unitcell composition

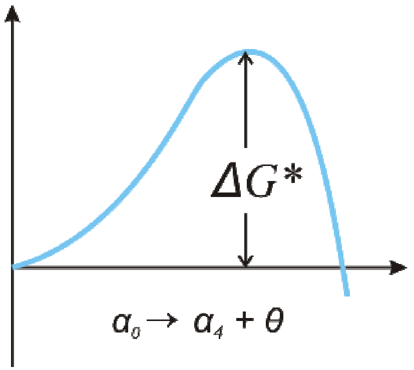
$Al_8Cu_4 = Al_2Cu$

Precipitation Hardening



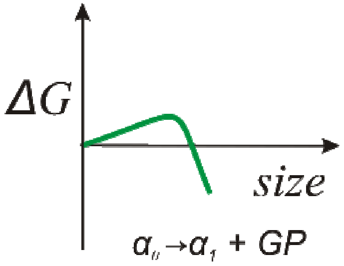
Schematic diagram showing the lowering of the Gibbs free energy of the system on sequential transformation:
GP zones → θ'' → θ' → θ

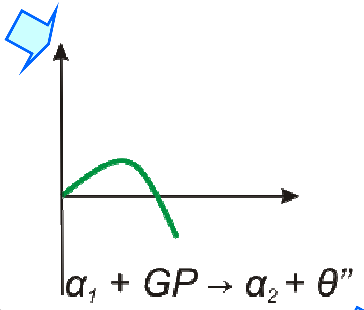
Precipitation Hardening

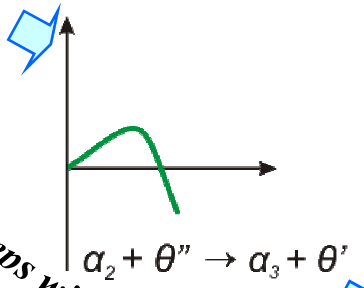


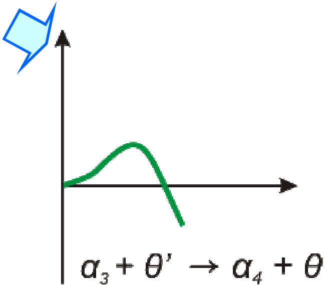
The activation barrier for precipitation of equilibrium (θ) phase is large

If the transformation is broken down into a series of steps with smaller activation barrier the processes can take place even with low thermal activation

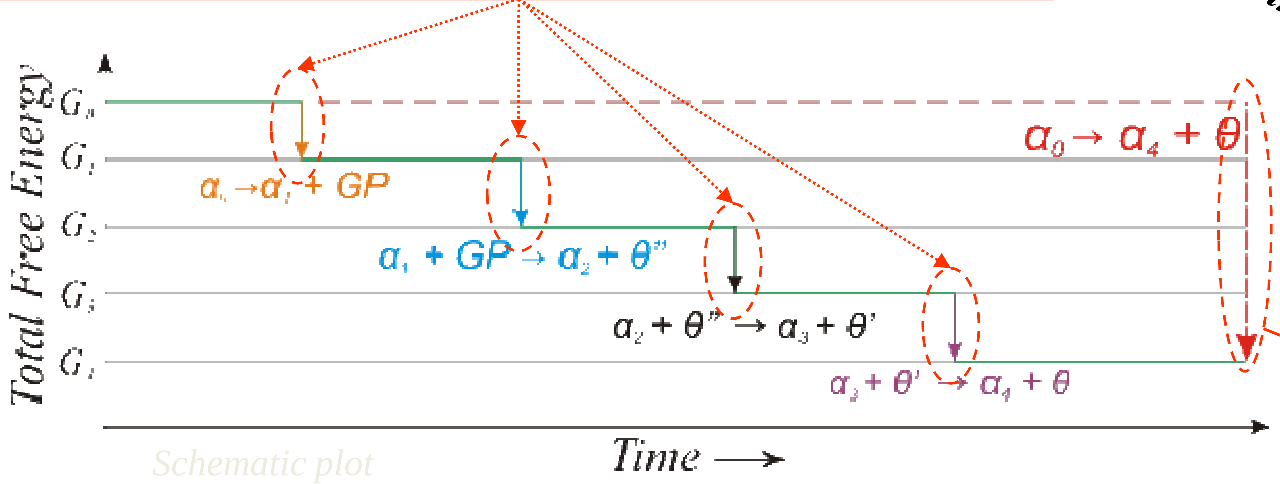








But, the free energy benefit in each step is small compared to the overall single step process

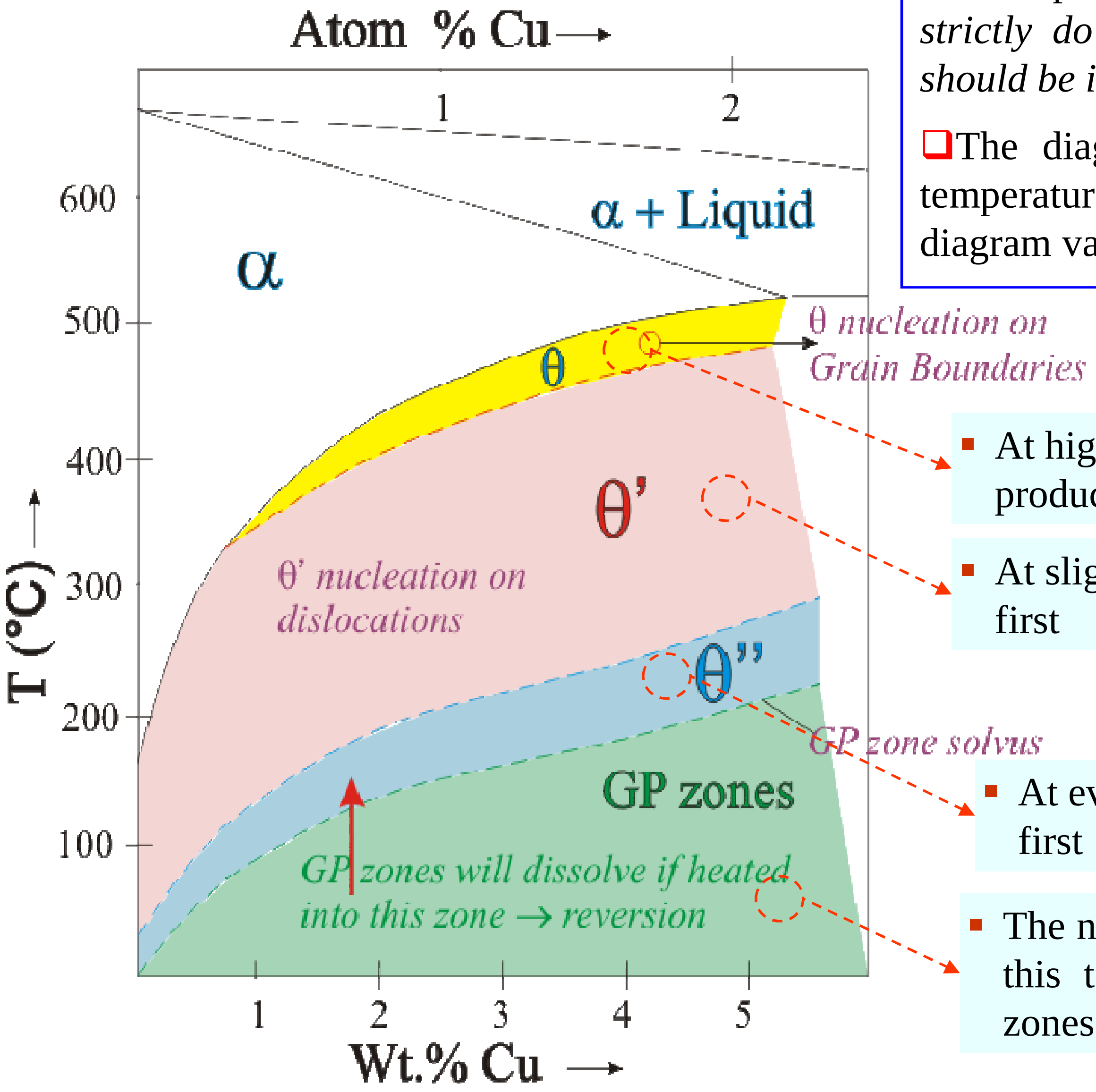


Single step ('equilibrium') process

Precipitation Hardening

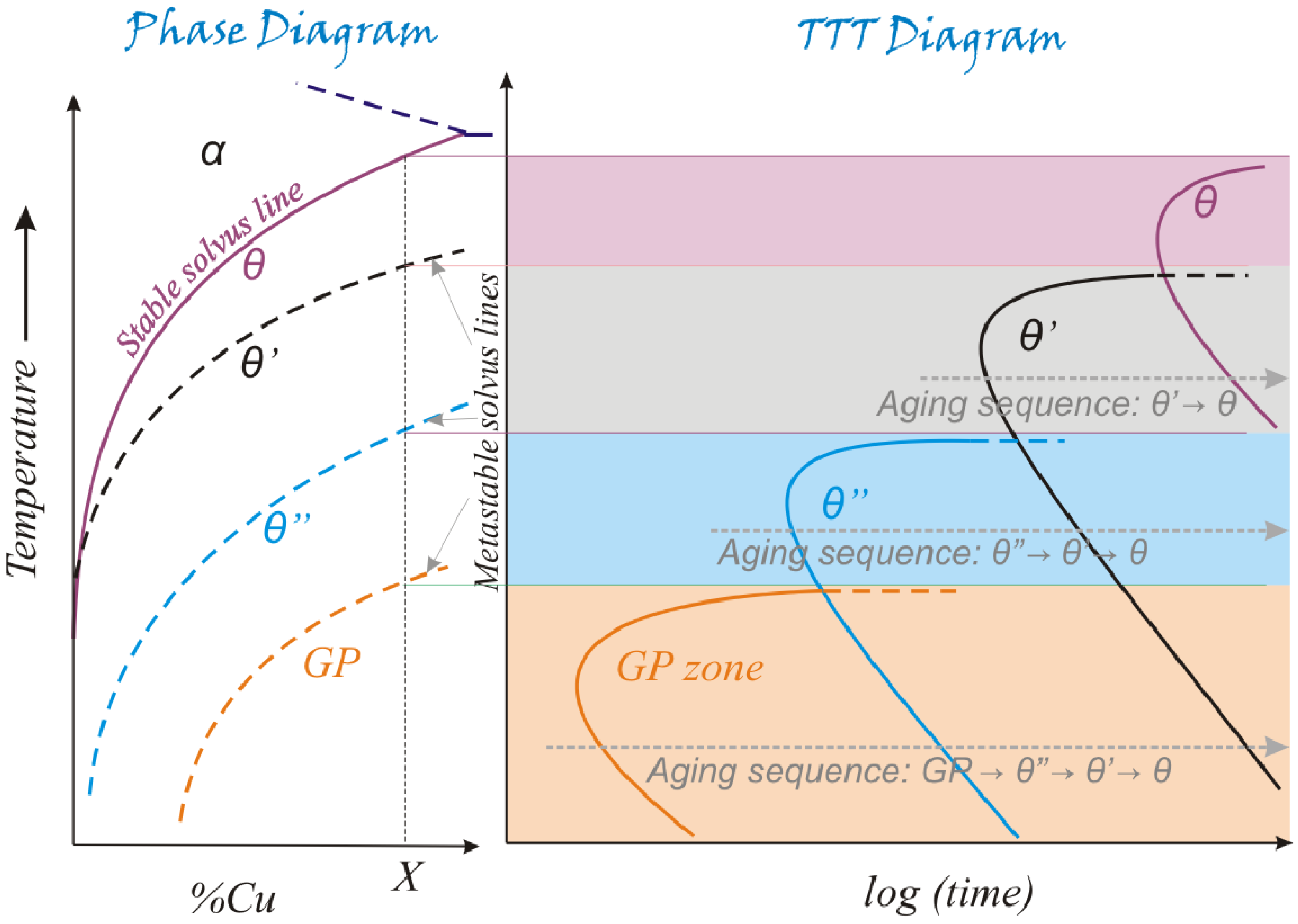
❑ In this diagram additionally information has been superposed onto the phase diagram *(which strictly do not belong there- hence this diagram should be interpreted with care)*

❑The diagram shows that on aging at various temperatures in the α + θ region of the phase diagram various precipitates are obtained first



- At higher temperatures the stable θ phase is produced directly
- At slightly lower temperatures θ' is produced first
- At even lower temperatures θ'' is produced first
- The normal artificial aging is usually done in this temperature range to give rise to GP zones first

Phase and TTT diagrams



Phase and TTT diagrams

- ❑ In previous slide, we show the Al-rich portion of the Al-Cu phase diagram (schematically). From the phase diagram, it is clear that the Al with a few percent copper is cooled from high temperature leads to the formation of a microstructure in which the θ phase precipitates out of the supersaturated α matrix.
- ❑ However, if an alloy of composition Al - 4 wt. %Cu is solutionised at say, 540°C, and the resultant phase is rapidly quenched to room temperature, the solid solution is largely retained; if this alloy is kept at room temperature (or at any temperature below 180°C), a metastable phase known as Guinier-Preston zones (GP zones) is formed.
- ❑ Similarly, the aging treatment at other temperatures can produce other precipitates such as θ'' and θ'.
- ❑ The solvus for these metastable phases in shown in Fig. Further, we also show the corresponding time-temperature-transformation curves for these metastable phase as well as the stable phase.
- ❑ we already discussed the crystallography and interface structure of all these phases as well as the reasons for their formation.

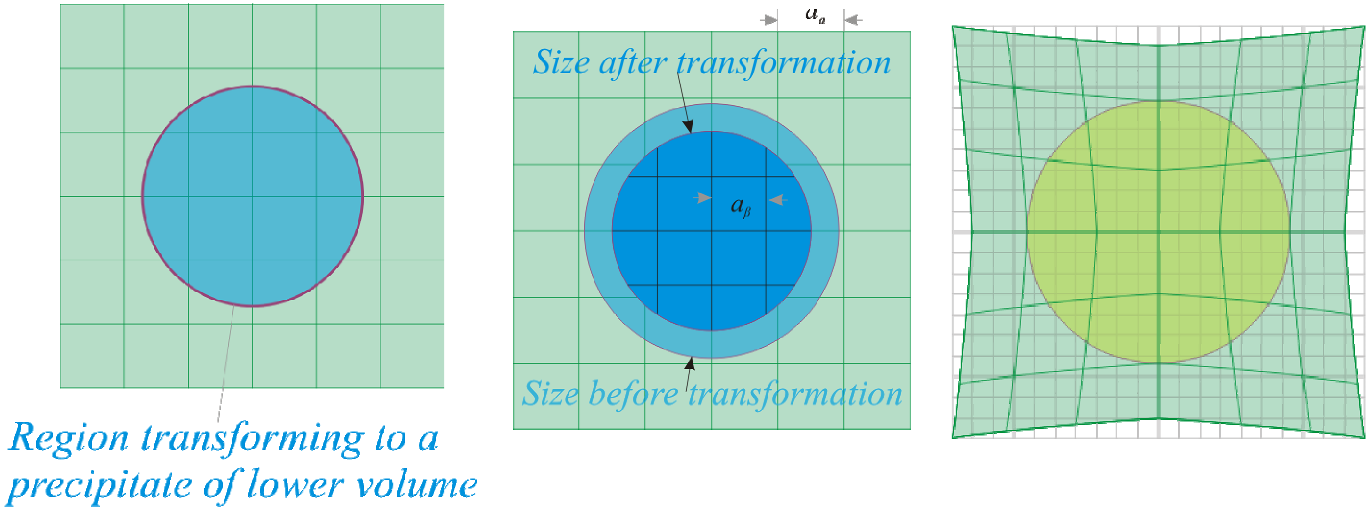
Misfit strain effects : Coherent precipitate

- The equilibrium shape of a coherent precipitate or zone is, when the misfit between the precipitate and matrix is small.
- When misfit is present is present the formation of coherent interfaces raises the free energy of the system on accounted of the elastic strain fields that arise.
- If the elastic strain energy is denoted by ΔG_s the condition for equilibrium becomes

$$\boxed{\sum A_i \gamma_i + \Delta G_s = \min imum}$$

- If the lattice parameters of the unstrained precipitate and matrix are a_p and a_m , respectively, the unconstrained misfit (δ) is defined by

$$\boxed{\delta = \frac{a_p - a_m}{a_m}}$$

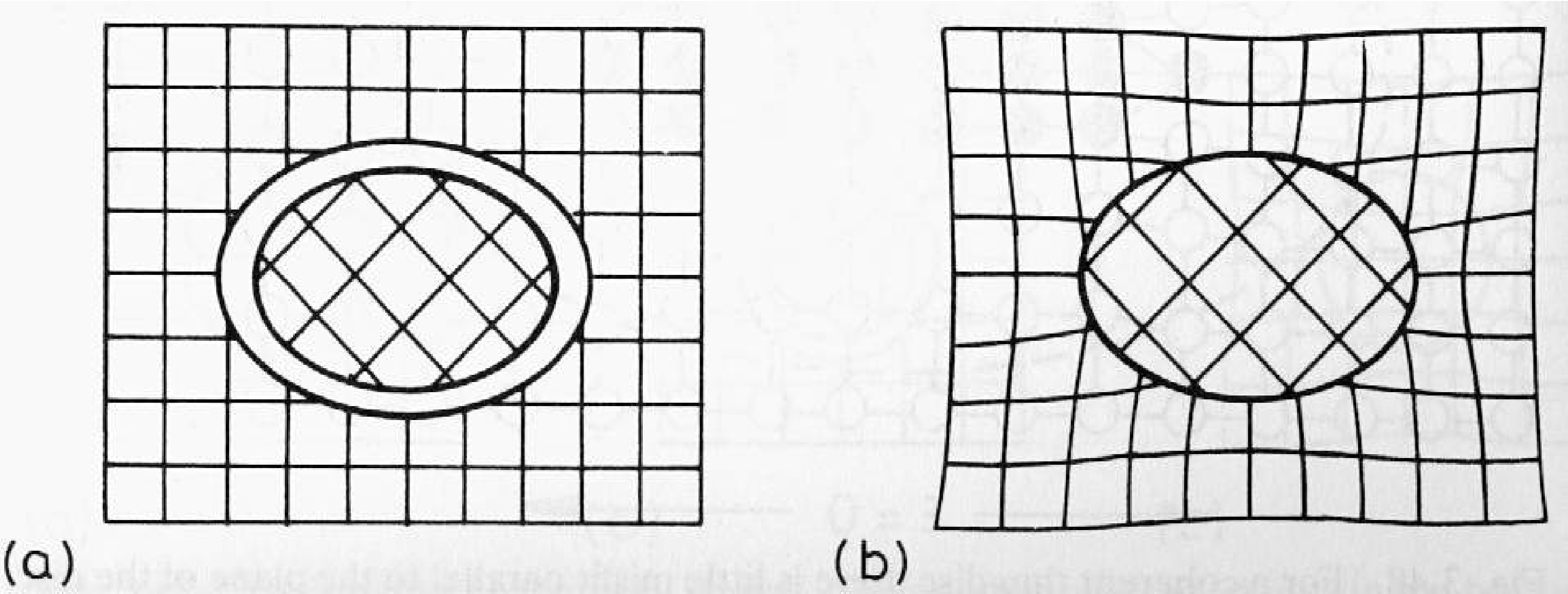


Schematic showing a coherent precipitate and the origin of coherency strains

Misfit strain effects : Coherent precipitate

- ❑ When the precipitate is incoherent with the matrix, there is an attempt at matching the two lattices and lattice sites are not conserved across the interface.
- ❑ Under these circumstances there are no coherency strains. Misfit strains can, however, still arise if the precipitate is the wrong size for the hole it is located.
- ❑ In this case the lattice misfit δ has no significance and it is better to consider the volume misfit Δ as defined by

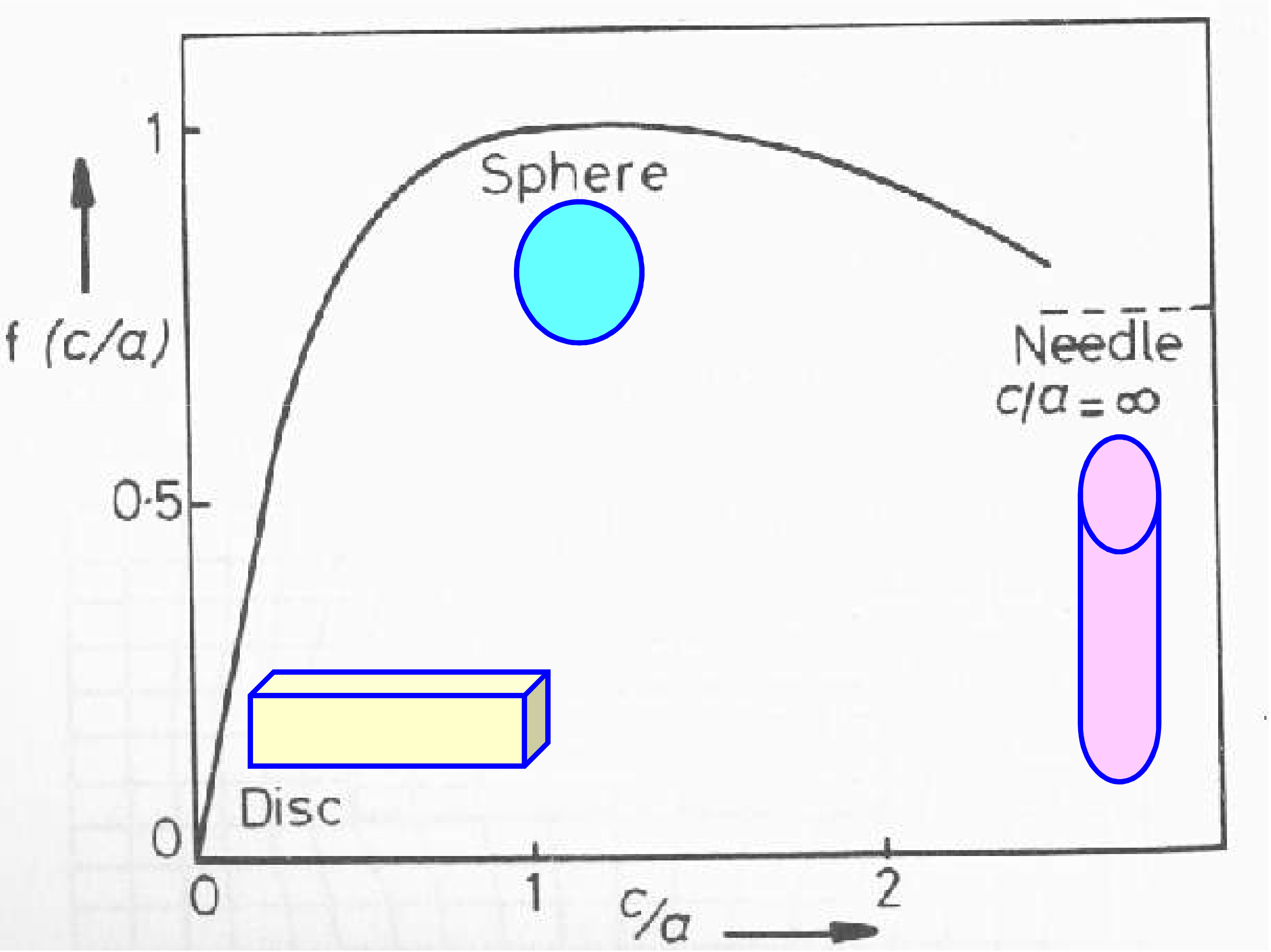
$$\Delta = \frac{V_p - V_m}{V_m}$$



The origin of misfit strain for an incoherent precipitate (no lattice matching

Misfit strain effects : Coherent precipitate

- ☐ Choose particle shape → minimize the free energy of system



The variation of misfit strain energy with aspect ratio of ellipsoid shape

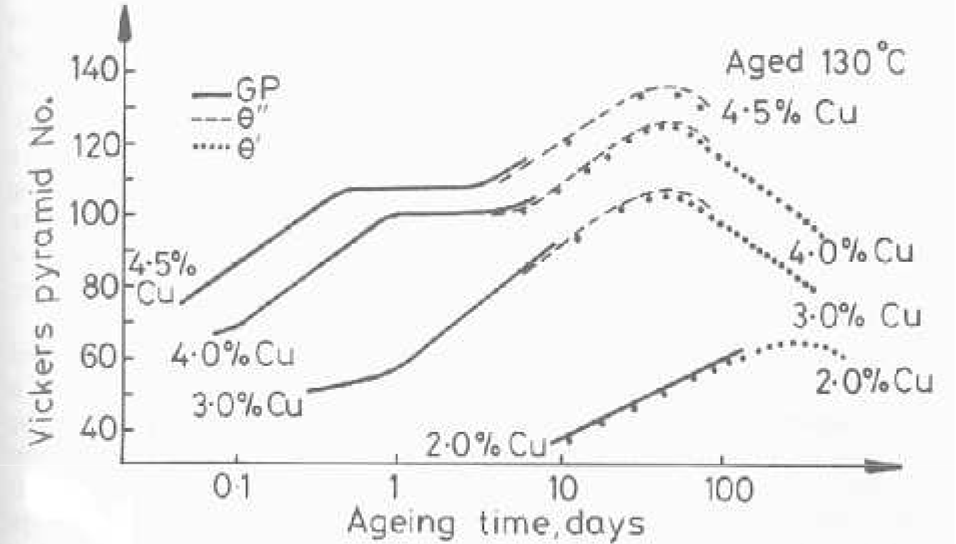
Precipitation Hardening

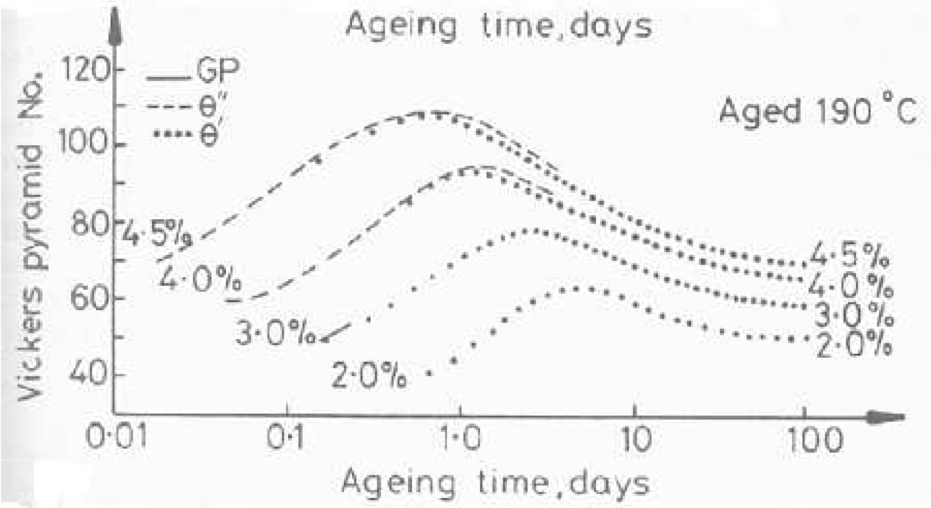
Precipitation Sequence in some precipitation hardening systems

Base Metal	Alloy	Precipitation Sequence
Aluminium	Al-Ag	GPZ (spheres) → γ' (plates) → γ (Ag_2Al)
	Al-Cu	GPZ (discs) → θ'' (discs) → θ' (plates) → θ ($CuAl_2$)
	Al-Cu-Mg	GPZ (rods) → S' (laths) → S ($CuMgAl_2$) (laths)
	Al-Zn-Mg	GPZ (spheres) → η' (plates) → η ($MgZn_2$) (plates or rods)
	Al-Mg-Si	GPZ (rods) → β' (rods) → β (Mg_2Si) (plates)
Copper	Cu-Be	GPZ (discs) → γ' → γ (CuBe)
	Cu-Co	GPZ (spheres) → β (Co) (plates)
Iron	Fe-C	ε-carbide (discs) → Fe_3C
	Fe-N	α'' (discs) → Fe_4N
Nickel	Ni-Cr-Ti-Al	γ' (cubes or spheres)

Precipitation Hardening

Details in ‘practical’ aging curves



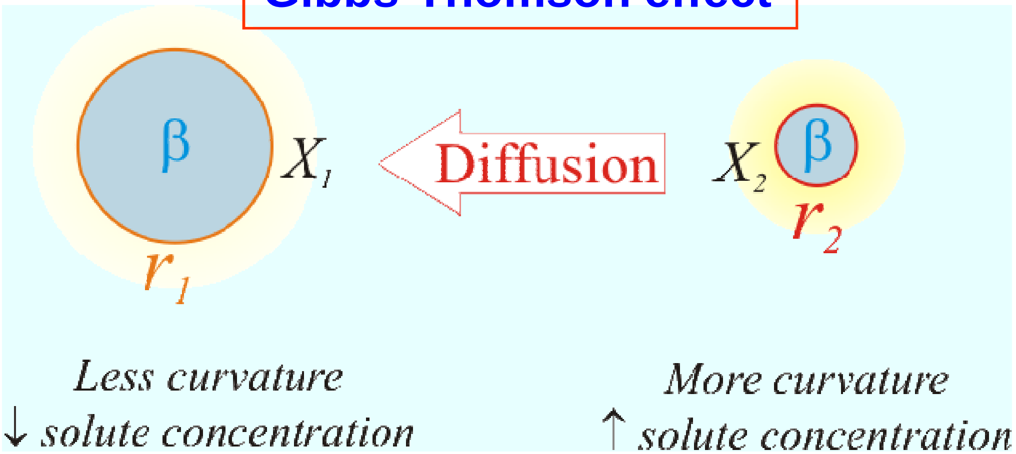


- In low T aging (130°C)→The aging curves have more detail than the single peak as discussed schematically before.
- In low T aging (130°C)→ the full sequence of precipitation is observed (GPZ →θ''→ θ').
- At high T aging (190°C)→ θ'' directly forms (i.e. the full precipitation sequence is not observed).
- Peak hardness increases with increasing Cu%.
- For the same Cu%, the peak hardness is lower for the 190°C aging treatment as compared to the 130°C aging treatment.
- Peak hardness is achieved when the microstructure consists of a θ' or combination of (θ' + θ'').

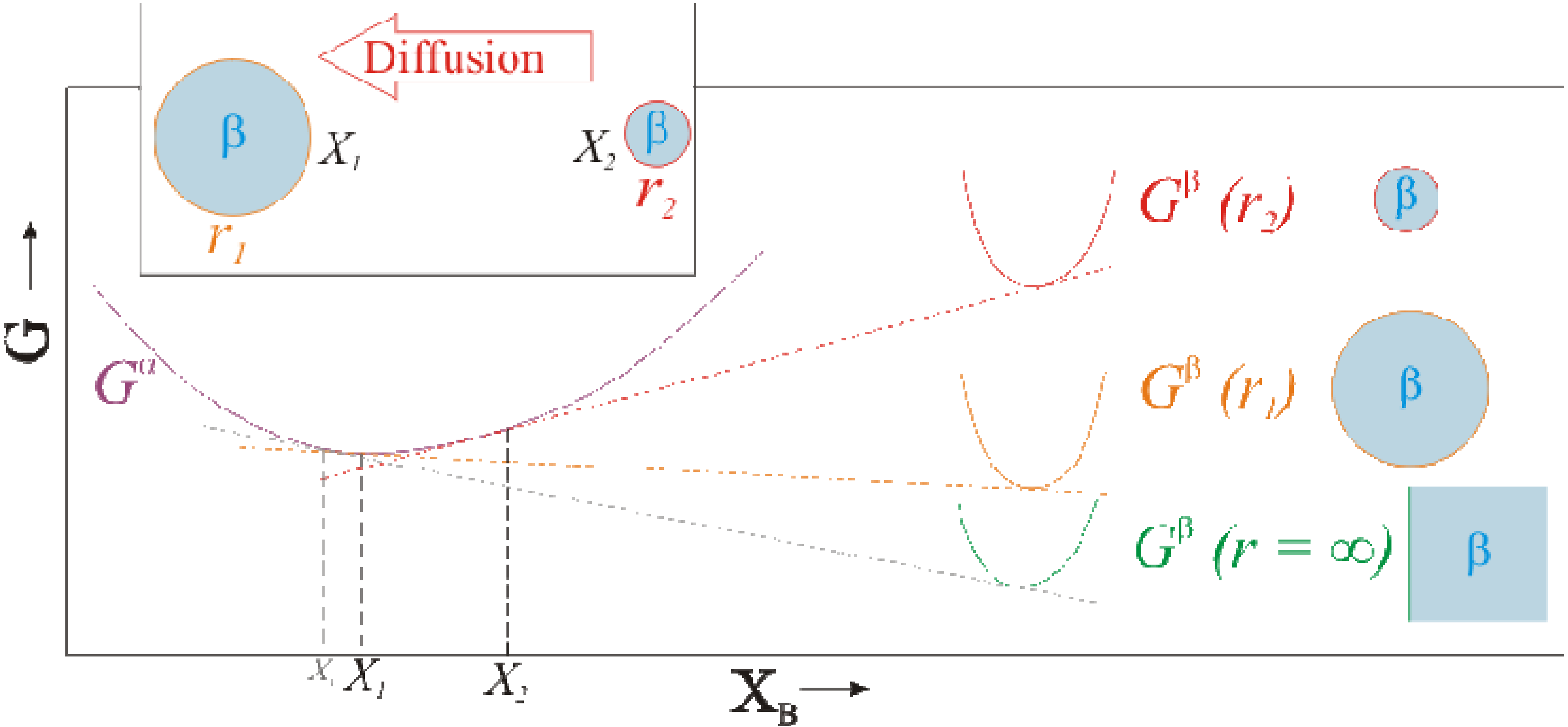
Particle/precipitate Coarsening

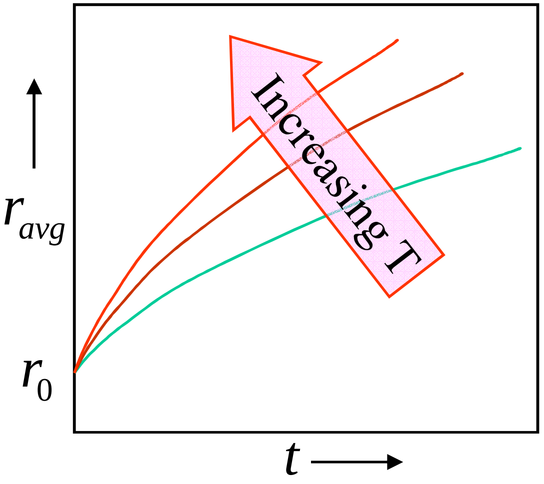
- ☐ There will be a range of particle sizes due to time of nucleation and rate of growth
- ☐ As the curvature increases the solute concentration (X_B) in the matrix adjacent to the particle increases
- ☐ Concentration gradients are setup in the matrix → solute diffuses from near the small particles towards the large particles
  ⇒ small particles shrink and large particles grow
- ☐ ⇒ with increasing time * Total number of particles decrease
  * Mean radius (r_{avg}) increases with time

Gibbs-Thomson effect



Particle/precipitate Coarsening





$$\boxed{r_{avg}^3 - r_0^3 = kt}$$

$$\boxed{k \propto D\gamma X_e}$$

- $r_0 \rightarrow r_{avg}$ at $t = 0$
- D → Diffusivity
- $X_e \rightarrow X_B\ (r = \infty)$

D is a exponential function of temperature
⇒ coarsening increases rapidly with T

Particle/precipitate Coarsening

Rate controlling factor

- Volume diffusion rate
  - $$\frac{dr_{avg}}{dt} \propto \frac{k}{r_{avg}^2}$$ $\Rightarrow$ *small ppts coarsen more rapidly*
  - Linear r_{avg}^3 versus t relation may break down due to diffusion short-circuits or if the process is interface controlled
- Interface diffusion rate

Rate of coarsening

- Diffusion coefficient (D)
- Interfacial energy
- Equilibrium solubility of very large particles (X_e)

- Precipitation hardening systems employed for high-temperature applications must avoid coarsening by having low: γ, X_e or D

Rate of coarsening

Low γ

- In superalloys, Strength obtained by fine dispersion of γ' [ordered FCC $Ni_3(TiAl)$] precipitate in FCC Ni rich matrix
- Matrix (Ni SS)/ γ' matrix is fully coherent [low interfacial energy γ = 30 mJ/m^2]
- Misfit = f(composition) → varies between 0% and 0.2%
- Creep rupture life increases when the misfit is 0% rather than 0.2%

Low X_e

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix)*

- Oxides are insoluble in metals
- Stability of these microstructures at high temperatures due to low value of X_e
- The term $D\gamma X_e$ has a low value

Low D

ThO_2 dispersion in W (or Ni) *(Fine oxide dispersion in a metal matrix)*

- Cementite dispersions in tempered steel coarsen due to high D of interstitial C
- If a substitutional alloying element is added which segregates to the carbide → rate of coarsening ↓ due to low D for the substitutional element

Spinodal decomposition/Spinodal clustering

- Phase diagrams showing miscibility gap correspond to solid solutions which exhibit clustering tendency.
- Within the miscibility gap the decomposition can take place by either
  - *Nucleation and Growth* *(First order)* or by
  - *Spinodal Mechanism* *(First order)*
- If the second phase is not coherent with the parent then the region of the spinodal is called the chemical spinodal
- If the second phase is coherent with the parent phase then the spinodal mechanism is operative only inside the coherent spinodal domain
- As coherent second phases cost additional strain energy to produce (as compared to a incoherent second phase – only interfacial energy involved) → this requires additional undercooling for it to occur
- Spinodal decomposition is not limited to systems containing a miscibility gap
- Other examples are in binary solid solutions and glasses
- All systems in which GP zones form (e.g.) contain a metastable coherent miscibility gap → THE GP ZONE SOLVUS
- Thus at high supersaturations it is GP zones can form by spinodal mechanism.

Spinodal mechanism

- In phase separating systems, at low temperatures, the Gibbs free energy consists of regions of concave curvature (as shown Fig. 1) and in such regions the binary alloy separated into a mechanical mixture of A and B-rich regions instead of remaining a solid solution. This is because such a phase separation into mechanical mixture reduces the free energy of the system.
- Further, in such systems with concavity of free energy, for certain compositions, the mechanism of phase separation changes from the classical nucleation and growth to spinodal decomposition. The change over in the mechanism is related to the curvature of the free energy curve as shown in Fig. 2.

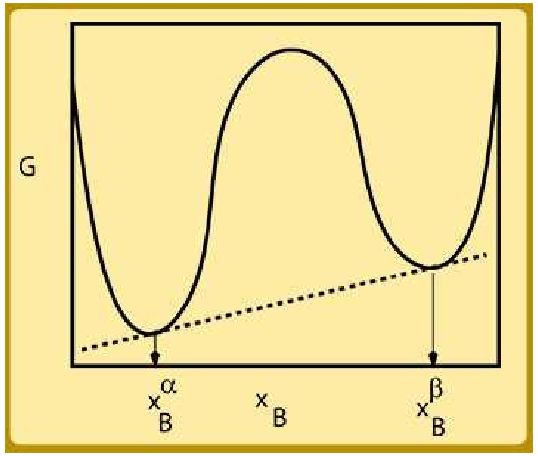


Fig. 1

The free energy of a system with concave curvature. In the concave curvature region, the system becomes a mechanical mixture of A rich and B rich phases with the given compositions marked in this figure.

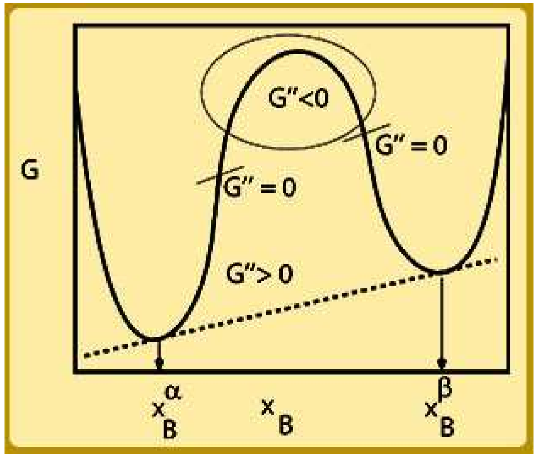
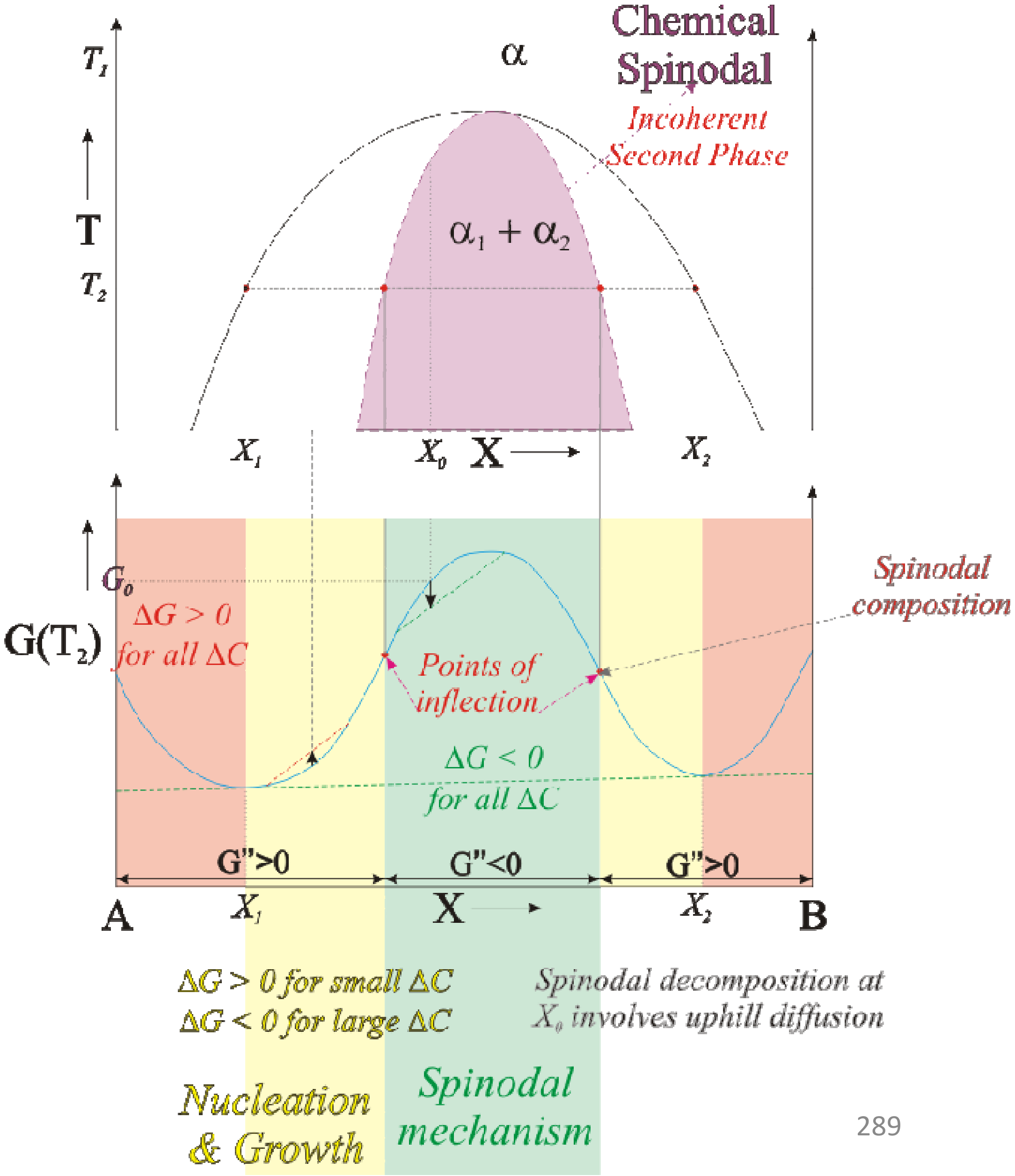


Fig. 2

Positive curvature (nucleation) and negative curvature (spinodal) regions of the free energy versus composition diagram; phase separation mechanism changes from nucleation to spinodal at the point of zero curvature.

Spinodal mechanism

- ❑ In this figure we show the phase separation region along with the points at every temperature at which the curvature of the free energy versus composition plot changes its sign; the locus of these points is as shown and is known as chemical spinodal.
- ❑ In the case of spinodal phase separation, any small composition fluctuation grows leading to A-rich regions becoming richer in A and B-rich regions becoming richer in B. This is because such a process leads to a decrease in free energy.
- ❑ Thus, the process of spinodal decomposition is in contrast to the classical diffusion equation scenario which predicts that regions with positive curvature for composition profile grow in time while those with negative curvature decay leading to homogenisation.



Spinodal mechanism

- Consider a system with an interdiffusion coefficient D and undergoing spinodal decomposition. Within the spinodal region, the composition fluctuations grow as shown in Fig. (previous slide); the fluctuations grow with a characteristic time constant

$$\boxed{\tau = -\lambda^2 / 4\pi^2 D}$$

where λ is the wavelength of the composition modulation (assuming one-dimensional modulations).

- Thus, for smaller λ, the rate of transformation becomes high; however, there is a minimum λ below which spinodal decomposition cannot occur; this is because, during spinodal decomposition, as A- and B-rich regions are forming, there are also interfaces between these regions where AB bonds are formed which are energetically costlier; these regions give rise to an increase in free energy; the `incipient' interfacial energy associated with the formation of these regions with large AB bonds are the ones which set the lower wavelength limit. The lower limit on the wavelength λ can be obtained using the following argument.
- Consider a homogeneous alloy of composition x_B^0 decomposing into two parts: one with composition $x_B^0 + \Delta x$ and another with composition . It can be shown that the total free energy change associated with this decomposition is

$$\boxed{\Delta G_{chem} = \frac{1}{2}\frac{d^2G}{dx_B^2}(\Delta x)^2}$$

Spinodal mechanism

- As noted earlier, the AB bonds in the incipient interface regions also contribute to the free energy; this free energy contribution, thus, is associated with the gradients in composition. Consider a sinusoidal composition modulation of wavelength λ and amplitude Δx ; the maximum composition gradient is thus Δx/λ and the gradient energy contribution is

$$\Delta G_{grad} = \kappa \left(\frac{\Delta x}{\lambda} \right)^2$$

where ΔG_{grad} is a proportionality constant which is dependent on the difference between AB and AA and BB bond energies.

- The total change in free energy associated with a composition fluctuation of wavelength λ is thus given by the addition of the chemical and gradient terms

$$\Delta G = \Delta G_{chem} + \Delta G_{grad} = \left(\frac{d^2 G}{dx_B^2} + \frac{2\kappa}{\lambda^2} \right) \frac{(\Delta x)^2}{2}$$

- From the above expression, it is clear that for spinodal decomposition

$$-\frac{d^2 G}{dx_B^2} > \frac{2\kappa}{\lambda^2}$$

- Or

$$\lambda^2 > -\frac{2\kappa}{\frac{d^2 G}{dx_B^2}}$$

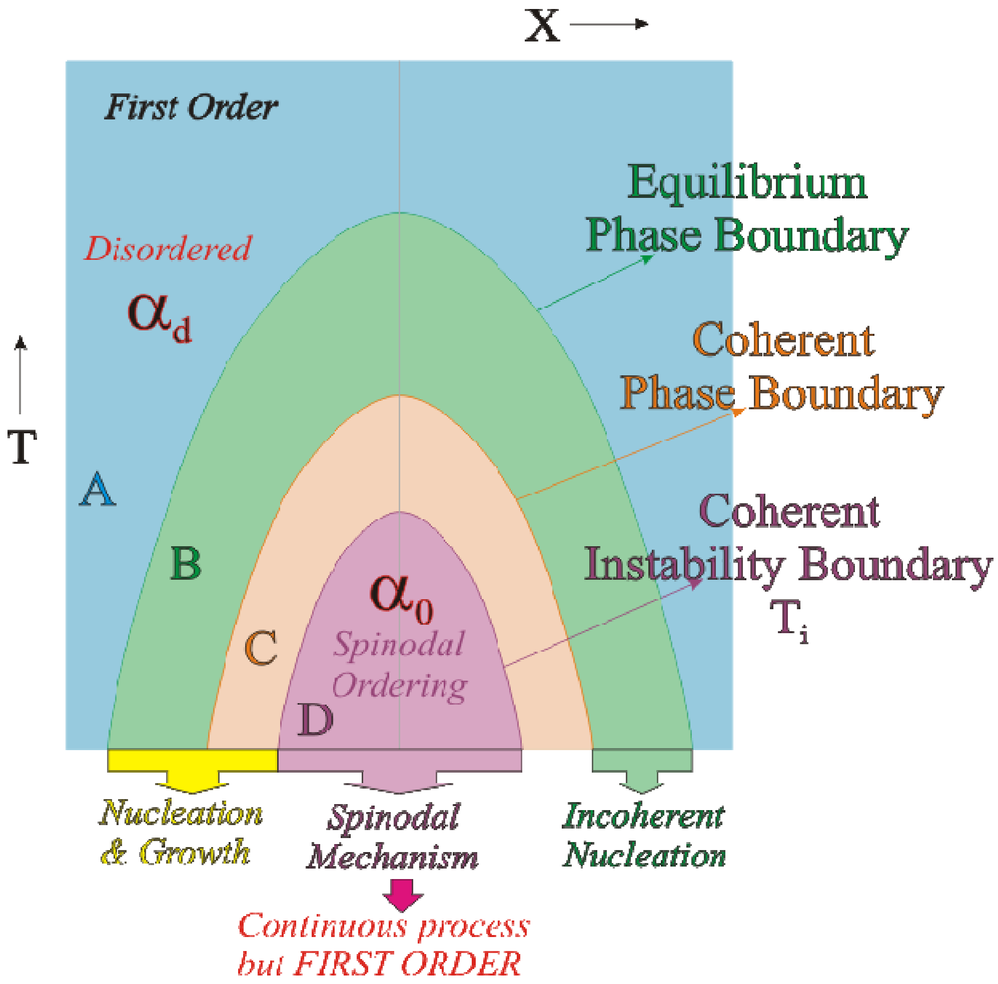
Spinodal Ordering

- Ordering leads to the formation of a superlattice
- Ordering can take place in *Second Order or First Order (in continuous mode below* T_i*)* modes
- Any change in the lattice dimensions due to ordering introduces a third order term in the Landau equation

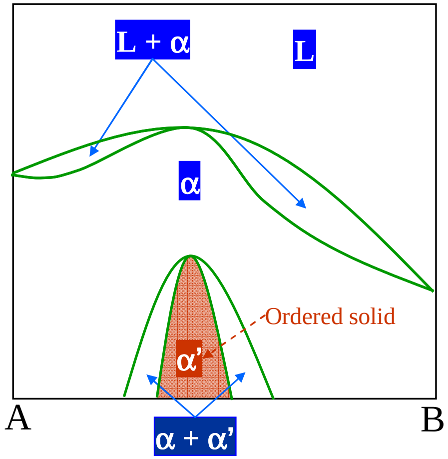
$$\Delta G = A\eta^2 + \underbrace{B}_{\text{Not zero}}\eta^3 + C\eta^4 \ldots$$

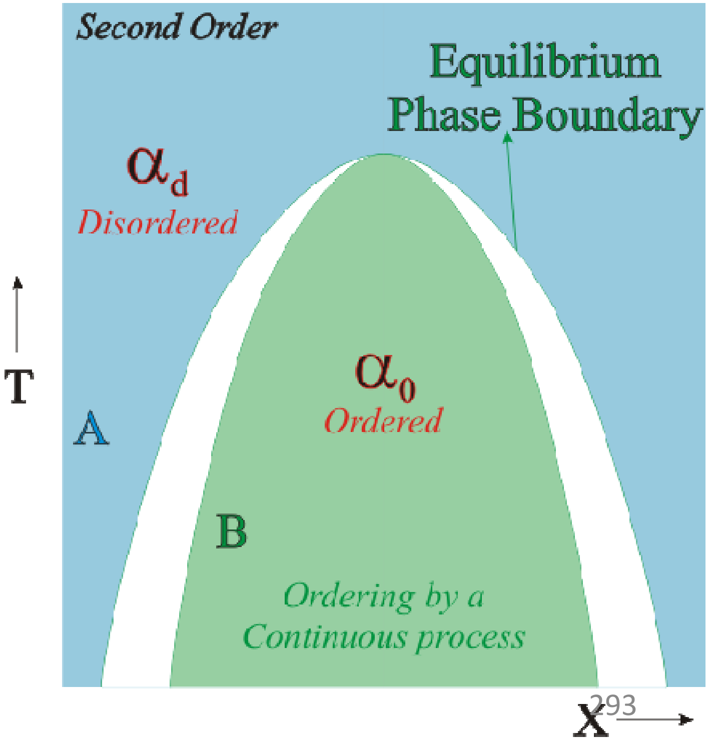
- Continuous ordering as a first order transformation requires a finite supercooling below the Coherent Phase Boundary to the Coherent Instability (T_i) boundary
- These (continuous ordering) 1st order transitions are possible in cases where the symmetry elements of the ordered structure form a subset of the parent disordered structure

Spinodal Ordering



A→Disordered solid solution
B→Nucleation of incoherent ordered phase
C→Nucleation of coherent ordered phase
D→Ordered phase by Spinodal mechanism

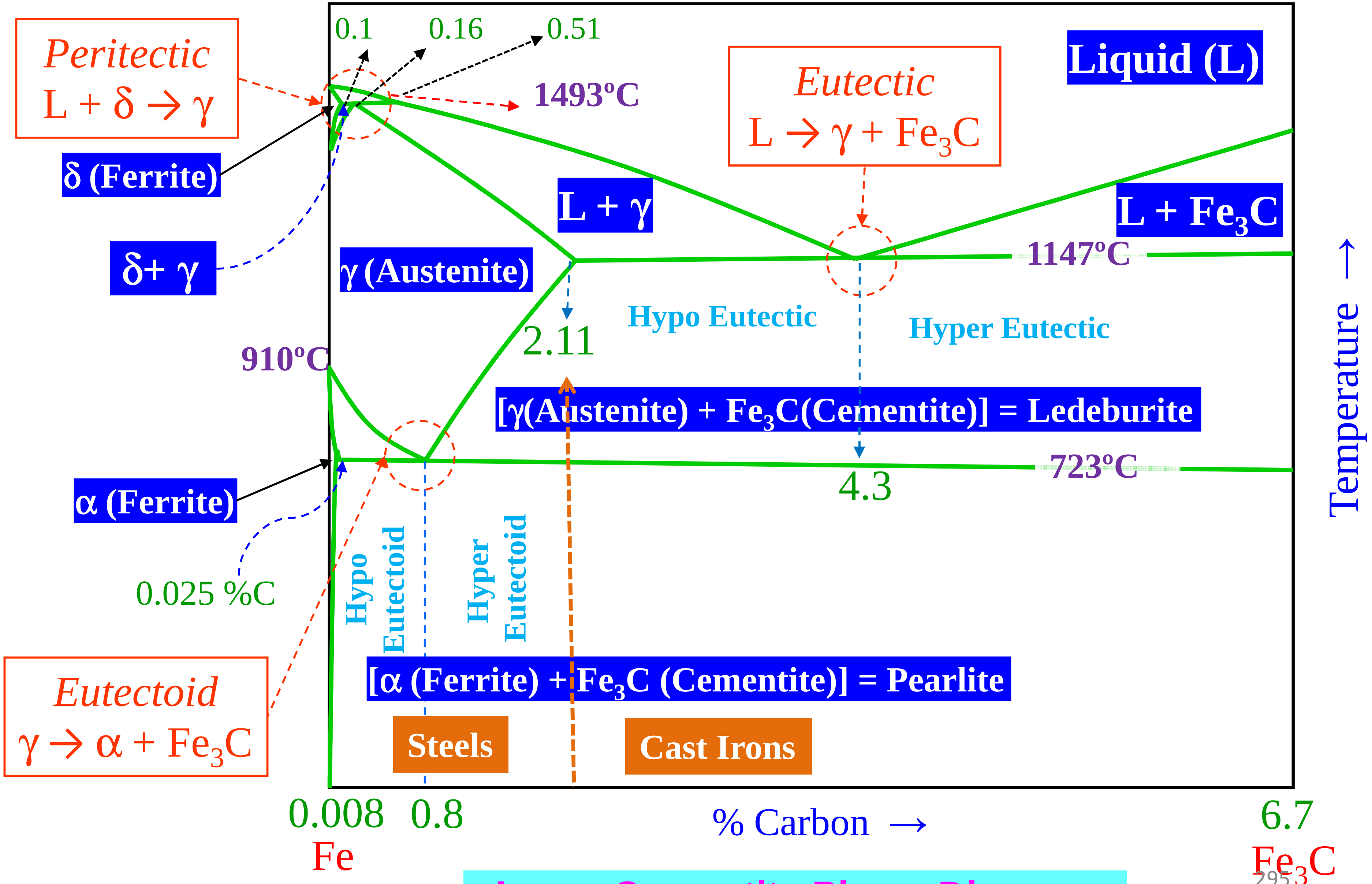




Summary

Nucleation & Growth	Spinodal
The composition of the second phase remains unaltered with time	A continuous change of composition occurs until the equilibrium values are attained
The interfaces between the nucleating phase and the matrix is sharp	The interface is initially very diffuse but eventually sharpens
There is a marked tendency for random distribution of both sizes and positions of the equilibrium phases	A regularity- though not simple- exists both in sizes and distribution of phases
Particles of separated phases tend to be spherical with low connectivity	The separated phases are generally non-spherical and posses a high degree of connectivity

Eutectoid Transformation in Fe-Fe_3C phase diagram



Iron – Cementite Phase Diagram

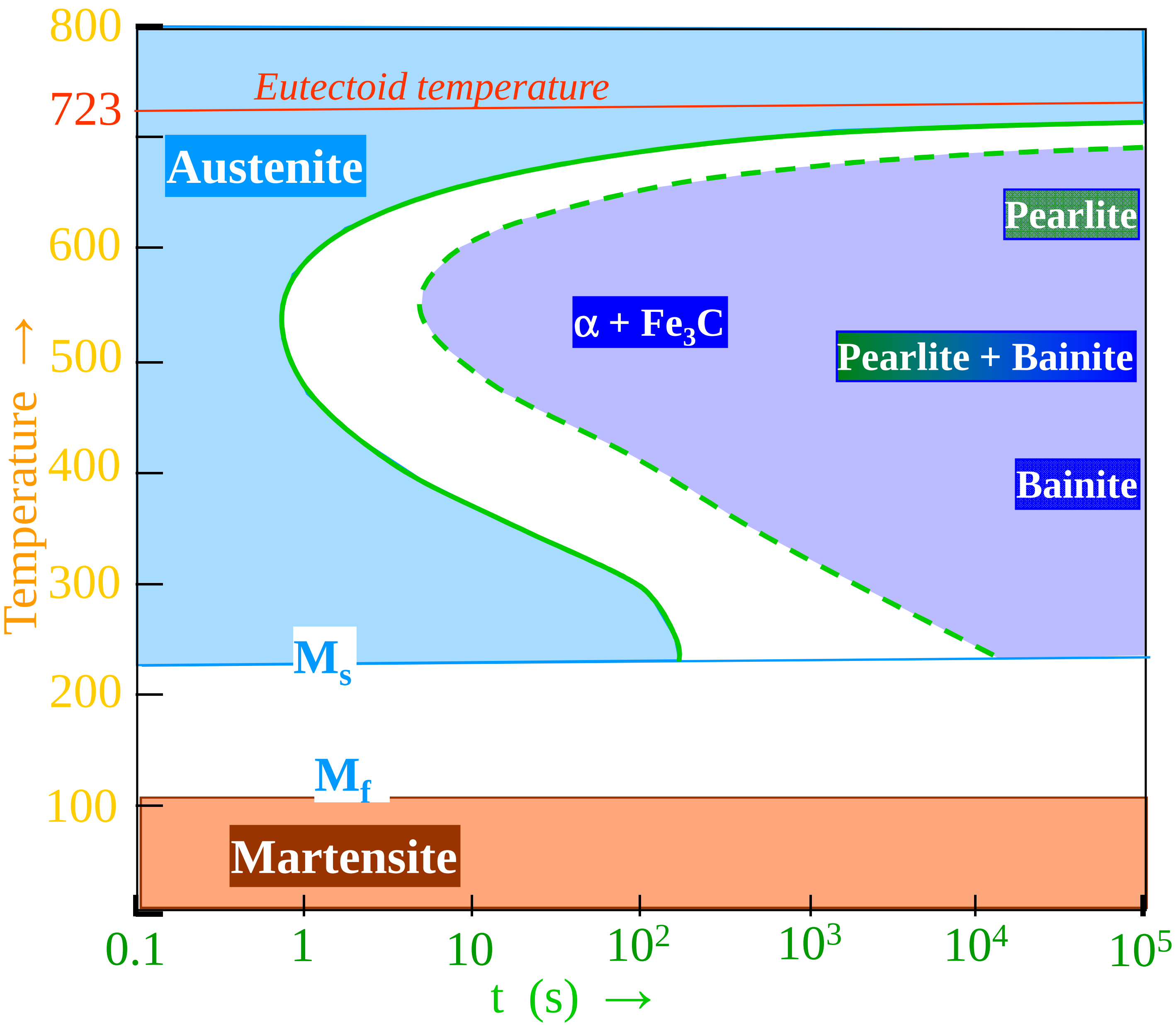
Isothermal Transformation diagram for eutectoid steel

Important points to be noted:

✓ The x-axis is log scale. 'Nose' of the 'C' curve is in ~sec and just below T_E transformation times may be ~day.

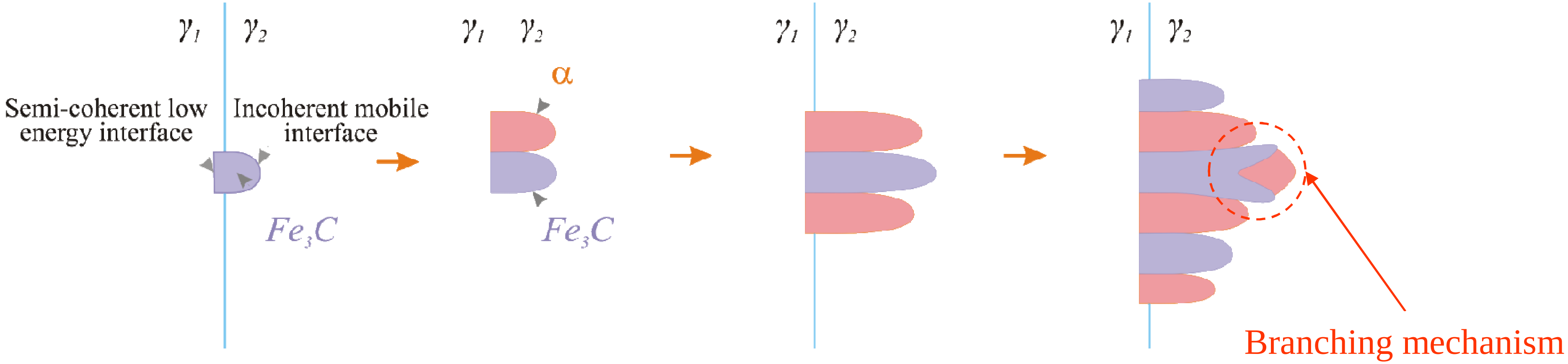
✓ The starting phase (left of the C curve) has to γ.

✓ To the right of finish C curve is (γ+ Fe3C) phase field. This phase field has more labels included.



Eutectoid Transformation : Nucleation of Pearlite

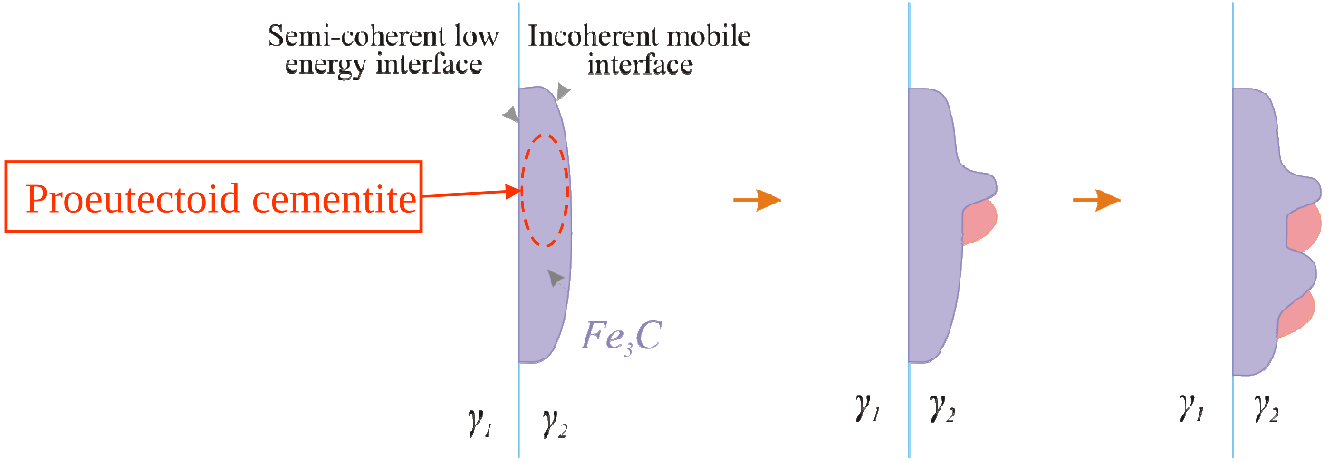
- ❑ Pearlite typically forms on the grain boundaries of the austenite phase by the nucleation of either the ferrite or cementite; the exact phase that nucleates is decided both by the composition and the structure of the grain boundary.
- ❑ The nucleation is such that the barrier for nucleation is the lowest; in other words, the nuclei has a orientation relationship with one of the grains such that the interfacial free energy is minimized.
- ❑ Suppose the first phase to nucleate is cementite; this leads to a depletion of the carbon surrounding this region leading to ferrite nucleation. Ferrite nucleation is also such that the interfacial free energy is minimized; thus, it also has an orientation relationship with the cementite. This process is repeated with the entire grain boundary coated with alternating cementite and ferrite nuclei.



Nucleation of the eutectoid phases in a system with eutectoid composition

Eutectoid Transformation : Nucleation of Pearlite

- ❑ If the composition of the steel is not the eutectoid composition, then, it is possible that proeutectoid ferrite or cementite is nucleated at the grain boundary. The other phase, be it cementite or ferrite, then forms on the incoherent boundary of this proeutectoid phase. This process is shown schematically in Fig.



Orientation Relation: Kurdyumov-Sachs

$$(100)_c \parallel (1\bar{1}1)_\gamma$$

$$(010)_c \parallel (110)_\gamma$$

$$(001)_c \parallel (\bar{1}12)_\gamma$$

Nucleation of the eutectoid phases in a system with pro-eutectoid composition

- ❑ The development of Pearlitic microstructure requires cooperative growth of Ferrite and Cementite
- ❑ If this cooperation is not established then the resulting microstructure is non-lamellar → *Degenerate Pearlite*

Eutectoid Transformation : Nucleation of Pearlite

Eutectoid Transformations

Nucleation at GB

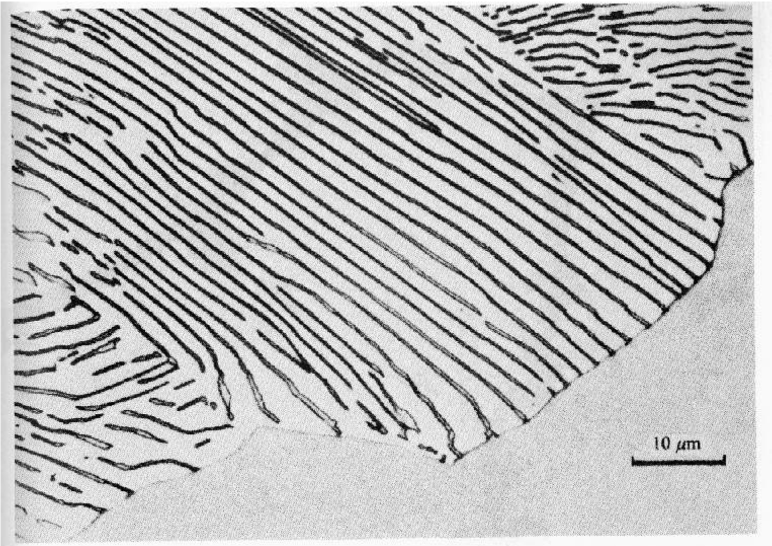
Pearlite in Fe-C alloys $\boxed{\gamma \to \alpha + Fe_3C}$

Low undercooling (below A_1)

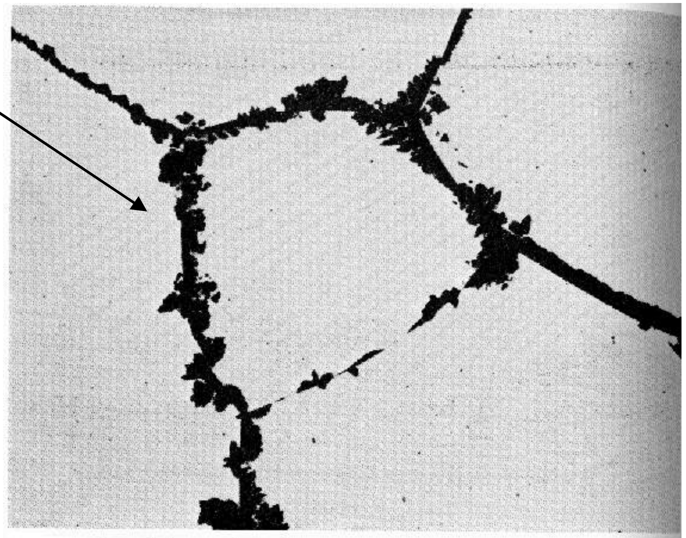
Small number of nuclei form which grow without interference

Large undercooling (below A_1)

High nucleation rate $\to$ *Site saturation along GB*



A pearlite colony advancing into an austenite grain. (After L.S. Darken and R.M. Fisher in *Decomposition of Austenite by Diffusional Processes*, V.F. Zackay and H.I. Aaronson (Eds.), by permission of The Metallurgical Society of AIME.



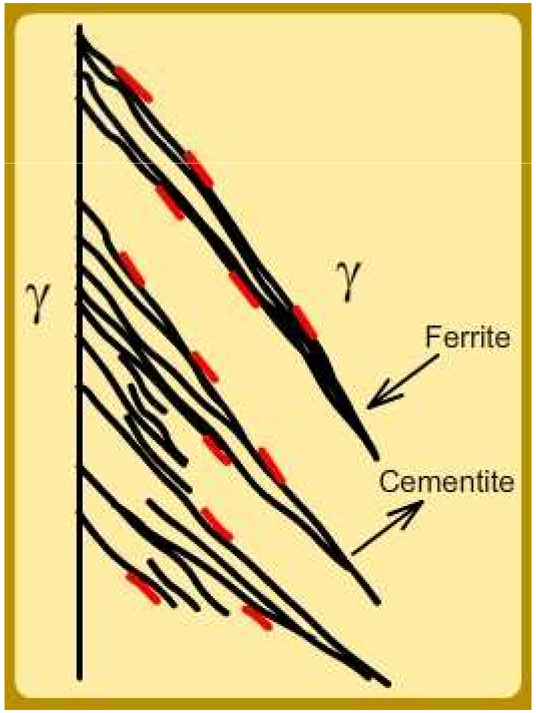
A partially transformed eutectoid steel. Pearlite has nucleated on grain boundaries and inclusions (× 100). (After J.W. Cahn and W.C. Hagel in *Decomposition of Austenite by Diffusional Processes*, V.F. Zackay and H.I. Aaronson (Eds.), 1962, by permission of The Metallurgical Society of AIME.)

Eutectoid Transformation : Bainite transformation

- ❑ At relatively larger supersaturations (austenite cooled below the nose of the pearlite transformaton), there is another eutectoid product that develops known as bainite; bainite is also a mixture of ferrite and cementite; however, it is microstructurally quite distinct. In the next two subsections, we discuss these microstructural features.

Upper bainite

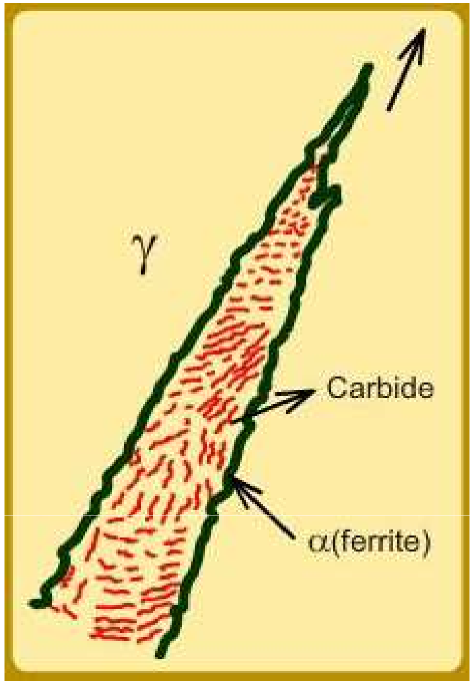
- ❑ At the higher end of the temperatures (350-550˚C), the microstructure consists of needles of laths of ferrite nucleated at the grain boundary and grown into one of the grains with cemetite precipitates between the ferrites; see in Fig.
- ❑ The ferrite formed is Widmanstatten; it has a Kurdjumov-Sachs orientation relationship with the austenite grain into which it is growing; it is in this respect, namely the orientation relationship between the ferrite/cementite and the austeinite grain in which they grow, that the bainite differs from pearlite.



Eutectoid Transformation : Bainite transformation

Lower bainite

- ❑ At low enough temperatures, the bainitic microstructure changes to that of plates of ferrite and very finely dispersed carbides; since the diffusion of carbon is very low at these temperatures (especially in the austenite phase as compared to ferrite), the carbides precipitate in ferrite (and, with an orientation relationship). These carbides that precipitate could be the equilibrium cementite or metastable carbides (such as ε carbide for example). A schematic of lower bainite plate that is formed is shown in Fig.

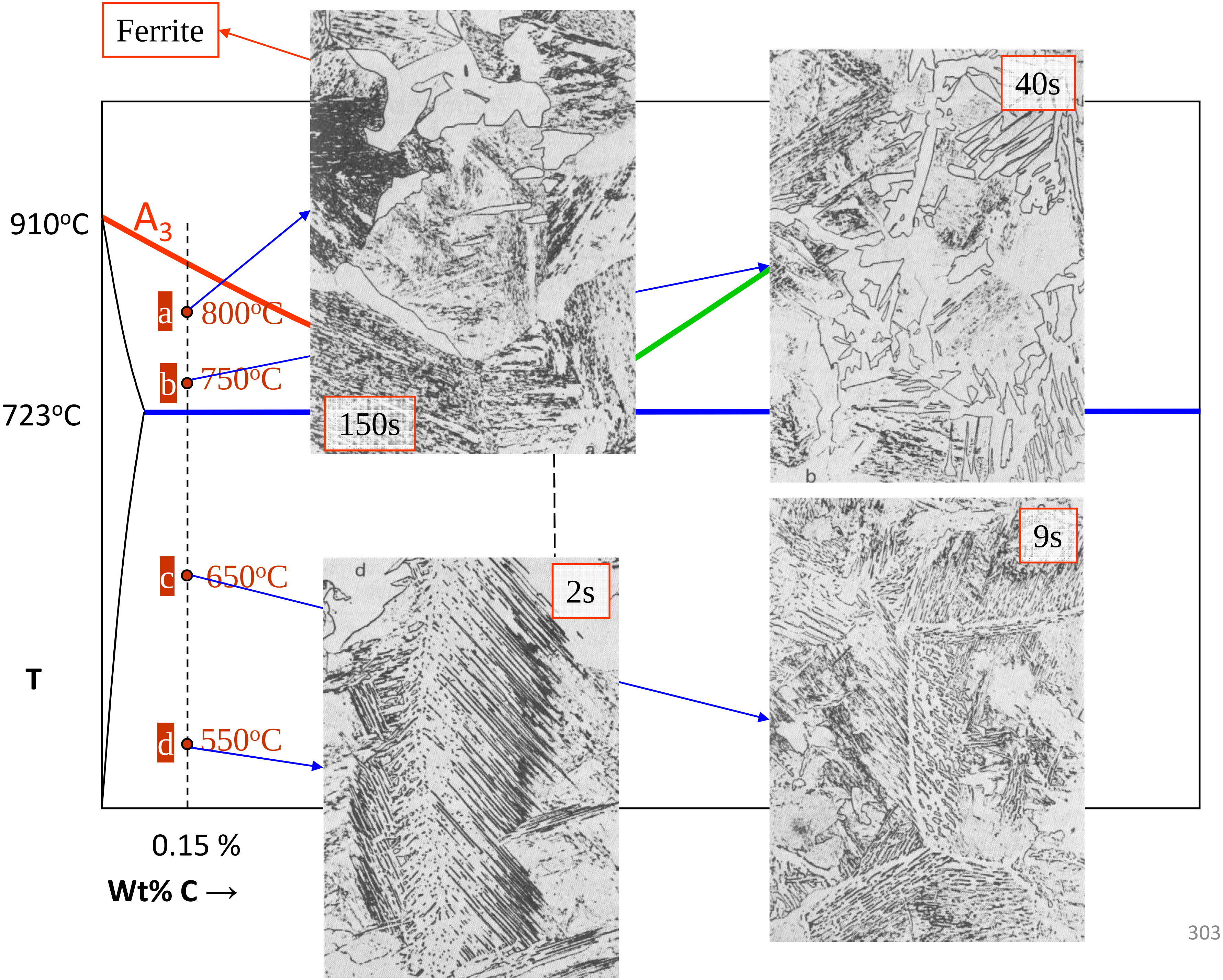


$$\gamma \rightarrow \alpha + Fe_3C^{**}$$

- ❑ Pearlite is nucleated by a carbide crystal, bainite is nucleated by a ferrite crystal, and this results in a different growth pattern.
- ❑ Acicular, accompanied by surface distortions
- ❑ ** Lower temperature → carbide could be ε carbide (hexagonal structure, 8.4% C)
- ❑ Bainite plates have irrational habit planes
- ❑ Ferrite in Bainite plates possess different orientation relationship relative to the parent Austenite than does the Ferrite in Pearlite

Precipitation of Ferrite from Austenite

- AtIn this topic we will be concerned with phase transformations in which the first phase to appear is that given by the equilibrium phase diagram.
- Here we will consider to the diffusional transformation of Fe-C austenite into ferrite.
- However, many of the principles are quite general and have analogues in other systems where the equilibrium phases are not preceded by the precipitation of transition phases.
- Under these conditions the most important nucleation sites are grain boundaries and the surface of inclusions.
- It can be seen in figure (next slide) that ferrite can also precipitate within the austenite grains (intragranular ferrite). Suitable heterogeneous nucleation sites are thought to be inclusions and dislocations. These precipitates are generally equiaxed at low undercoolings and more platelike at higher undercoolings.
- In general the nucleation rate within grains will be less than on grain boundaries. Therefore, whether or not intergranular precipitates are observed depends on the grain size of the specimen.
- In fine grained austenite for example, the ferrite that forms on grain boundaries will rapidly raise the carbon concentration with in the middle of the grains, thereby reducing the undercooling and making nucleation even more difficult.
- In a large grained specimen, however, it takes a longer time for the carbon rejected from the ferrite to reach the centers of the grains and meanwhile there will be time for nucleation to occur on the less favorable intragranular sites.


Ferrite
910°C
A3
a
800°C
b
750°C
723°C
c
650°C
d
550°C
T
0.15 %
Wt% C →
150s
40s
b
9s
d
2s

Ferrite nucleates on Austenite grain boundaries and grows with a blocky appearance
→ Grain Boundary Allotriomorphs

Small ΔT

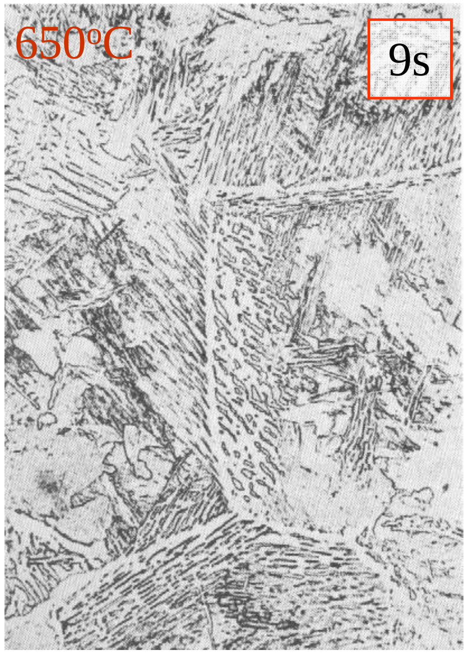
Curved interfaces → incoherent
Faceted interfaces → semicoherent

Larger undercooling – Ferrite grows as plates from GB
→ Widmannstätten side-plates

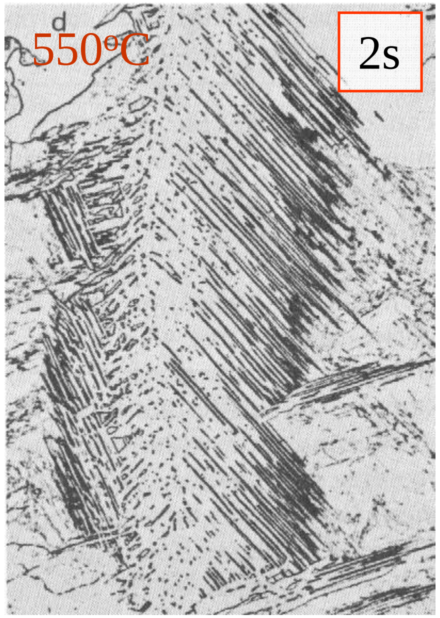
Large ΔT

Irrational habit planes

Ferrite can also nucleate within the γ grains heterogeneously at inclusions and dislocations → equiaxed at low undercoolings and plate-like at higher undercoolings.



Widmannstätten side-plates → *become finer with larger undercooling*

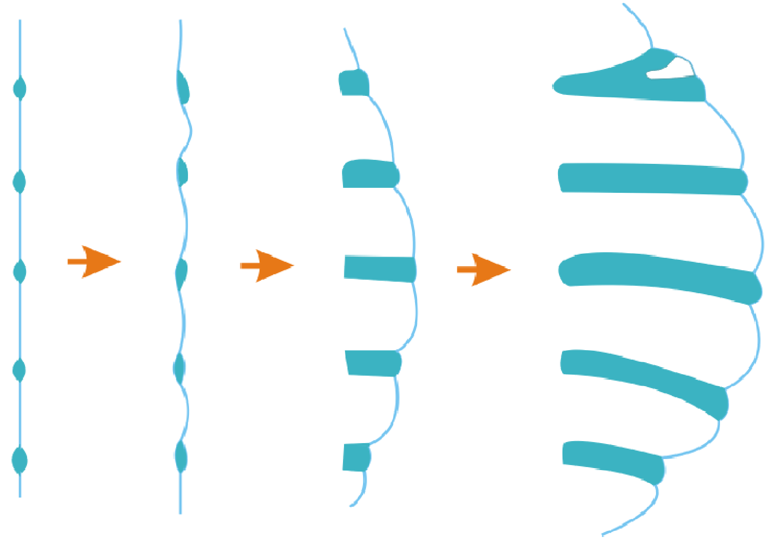


Very Large undercooling – Ferrite grows as needles GB → *Widmannstätten needles*

Cellular Precipitation (Discontinuous Precipitation)

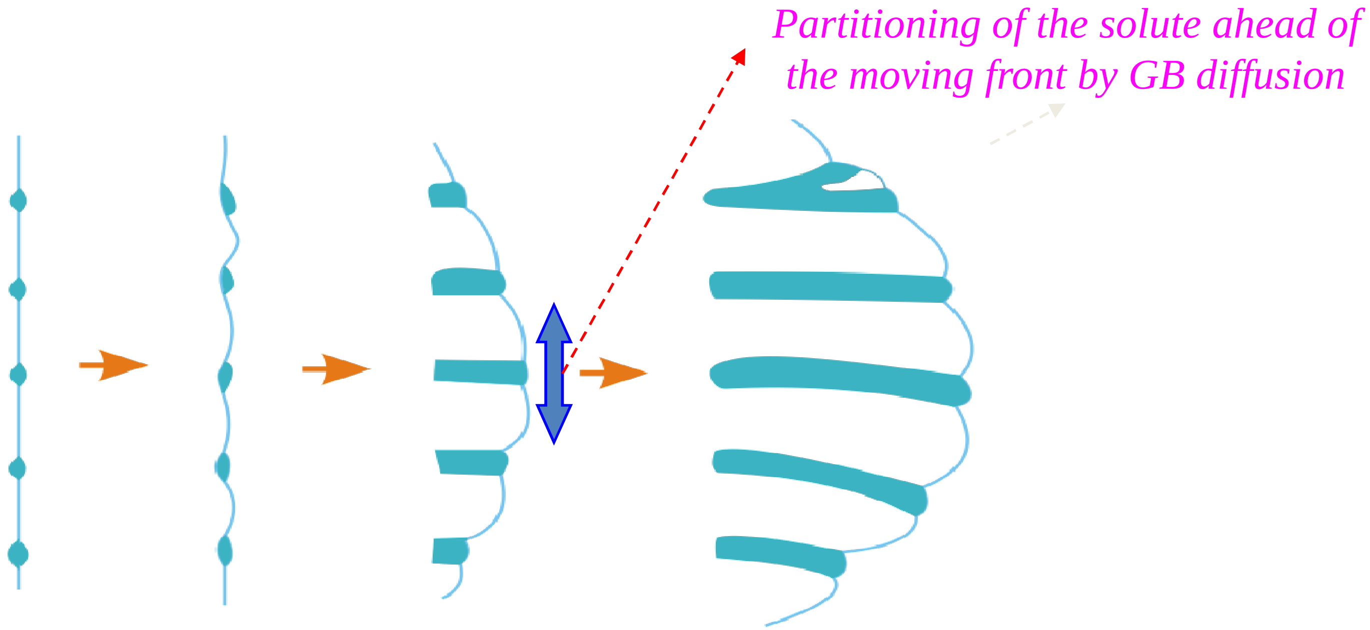
- ❑ Grain boundary precipitation may also occur by cellular precipitation *(apart from Allotriomorphs, Widmannstätten side plates & needles)*
- ❑ Main Feature → boundary moves with the tip of the precipitates
- ❑ The mechanism by which GB ppt. develops into cellular precipitation is system specific
- ❑ Called *discontinuous precipitation* as the composition of the matrix changes discontinuously as the cell front passes
- ❑ (Continuous precipitation- *not* cellular- occurs throughout the matrix and the matrix composition changes continuously with time

$$\boxed{\alpha'\text{(higher solute concentration)} \rightarrow \alpha\text{(lower solute concentration)} + \beta}$$



Cellular Precipitation (Discontinuous Precipitation)

- ☐ In the previous section, we discussed the effect of grain boundaries on the nucleation of precipitates with specific reference to ferrite (α) on austenite (γ). We saw that there exist two morphologies, namely, grain boundary allotriomorphs and Widmanstatten side plates.
- ☐ In some cases, the precipitates that are nucleated at the grain boundary, when they grow, also carry the grain boundary along with them. This process is shown schematically in Fig. Such a process leads to a cellular microstructure as shown. This kind of process is known as cellular precipitation.



Partitioning of the solute ahead of the moving front by GB diffusion

$$\alpha'\text{(higher solute concentration)} \rightarrow \alpha\text{(lower solute concentration)} + \beta$$

Cellular Precipitation (Discontinuous Precipitation)

- Cellular precipitation is also known discontinuous precipitation because of the sudden change in composition of matrix across the moving grain boundary as shown below; on the other hand, noncellular precipitation is known as continuous because the composition of the matrix phase decreases continuously at any point. In general, continuous precipitation leads to much better mechanical properties (due to the more uniform distribution of precipitates, which nucleate throughout the matrix (on dislocations for example) and hence, much smaller size distribution) as opposed to discontinuous precipitation.
- Cellular precipitation leads to microstructures that are very similar to eutectoid transformations. In fact, the only difference between cellular precipitation and eutectoid transformation is that while in eutectoid transformation both the phases that form are different from the original phase, in cellular precipitation one of the phases remains the same as the original phase (albeit with a different composition):

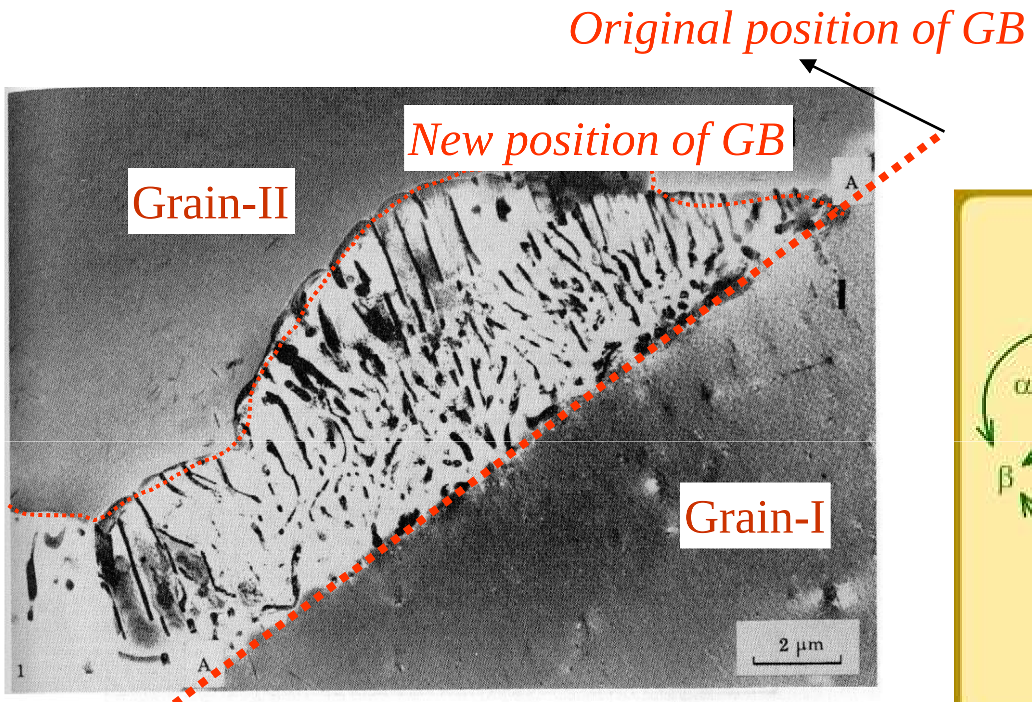
$$\boxed{\alpha' \rightarrow \alpha + \beta}$$

- α' is the supersaturated matrix, and is the matrix phase with a composition closer to equilibrium as compared to α ' and β is the precipitate phase.

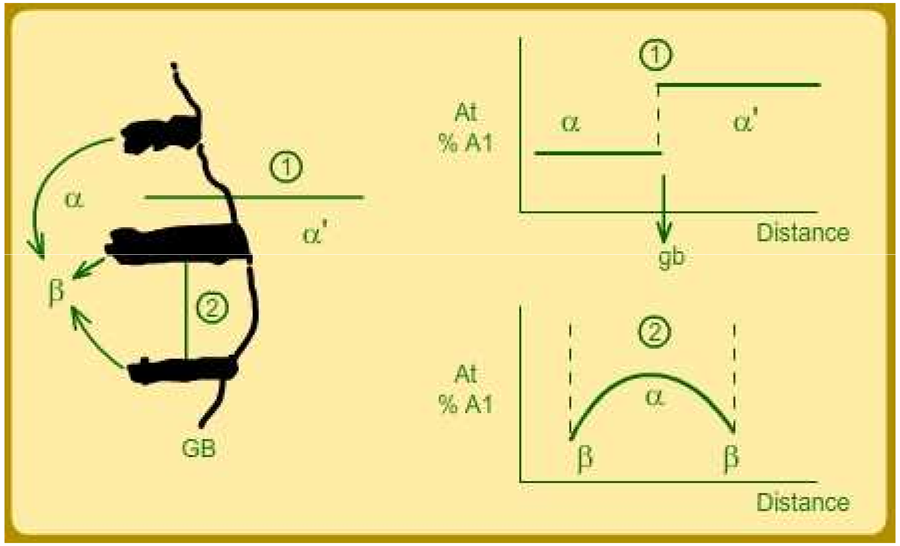
Cellular Precipitation (Discontinuous Precipitation)

- Consider the phase diagram of the Al-Mg system, The β phase is the $Mg_{17}Al_{12}$ phase and the phase is the solid solution of Mg and Al. Consider an alloy of 9 at % Al, which is solution treated (at, say 410°C) and aged for an hour at 220°C.
- The cellular precipitation that takes place during the aging treatment leads to microstructures as shown schematically in Fig. (next slide).
- The composition profiles across the boundary as well as parallel to the boundary are as shown in Fig. (next slide).
- The discontinuous nature of the composition in the phase across the moving boundary indicates that the mechanism of diffusion which leads to the formation of cellular structures is the diffusion of solutes through the moving grain boundary (since, if the diffusion took place through the matrix on either side of the boundary, it would have led to composition gradients).
- The composition of the α in the profile parallel to the moving boundary indicates that composition is still not equilibrated after the precipitation of β.
- When the mechanism of phase transformation changes from nucleation and growth to spinodal decomposition, it is possible for discontinuous spinodal to take place; in such cases, phase separation starts near the grain boundary and the boundary moves with the phase separation (reaction) front.

Cellular Precipitation (Discontinuous Precipitation)



Cellular precipitation of $Mg_{17}Al_{12}$ in an Mg–9 at% Al alloy solution treated and aged 1 h at 220 °C followed by 2 min at 310 °C. Some general $Mg_{17}Al_{12}$ precipitation has also occurred on dislocations within the grains.



The cellular precipitation that takes place during the aging treatment leads to microstructures

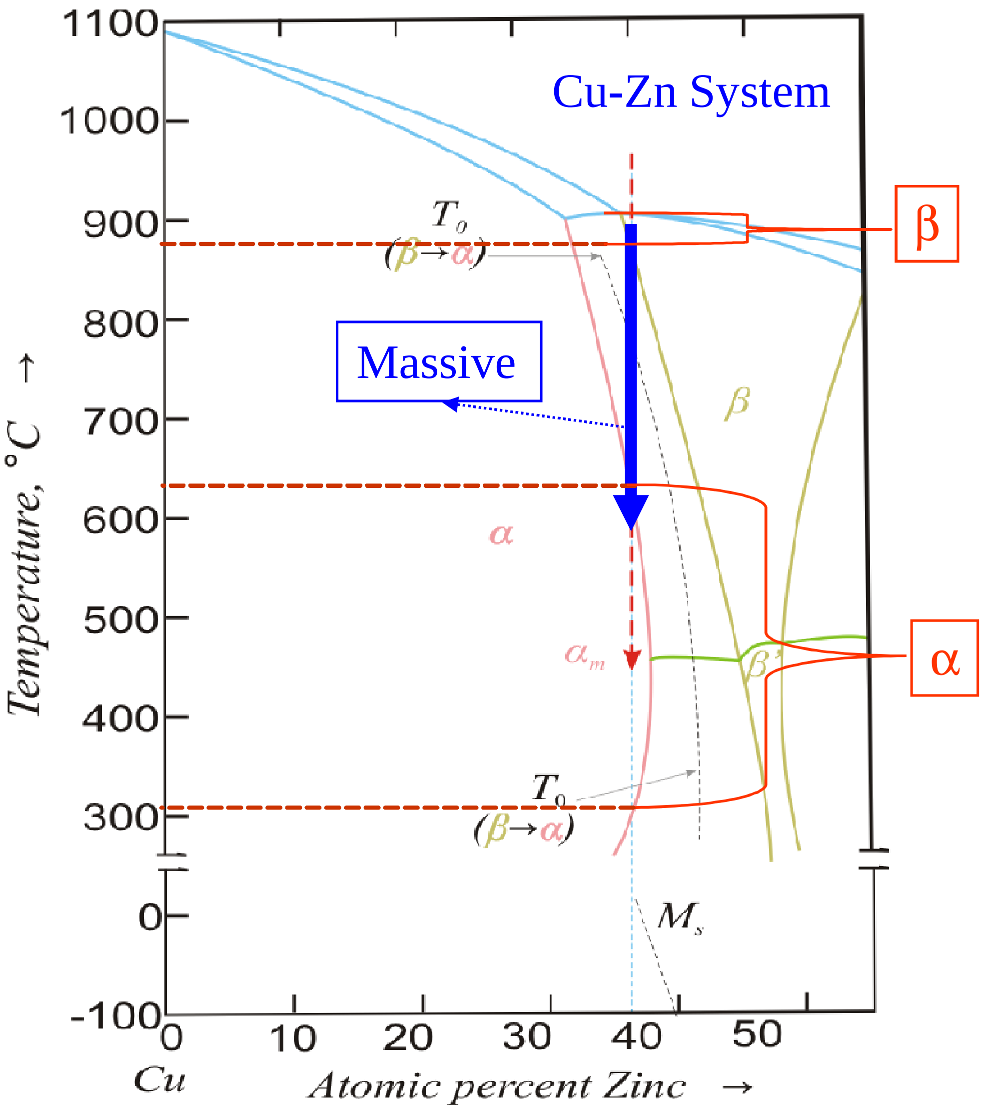
The composition profiles across the boundary as well as parallel to the boundary

Massive Transformation

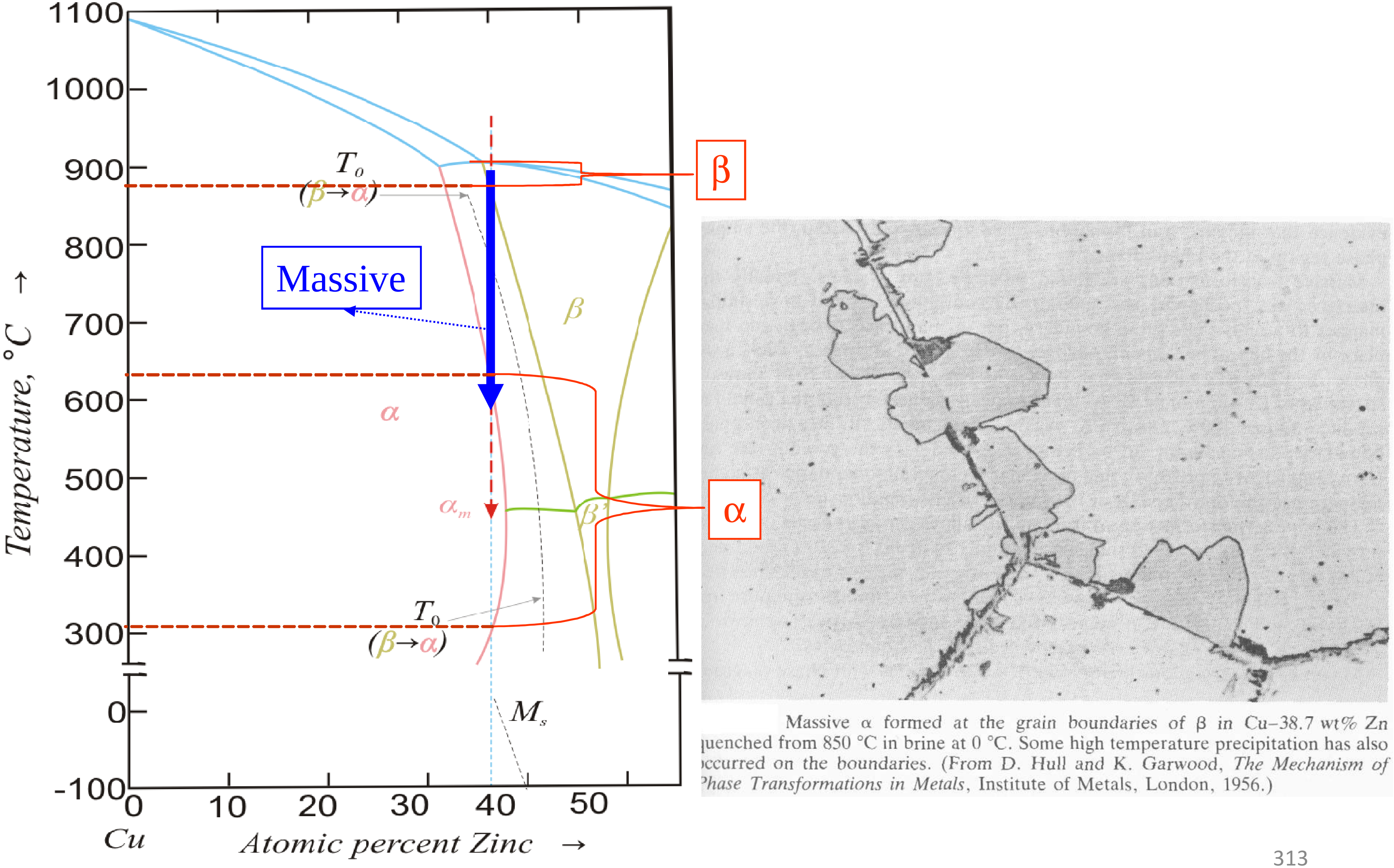
- The type of transformation that occurs in cooling (e.g. Cu-38 at% Zn alloy) depends on the cooling rate
  - Slow cooling → transformation at small undercoolings ⇒ equiaxed α
  - Faster cooling → transformation at lower T ⇒ *Widmannstätten α needles*
  - Even faster cooling (brine quench) → no time for diffusion ⇒ *Transformation of β →α without change in composition* (MASSIVE TRANSFORMATION)
- α richer in Cu ⇒ growth of α requires long-range diffusion of Zn away from advancing α/β interface
- MASSIVE Tr.
  - Nucleation at GB and rapid growth into β
  - Irregular appearance
  - No change in composition ⇒ Only short range jumps (thermally activated) across the interface (α/β) *(no long range diffusion required)→ fast growth rate (thermally activated migration of incoherent interfaces → diffusionless civilian)*
- Separate transformation curve (in TTT & CCT diagrams)
- ~ to GB migration during recrystallization → *but driving force v.high*

Massive Transformation

- An example of massive transformation is shown in Fig.: in Cu-Zn system, when an alloy of 38 at.% Zn is cooled from 850°C to say 400°C at fast enough cooling rates, the structure changes from that of β to α albeit with the same composition.
- Since the composition is the same, there is no need for long range diffusion and hence the transformation is very fast.
- Such changes in structure without changes in composition can be achieved in two ways: massive which is through thermally activated jumps of atoms from regions of one phase to another and martensitic which is through diffusionless (military)



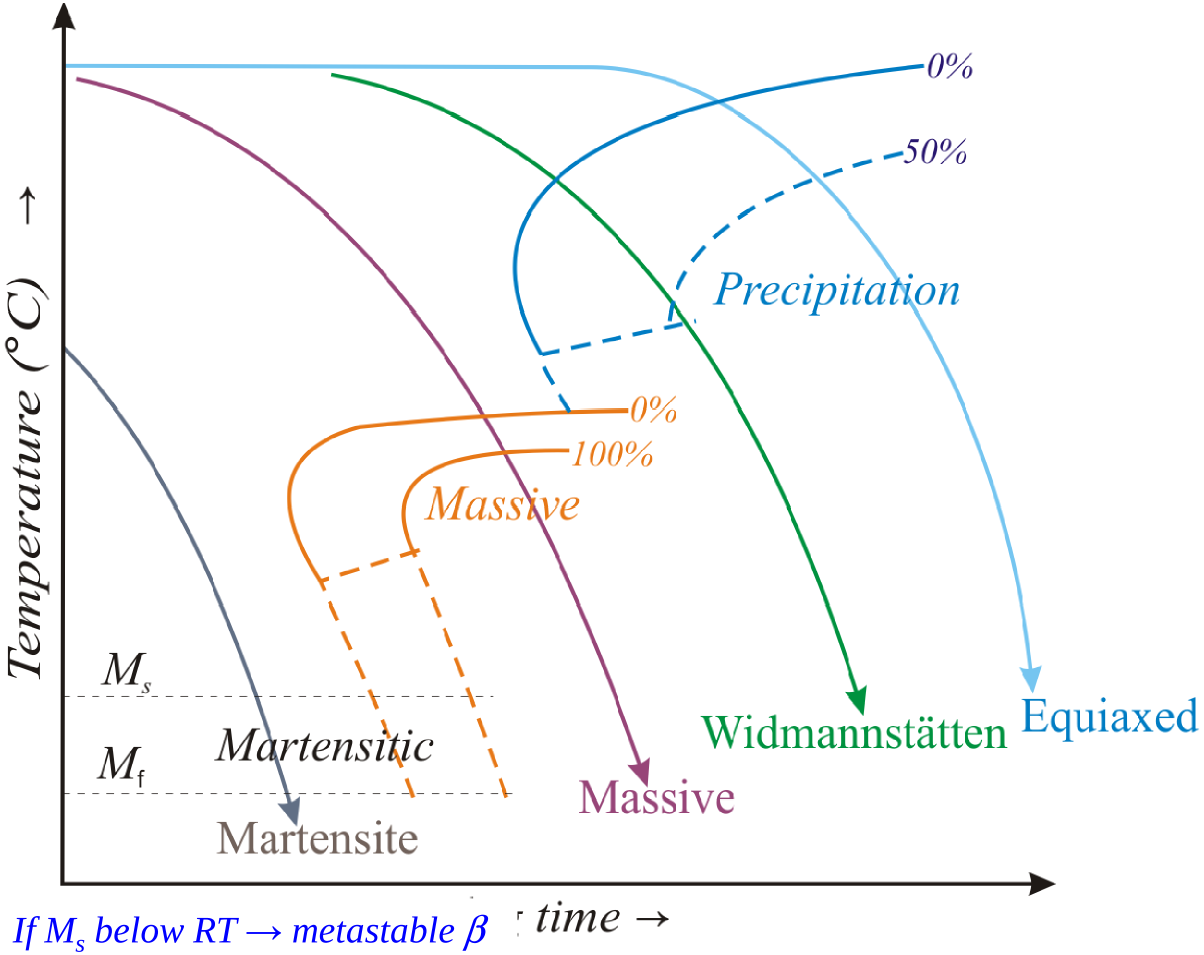
Massive Transformation



Massive α formed at the grain boundaries of β in Cu–38.7 wt% Zn uenched from 850 °C in brine at 0 °C. Some high temperature precipitation has also ccurred on the boundaries. (From D. Hull and K. Garwood, *The Mechanism of hase Transformations in Metals*, Institute of Metals, London, 1956.)

Massive Transformation

- ❑ Typically, systems which undergo massive transformation also undergo martensitic transformation at higher cooling rates; this is indicated in the schematic CCT diagram in Fig. The mechanism of formation of massive transformation can be understood with reference to this CCT diagram.

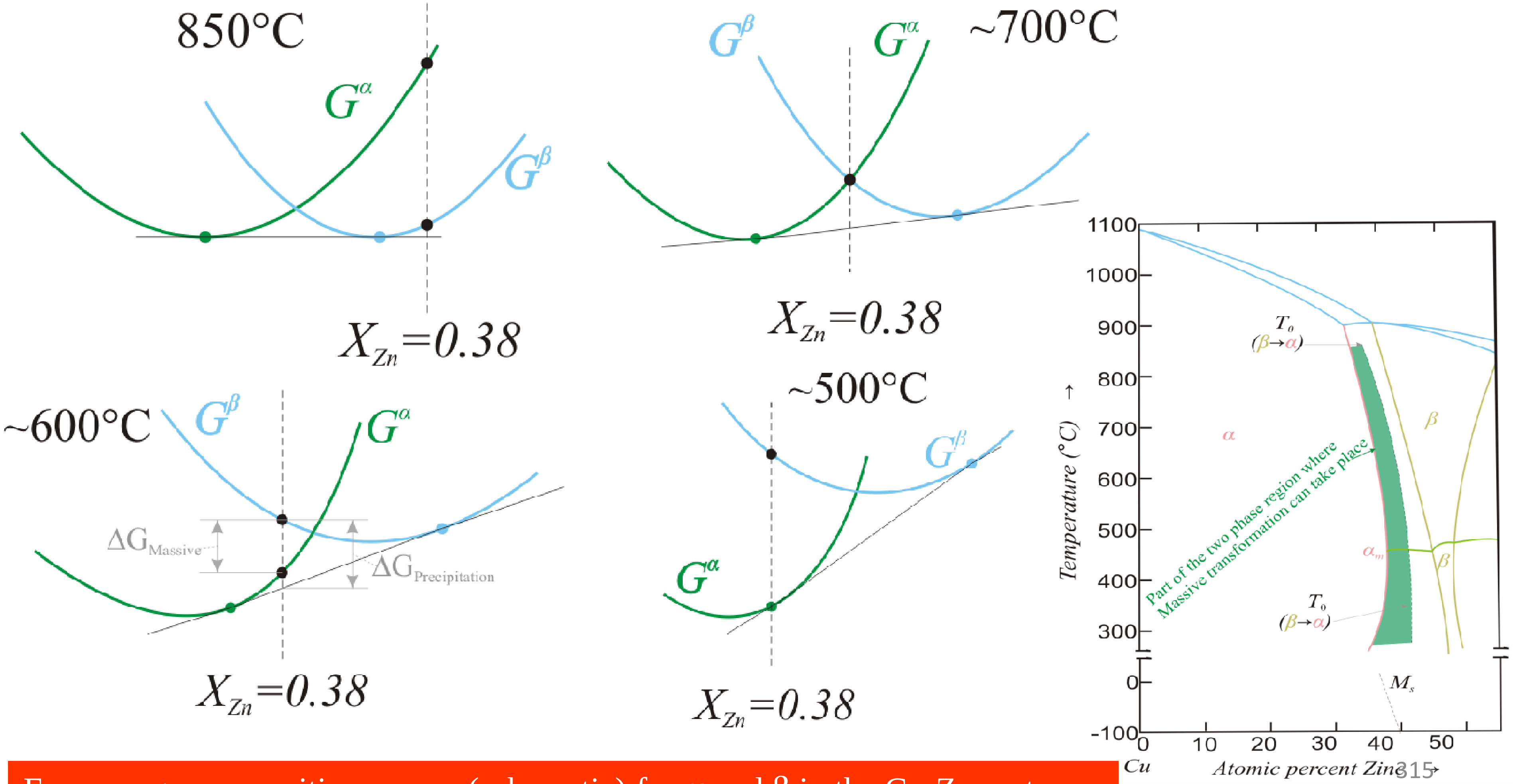


If M_s below RT → metastable β

- ❑ At slow cooling rates and at smaller undercoolings, precipitation and growth of α leads to equiaxed α. At higher cooling rates and larger undercoolings Widmanstatten α formation takes place.
- ❑ In both these cases, since the growth of α requires long range diffusion (see Cu-Zn phase diagram for example, where it is the long range diffusion of Zn that is needed), it requires long time to form.

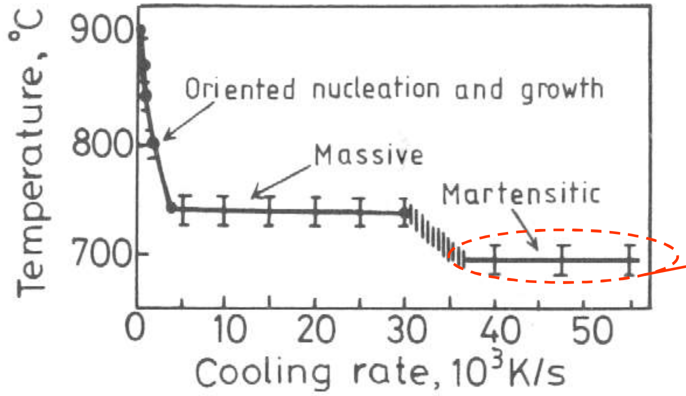
Massive Transformation

- However, relatively faster cooling rates would nucleate the α phase at the grain boundaries; since the growth of this α only requires that atoms jump across the α -β interface, and since the driving forces for the formation of α are very large (see in Fig.)



Free energy composition curves (schematic) for α and β in the Cu-Zn system

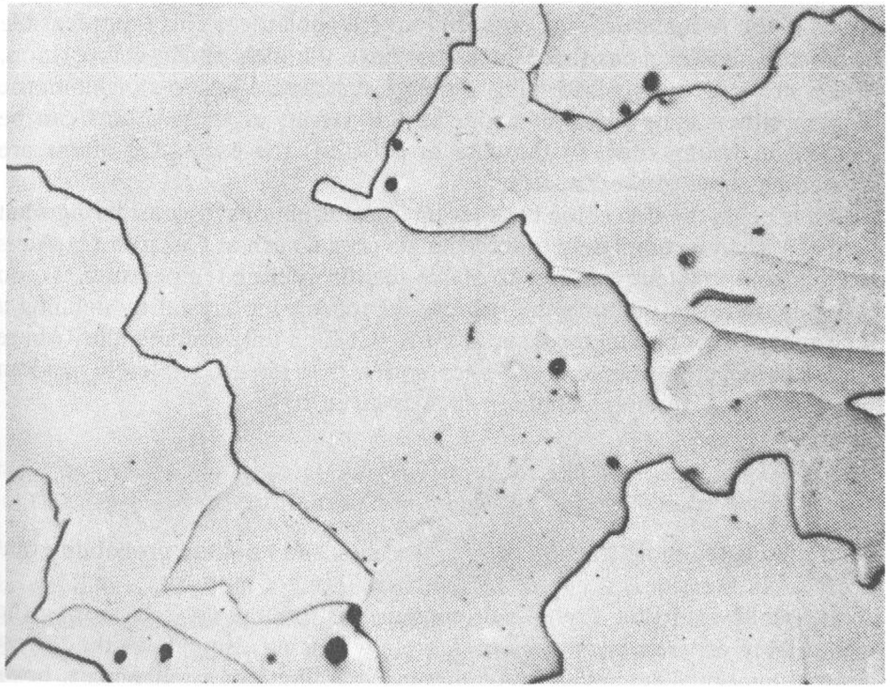
Massive Transformation



The effect of cooling rate on the transformation temperature of pure iron. (After M.J. Bibby and J.G. Parr, *Journal of the Iron and Steel Instit* 100.)

V.High cooling rate will produce Martensite

Massive Tr. can also occur in Fe-C system



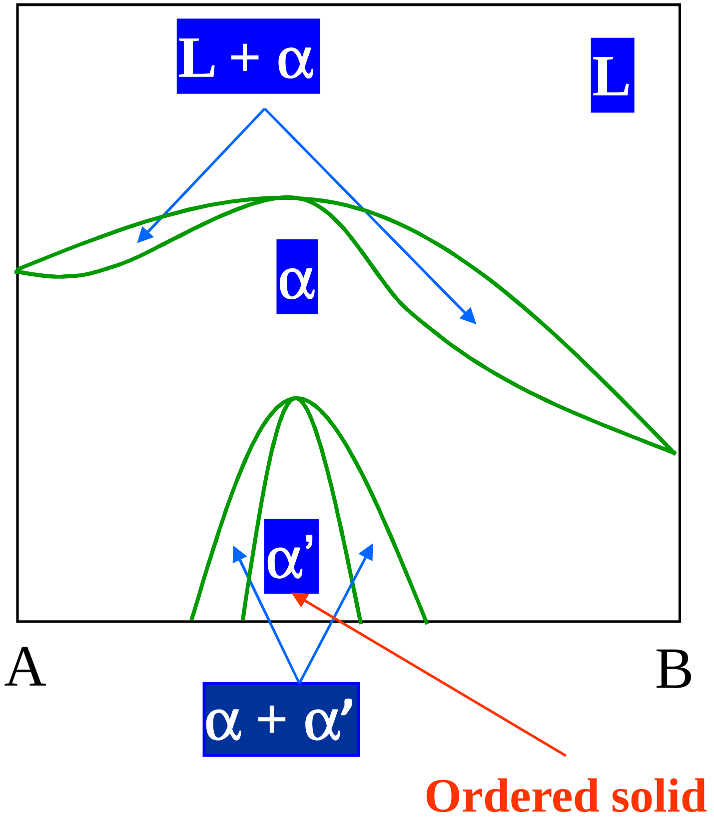
Massive α in an Fe–0.002 wt% C quenched into iced brine from 1000 °C. Note the irregular α/α boundaries. (After T.B. Massalski in *Metals Handbook*, 8th edn., Vol. 8, American Society for Metals, 1973, p. 186.)

Ordering Transformations

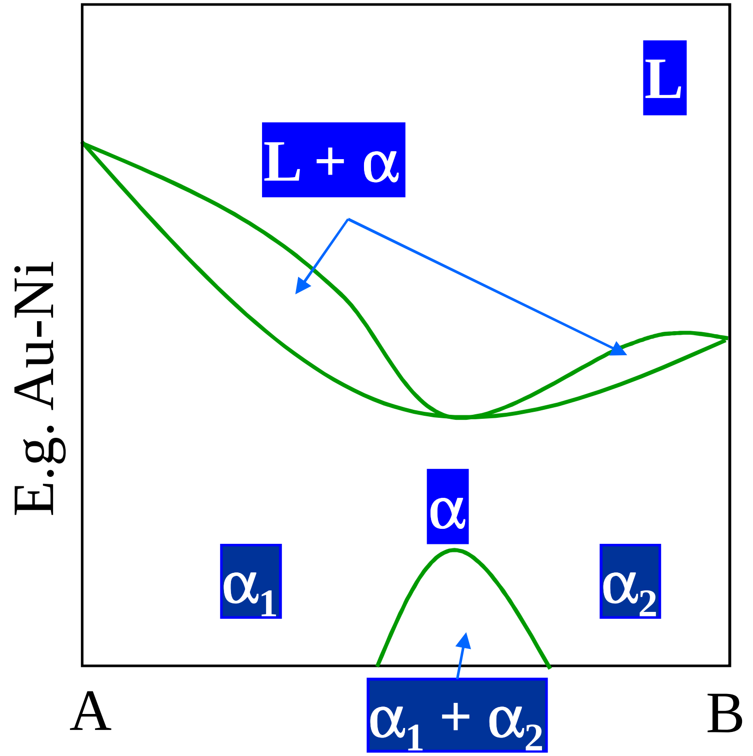
- In the thermodynamics & kinetics topic, we considered a system with $\Omega > 0$. In such systems, at lower temperatures, the free energy develosps a concave curvature leading to a phase separation into mechanical mixture.
- Now, consider a system with , that is, the AB bonds are preferred over AA/BB bonds. What happens to such systems at low temperatures?
- In systems with $\Omega > 0$, that is, systems in which AB bonds are preferred over AA/BB bonds are prefered, at lower temperatures, the system becomes ordered. This ordering is over and above the crystallographic ordering. In the crystalline lattice, specific lattice positions are occupied by specific atoms, thus leading to more of the preferred unlike bonds.
- Consider for example a bcc lattice occupied by A and B atoms. If it is disordered, then, the probability of the cube corners and cube centers are occupied by the A or B atoms is 50% (that is, the same as the alloy composition in at%). However, when this system orders, the cube corners preferentially occupy one of the positions, say, cube corners while the other preferentially occupies the cube centers.
- That is, the bcc lattice now can be considered to be consisting of two interpenetrating cubic lattices. Such a structure is known as B_2. Notice that in the (ideal) B_2 structure, there are only AB bonds and no AA/BB bonds. NiAl is a system in which, for example, such B_2 ordered structure is known. There are also fcc based ordered structures such as $L1_2$ (example: Ni3Al) and $L1_0$ (example: CuAu).

Ordering Transformations

- A–B bonds stronger than A–A and B–B bonds
- Solid stabilized → Ordered solid formation



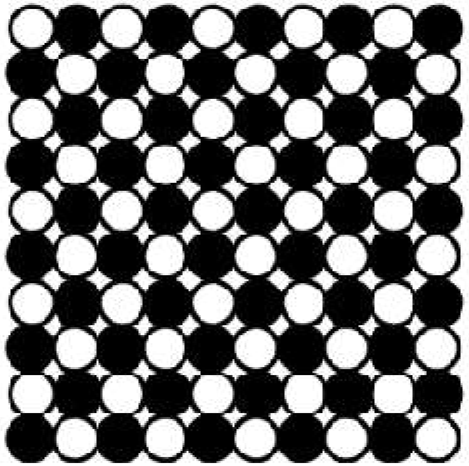
- A–A and B–B bonds stronger than A–B bonds
- Liquid stabilized → Phase separation in the solid state



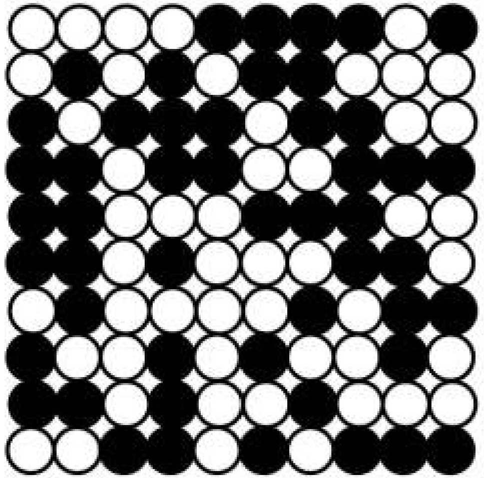
α_1 & α_2 are different only in lattice parameter

Variations to the isomorphous phase diagram

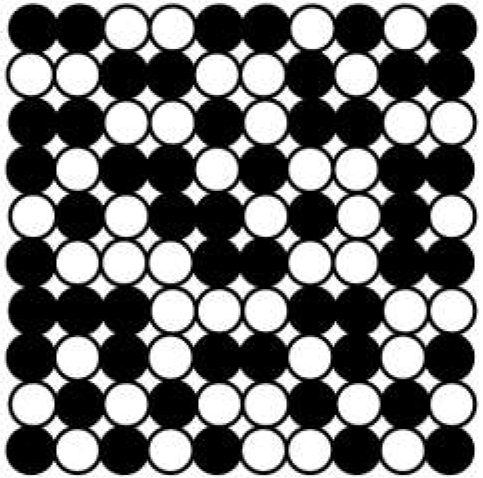
Ordered Phases



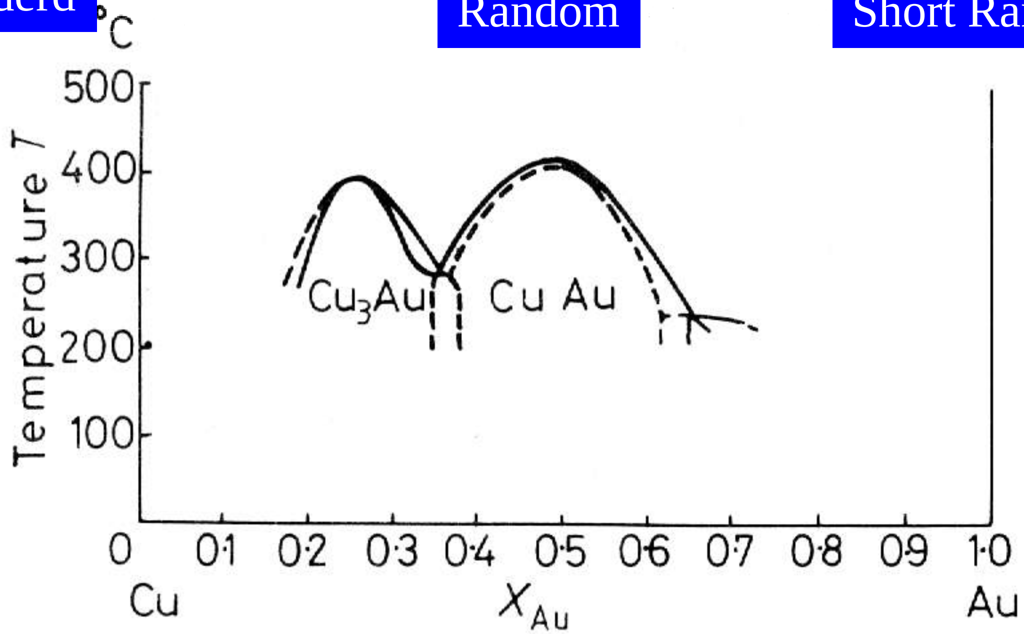
Orderd



Random

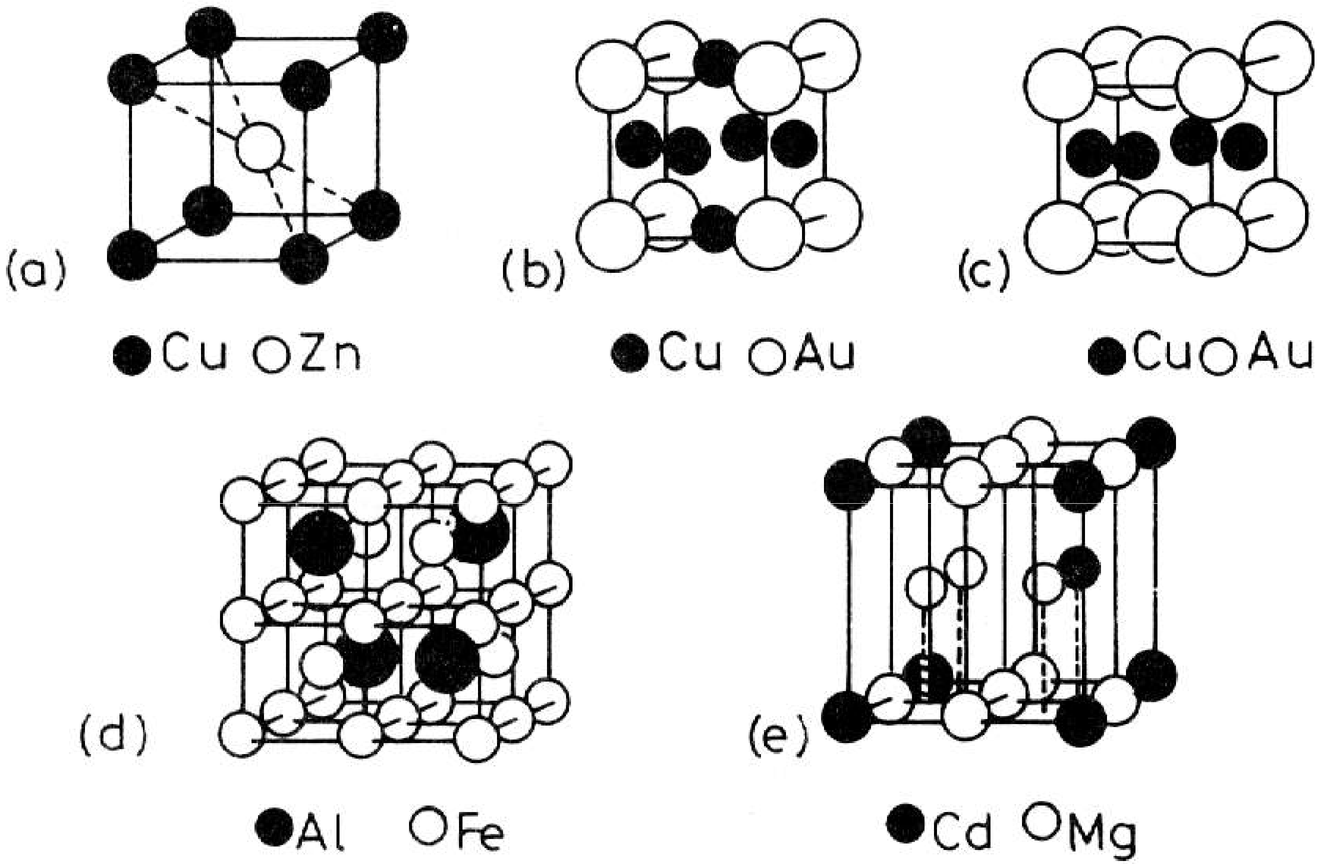


Short Range Orderd



Part of the Cu-Au phase diagram showing the regions where the Cu_3Au and CuAu superlatices are stable.

Ordered Phases



The five common ordered lattices, examples of which are: (a) $L2_0$: CuZn, FeCo, NiAl, FeAl, AgMg; (b) $L1_2$: Cu_3Au, Au_3Cu, Ni_3Mn, Ni_3Fe, Ni_3Al, Pt_3Fe; (c) $L1_0$: CuAu, CoPt, FePt; (d) $D0_3$: Fe_3Al, Fe_3Si, Fe_3Be, Cu_3Al; (e) $D0_{19}$: Mg_3Cd, Cd_3Mg, Ti_3Al, Ni_3Sn. (After R.E. Smallman, *Modern Physical Metallurgy, 3rd edition*, Butterworths, London, 1970.)

Long range and short range order parameters

- ☐ There are two different order parameters that one can define. The first is the short range order parameter (S) defined as :

$$S = \frac{P_{AB} - P_{AB}(random)}{P_{AB}(\max) - P_{AB}(random)}$$

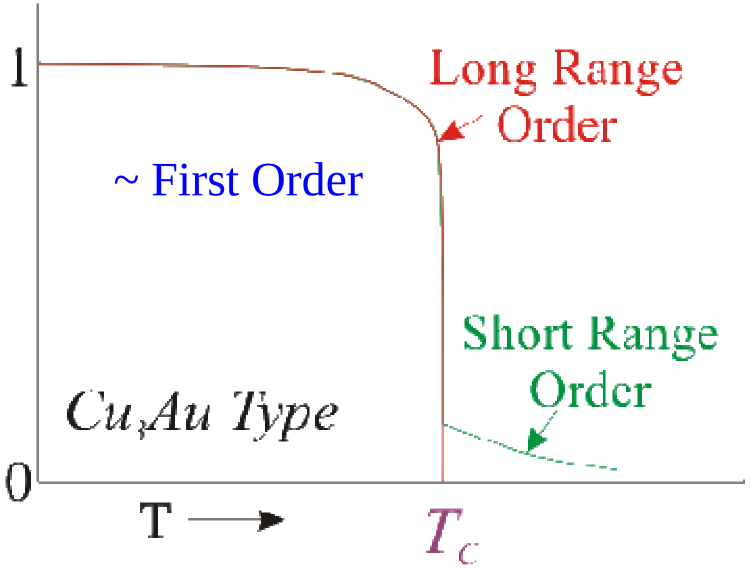
- ☐ Here, P_{AB}(max)and P_{AB}(random) refer to the maximum number of bonds that can exist and the number of bonds in a random solution. As one can see, the short range order parameter is closely related to the , regular solution parameter; this type of ordering is possible in alloys of all compositions.
- ☐ In case the alloy composition is in simple ratios of the constituent atoms, then, one can define the so called long range order parameter L in terms of the alloy composition as x given as:

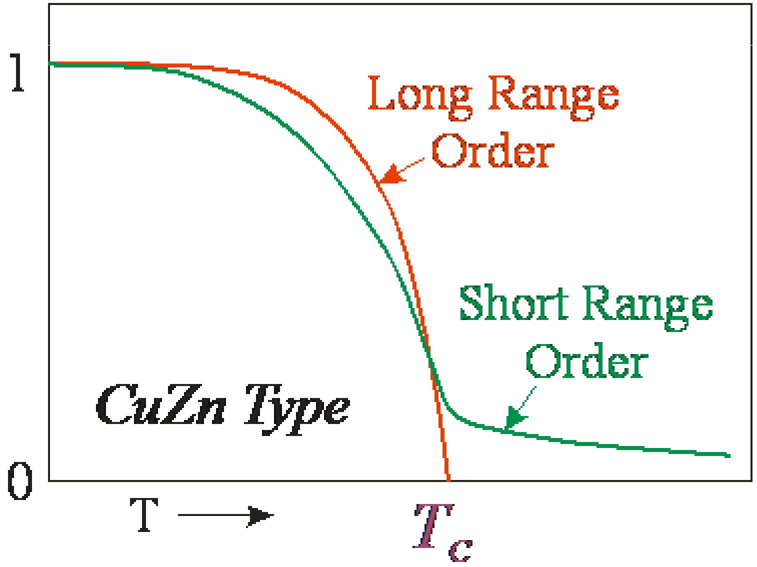
$$L = \frac{p - x}{1 - x}$$

- ☐ Where p is the probability of occupancy of the given site by the right kind of atom.
- ☐ At absolute zero, the system will choose a state with L = 1; however, as temperature increases, the effects of configurational entropy come into play; so the value of L decreases from unity and eventually reaches zero. The temperature at which this change of Long Range Order (LRO) from unity to zero takes place is known as the critical temperature (T_c) for the order-disorder transformation.

Long range and short range order parameters

- In Fig. we show the variation of *L* and *S* with temperature in two systems, namely, one that undergoes an order-disorder transformation from B_2 to disordered bcc and another that undergoes an order-disorder transformation from $L1_2$ to disordered fcc.
- It is clear from the figures, the changes are of two different types; in the equiatomic case of B_2 to bcc (CuZn type), the variation is continuous; however, in the case of $L1_2$ to fcc (Cu_3Au type), the variation is abrupt. These differences in the behaviour is a consequence of the differences in atomic configurations in the two ordered lattices.

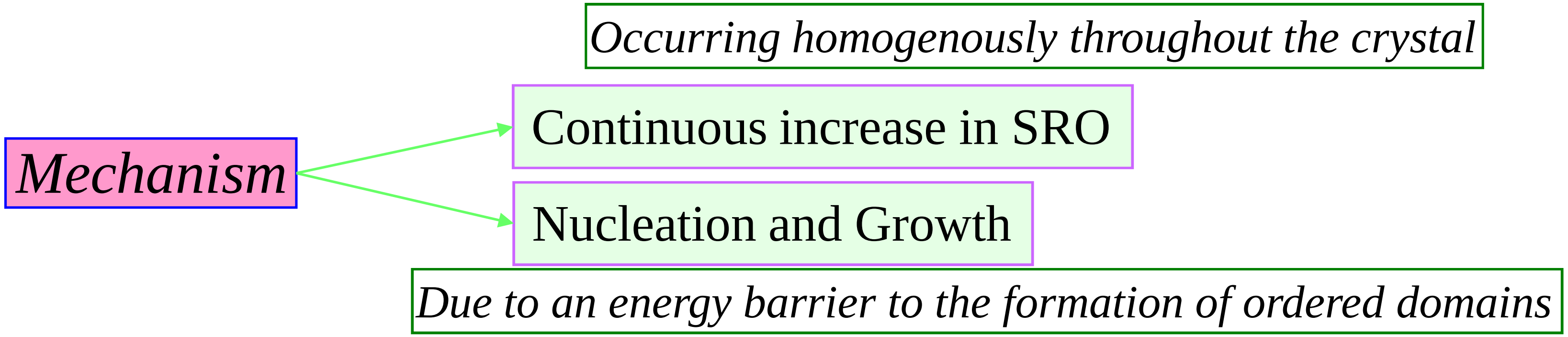




Order parameter variation with temperature: continuous (B_2 type) and abrupt ($L1_2$).

Ordering Transformations : Microstructural features

- The order-disorder transformation can take place both through the nucleation and growth mechanism and spinodal mechanisms. In spinodal mechanism there is continuous increase in, homogeneously all through the crystal leading to the transformation. In the nucleation and growth mechanism, small regions form overcoming an energy barrier and these regions grow.
- In ordered alloys, the two phases have near-identical lattice parameters and the interfacial energies between the ordered and disordered phases is very low. Hence, the barrier for nucleation is very small. Hence, order-disorder transformation, when takes place through the nucleation and growth mechanism, takes place through homogeneous nucleation.



Occurring homogenously throughout the crystal

Mechanism

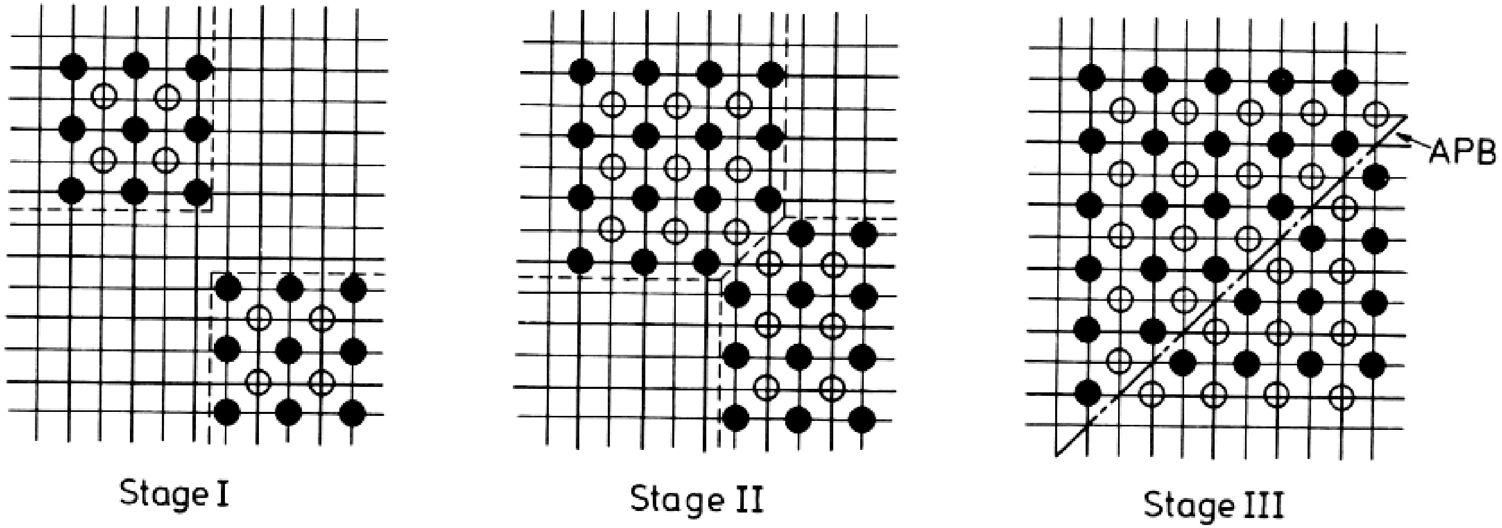
Continuous increase in SRO

Nucleation and Growth

Due to an energy barrier to the formation of ordered domains

Ordering Transformations : Microstructural features

- The surface defects that come about in ordered alloys is known as anti-phase boundaries (APB). These come into existence due to accidents of nucleation and growth. For example, in bcc-B_2 transformation, since the two sites in B_2 are completely equivalent, at some nuclei the cube corner is occupied by A while in some nuclei the cube corner is occupied by B.
- Hence, as these nuclei grow and the ordered regions impinge, there is predominant AA or BB bonds (unpreferred bonds). Such defects are known as APBs and in Fig. 11 we show, schematically, the formation of APBs. In Fig. we shown a schematic ordered microstructure in B_2 and $L1_2$ alloys. As is clear from the figures, the nature of APBs and hence the microstructures are different in these two cases.



The formation of an antiphase boundary (APB) when out of phase ordered domains grow together.
The diagram could represent a {1 0 0} plane in Cu_3Au in which case the black – Cu and white - Au

Diffusionless Transformations

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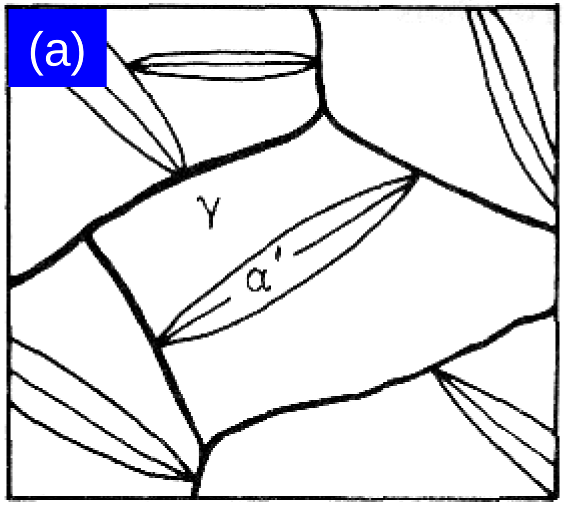
Martensitic transformations

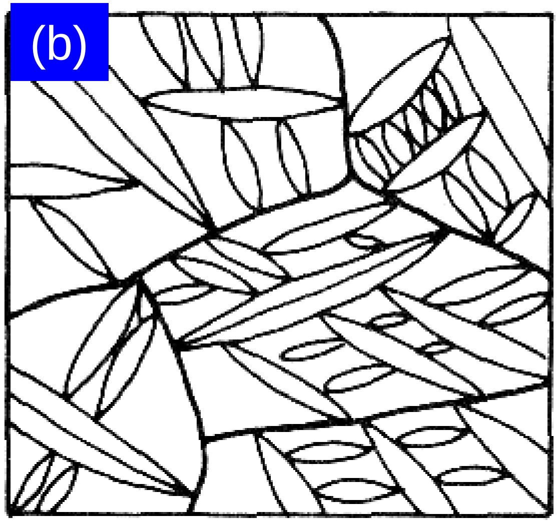
- The name martensite is after the German scientist Martens. It was used originally to describe the hard microconstituent found in quenched steels. Martensite remains of the greatest technological importance in steels where it can confer an outstanding combination of strength (> 3500 MPa) and toughness (> 200 MPa $m^{1/2}$).
- Martensitic transformation is the name for any transformation that takes place in a diffusionless and military manner - that is, these transformations take place through atomic movements which are less than one atomic spacing; and in these transformations atoms change their positions in a coordinated manner (unlike thermally activated diffusional, or, so-called, civilian processes).
- In shape memory alloys such as Ni-Ti (nitinol), it is the martensitic transformation that is responsible for the shape memory effect.
- In this topic, we describe some characteristic features of the martensitic transformations (with specific reference to steels in which, this transformation is repsonsible for hardening by quenching).
- Since martensitic transformations are diffusionless, necessarily, the composition does not change during the transformation. It is only the crystal structure that changes. For example, in Fe-C alloys, the austenite (fcc) transforms into martensite (bct);
- in Ni-Ti, an ordered bcc (called austenite) transforms to another ordered CsCl type structure (called martensite). Note that since martensitic transformation is diffusionless, if the austenitic phase is ordered, the martensitic phase is also ordered.

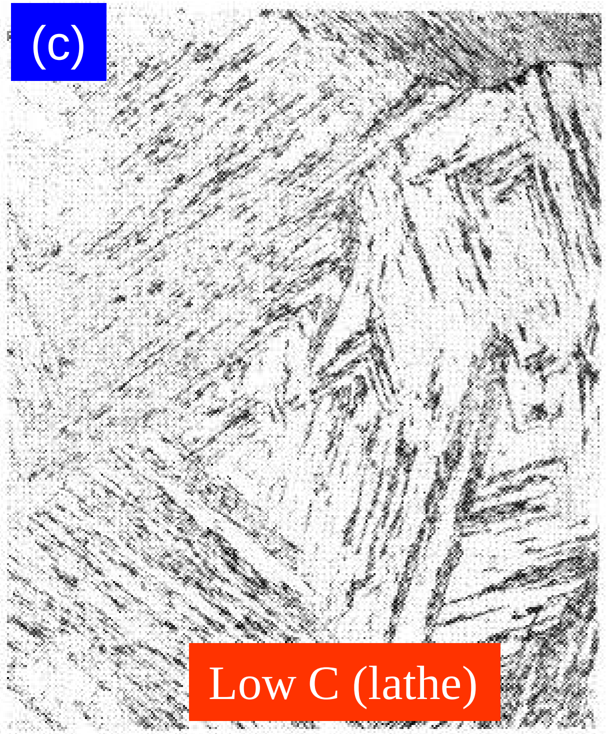
Characteristics of martensitic transformation

- Occur at high supersaturations, without change in composition
- No long range diffusion → Movement of atoms a fraction of the inter-atomic distance
- Nearest neighbour configuration remains unchanged
- Cooperative movement of a large group of atoms → transformation proceeds at the speed of sound in the material
- Thermal activation does not play a role in the growth of the martensitic phase
  Thermal activation may play a role in the nucleation of martensite
- Usually martensite crystals nucleate and grow across the whole grain (in some cases this growth is a function of temperature)
- In some cases the transformation occurs over a period of some time (due to thermally assisted nucleation)
- Martensitic crystals have a specific orientation relationship (OR) with the parent phase
- Planes of the parent lattice on which Martensitic crystals from → Habit planes *(irrational Indices)*
- Interface between Martensite and parent phase → Coherent or Semi-coherent
- At a given temperature (between M_s and M_f) the fraction transformed ↑ with plastic deformation (in some cases elastic stress also has a similar effect)
- With prior plastic deformation the transformation temperature can be increased to M_d

Characteristics of martensitic transformation







(a, b) Growth of martensite with increasing cooling below M_s
(c-e) Different martensite morphologies in iron alloys

Characteristics of martensitic transformation

- ❑ Shape of the Martensite formed → Lathe and Plate morphologies
- ❑ Associated with shape change (shear)
- ❑ But: Invariant plane strain *(observed experimentally)* → Interface plane between Martensite and Parent remains undistorted and unrotated
- ❑ This condition requires
  1) Bain distortion → Expansion or contraction of the lattice along certain crystallographic directions leading to homogenous pure dilation
  2) Secondary Shear Distortion → Slip or twinning
  3) Rigid Body rotation

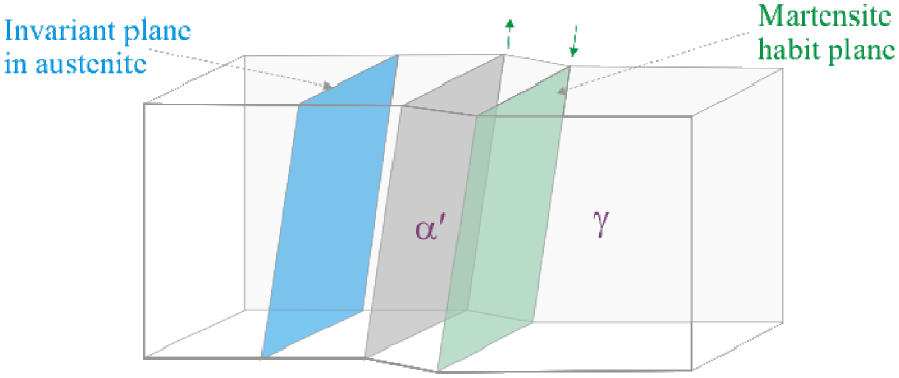
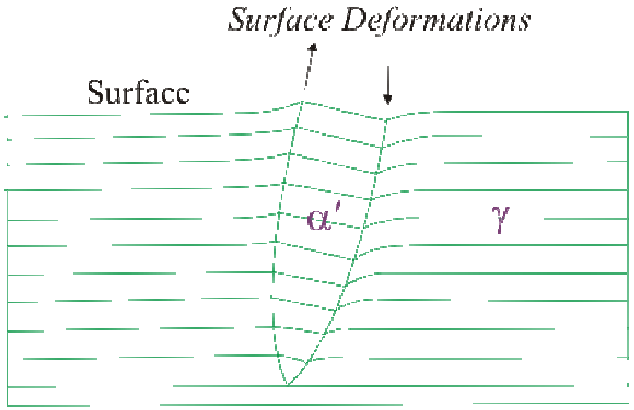


Illustration of the coherence of the martensitic plate with the surrounding austenite

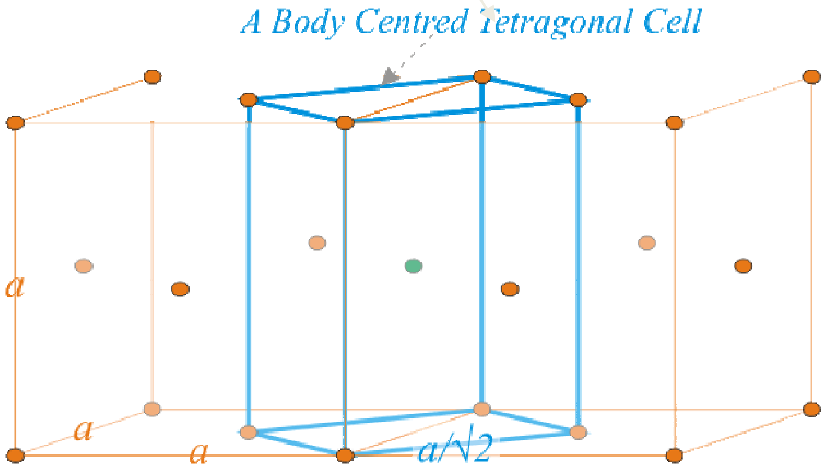


Characteristics of martensitic transformation

- Martensitic transformation can be understood by first considering an alternate unit cell for the Austenite phase as shown in the figure below.
- If there is no carbon in the Austenite (as in the schematic below), then the Martensitic transformation can be understood as a ~20% contraction along the c-axis and a ~12% expansion of the a-axis → accompanied by no volume change and the resultant structure has a BCC lattice (the usual BCC-Fe) → c/a ratio of 1.0.

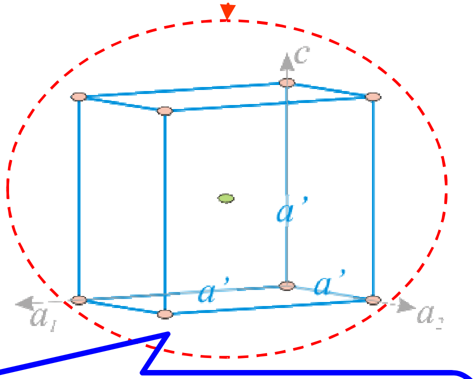
$$\underset{0.8\,\%C}{\gamma\,(FCC)} \xrightarrow{Quench} \underset{0.8\,\%C}{\alpha'\,(BCT)}$$

FCC Austenite alternate choice of Cell



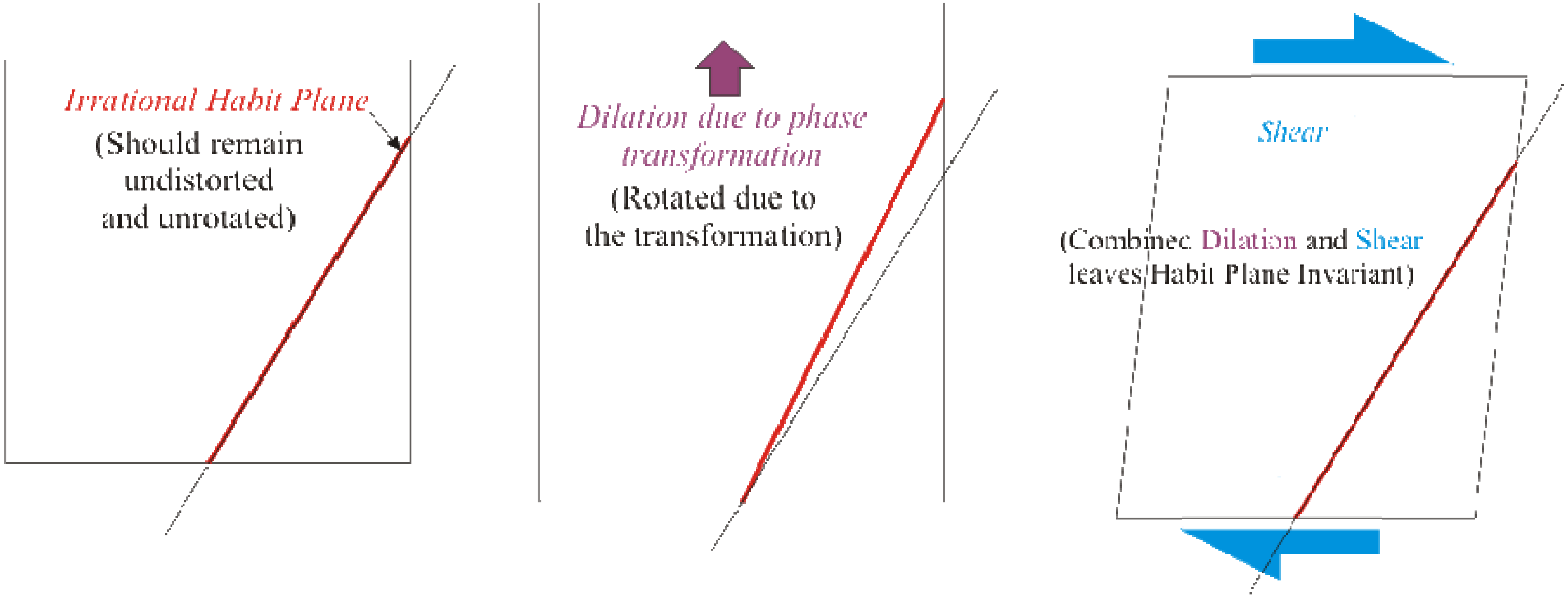
FCC → BCC

In Pure Fe after
the Martensitic transformation
$c = a$



~20% contraction of *c-axis*
~12% expansion of *a-axis*

Characteristics of martensitic transformation



Irrational Habit Plane

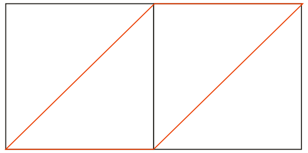
(Should remain undistorted and unrotated)

Dilation due to phase transformation

(Rotated due to the transformation)

Shear

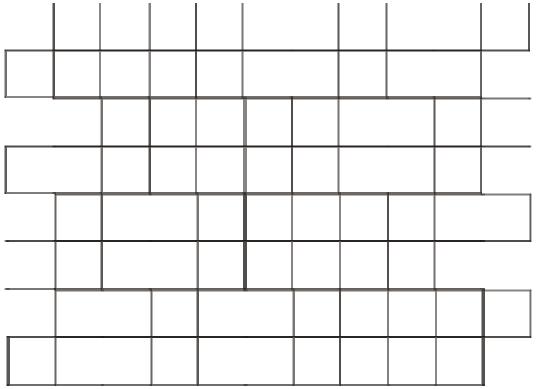
(Combined Dilation and Shear leaves Habit Plane Invariant)



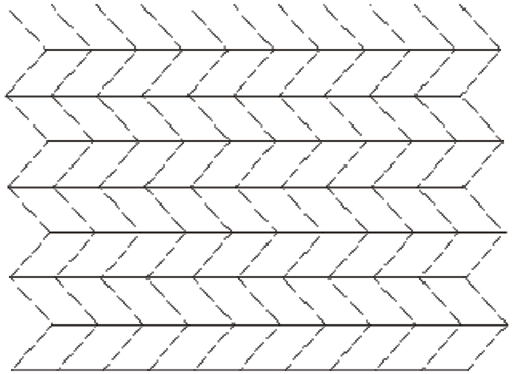
But shear will distort the lattice!

Slip

Twinning



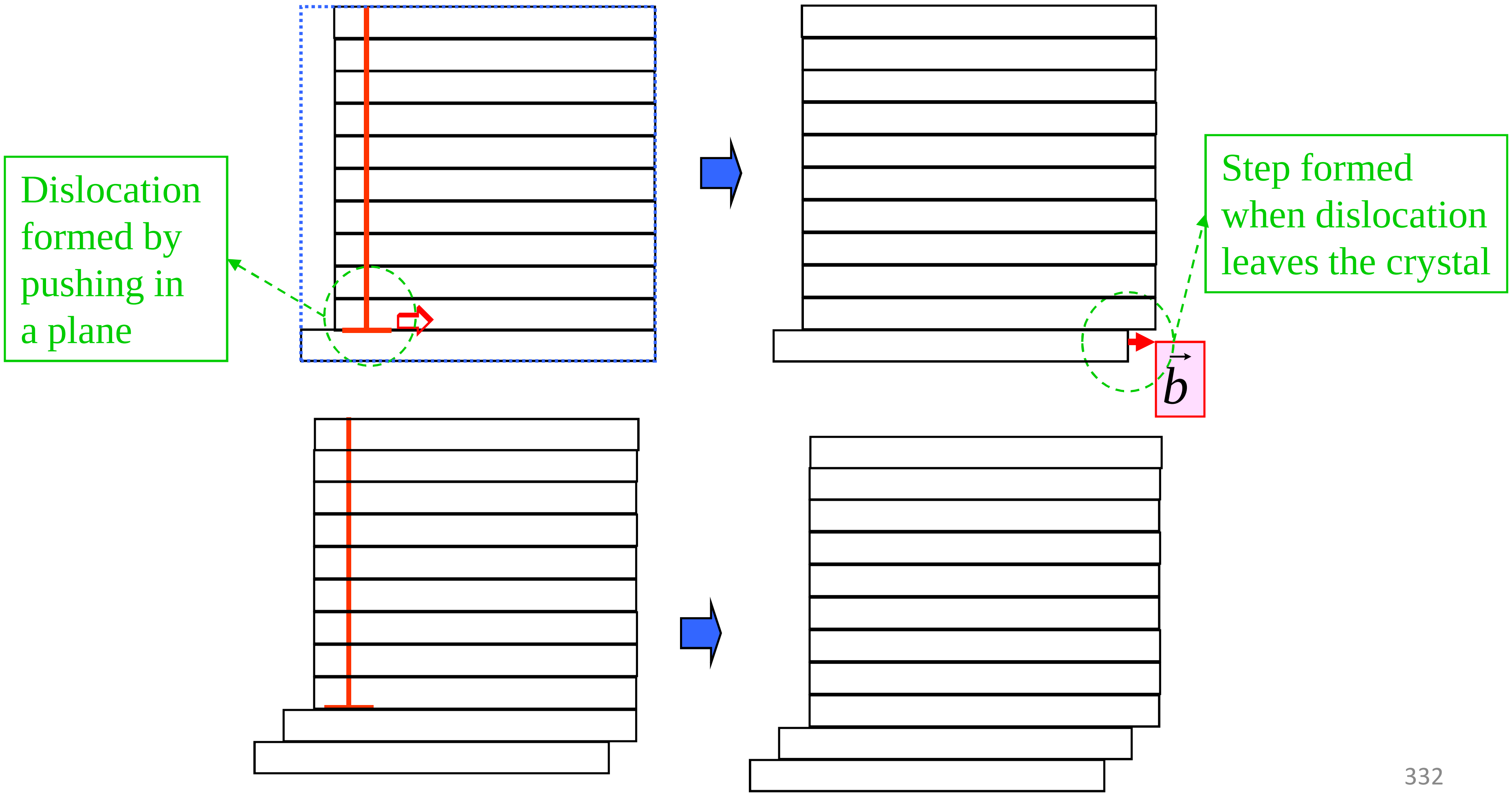
Average shape remains undistorted



Characteristics of martensitic transformation

How does the motion of dislocations lead to a macroscopic shape change?

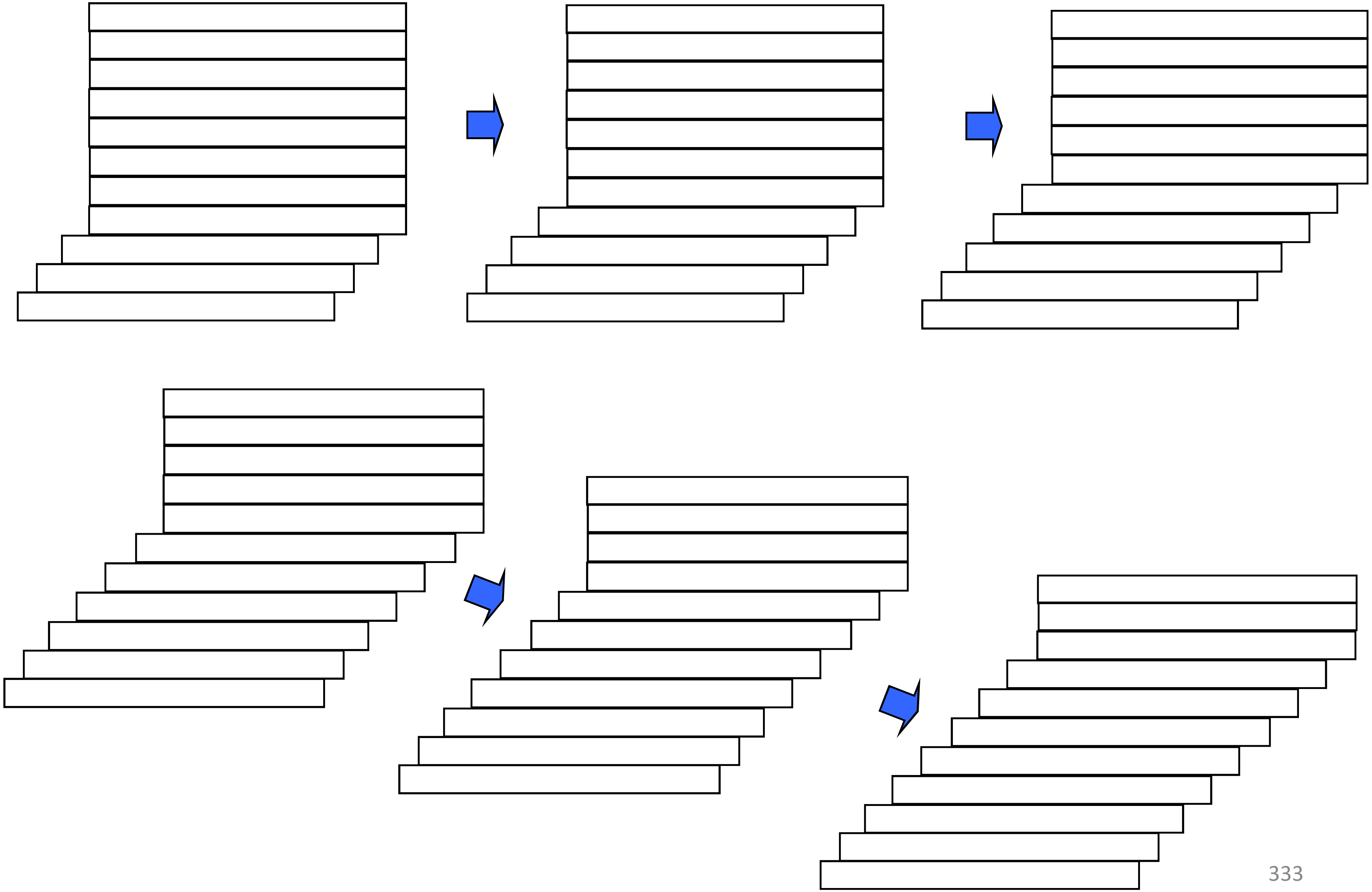
(From microscopic slip to macroscopic deformation ⇨ a first feel!)



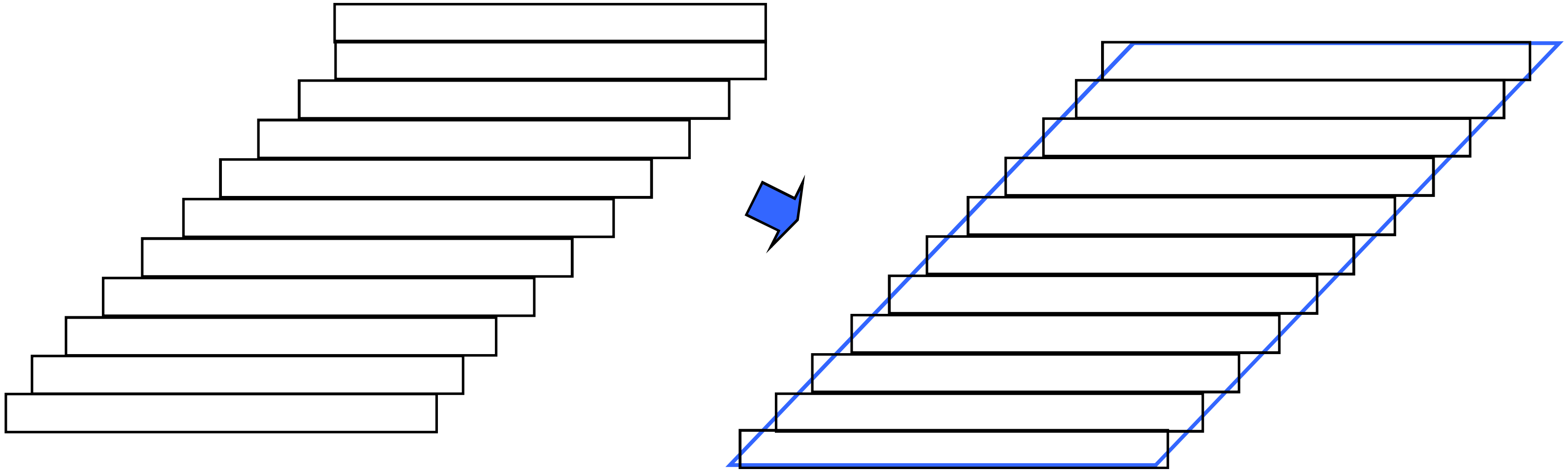
Dislocation formed by pushing in a plane

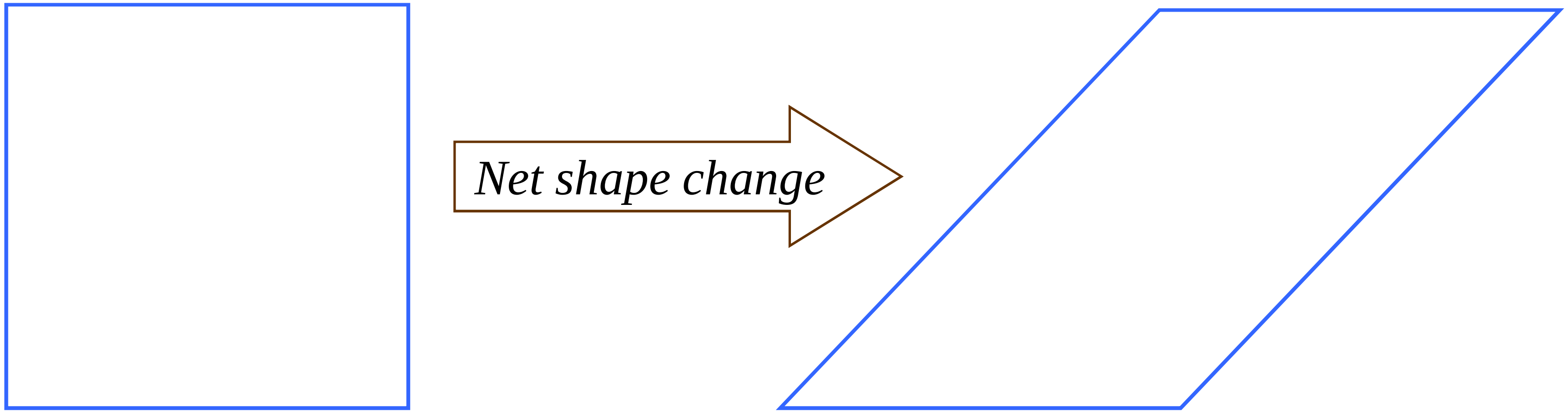
Step formed when dislocation leaves the crystal

Characteristics of martensitic transformation



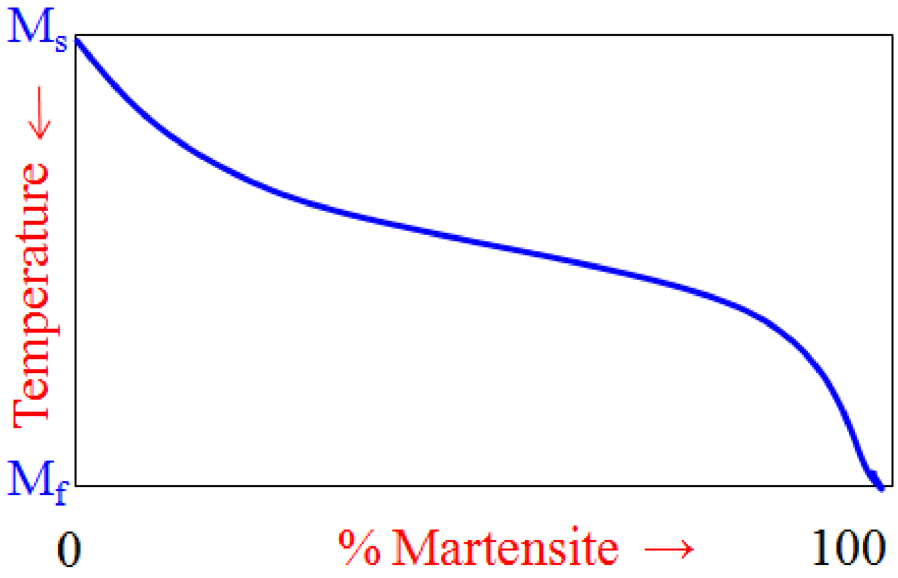
Characteristics of martensitic transformation

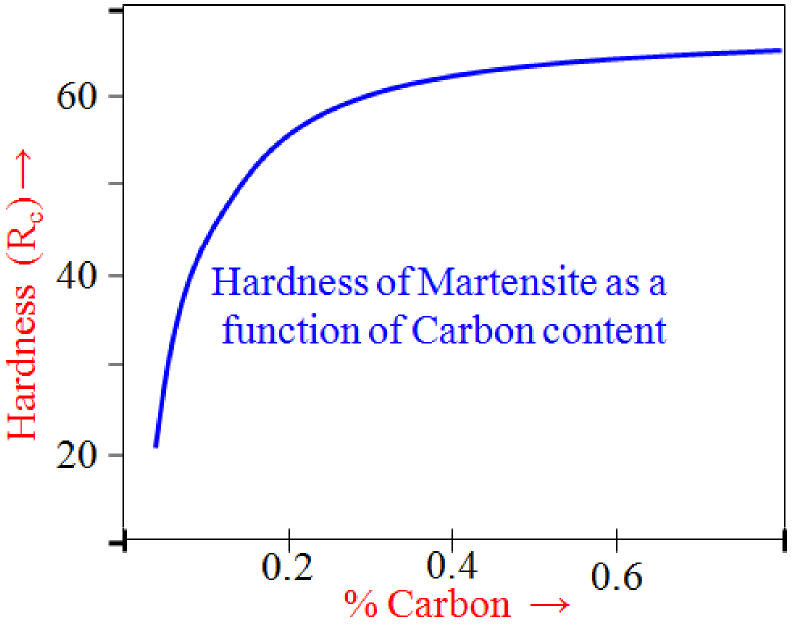




Net shape change

Characteristics of martensitic transformation

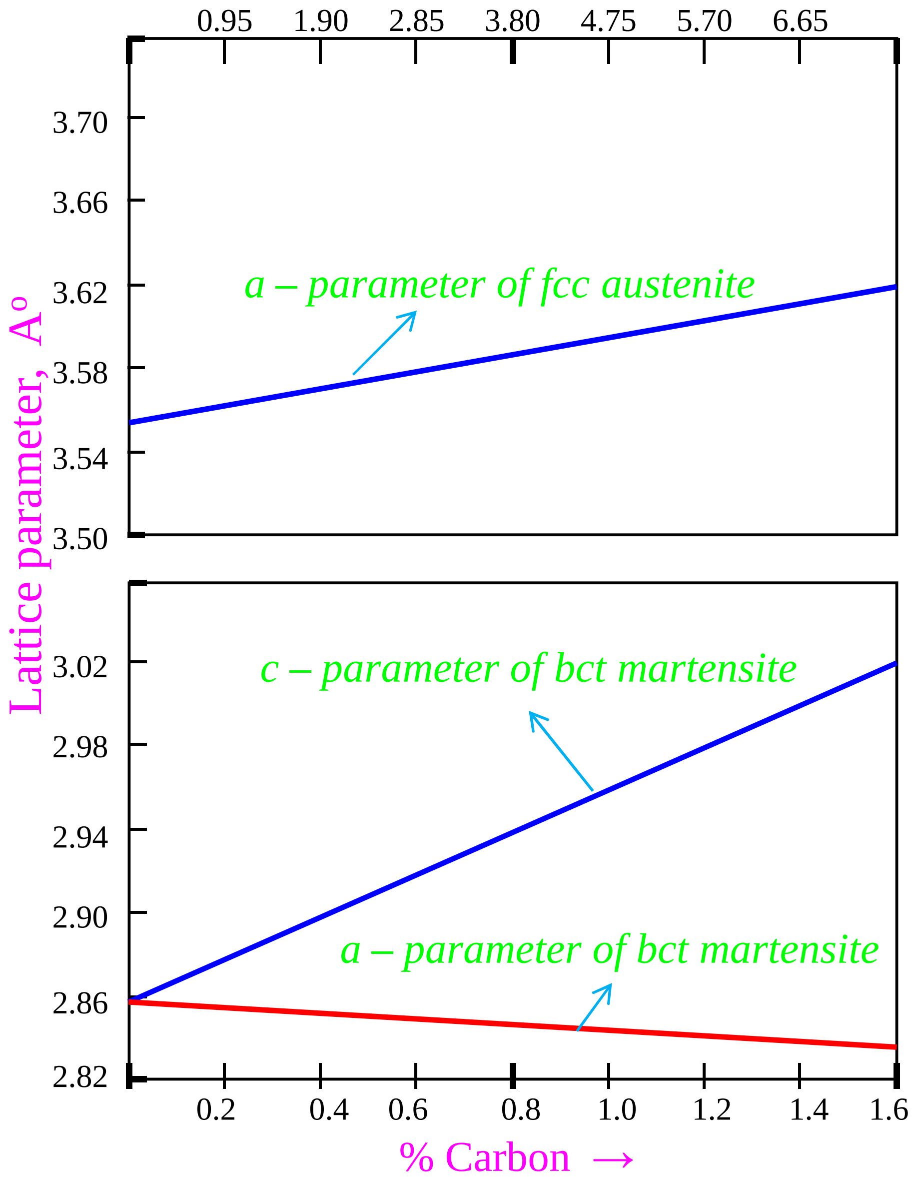


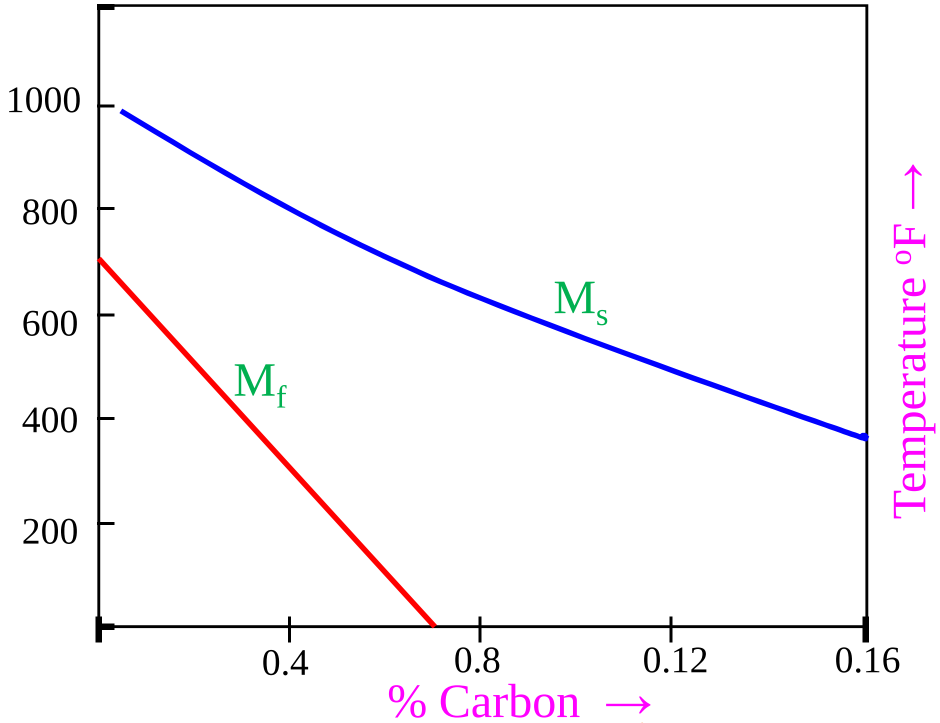


Hardness of Martensite as a function of Carbon content

Properties of 0.8% C steel		
Constituent	Hardness (R_c)	Tensile strength (MN / m^2)
Coarse pearlite	16	710
Fine pearlite	30	990
Bainite	45	1470
Martensite	65	-
Martensite tempered at 250 °C	55	1990

Characteristics of martensitic transformation





Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite

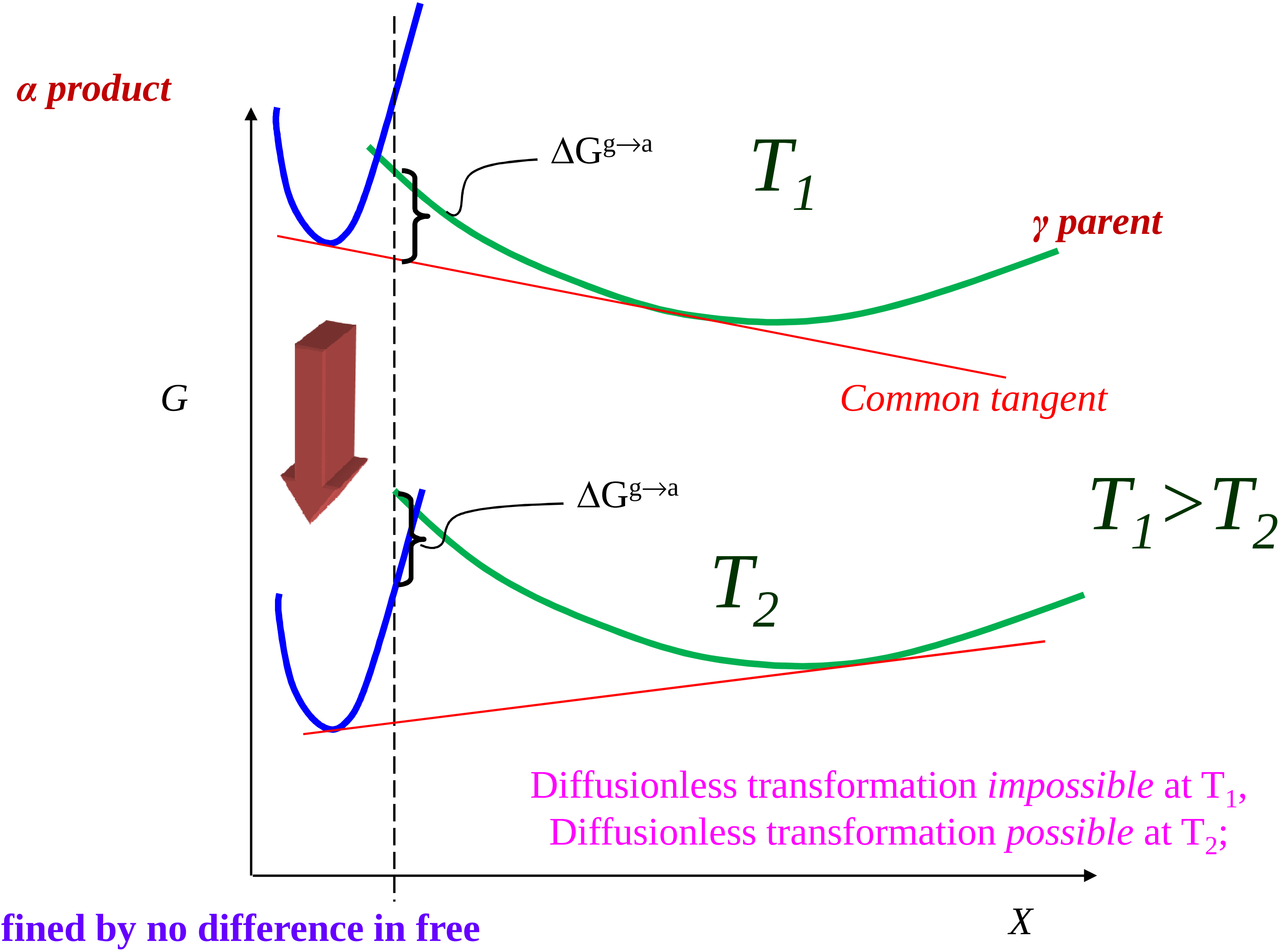
Driving force for martensitic transformation

- Diffusionless transformations require larger driving forces than for diffusional transformations
- Why? In order for a transformation to occur without long range diffusion, it must take place *without a change in composition*
- This leads to the so-called T_0 concept, which is the temperature at which the new phase can appear with a net decrease in free energy *at the same composition as the parent (matrix) phase*.
- As the following diagram demonstrates, the temperature, T_0, at which segregation-less transformation becomes possible (i.e. a decrease in free energy would occur), is always less than the solvus (liquidus) temperature.
- The driving force for a martensitic transformation can be estimated in exactly the same way as for other transformations such as solidification.
- Provided that an enthalpy (latent heat of transformation) is known for the transformation, the driving force can be estimated as proportional to the latent heat and the undercooling below T_0.

$$\Delta G^{\gamma \rightarrow \alpha'} = \Delta H^{\gamma \rightarrow \alpha'} \frac{T_0 - M_S}{T_0}$$

.

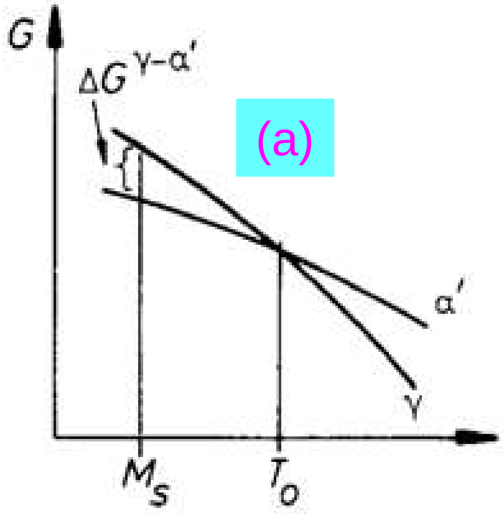
Driving force for martensitic transformation

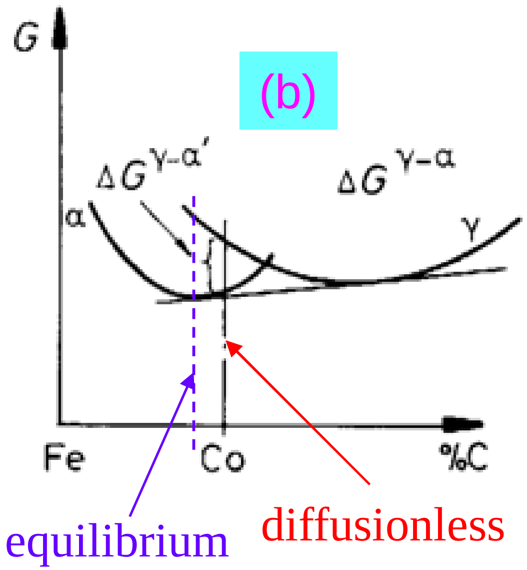


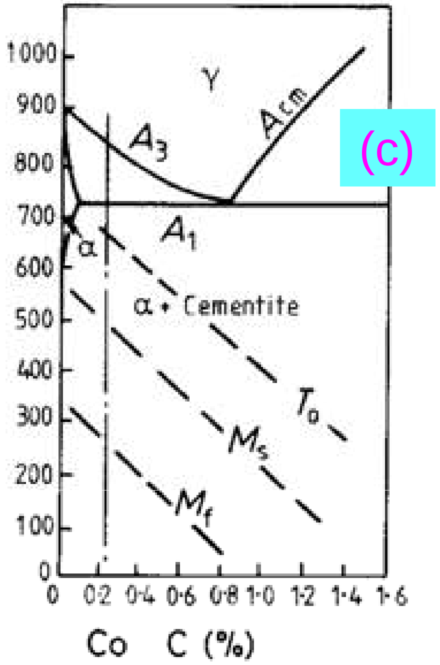
Diffusionless transformation *impossible* at T_1,
Diffusionless transformation *possible* at T_2;

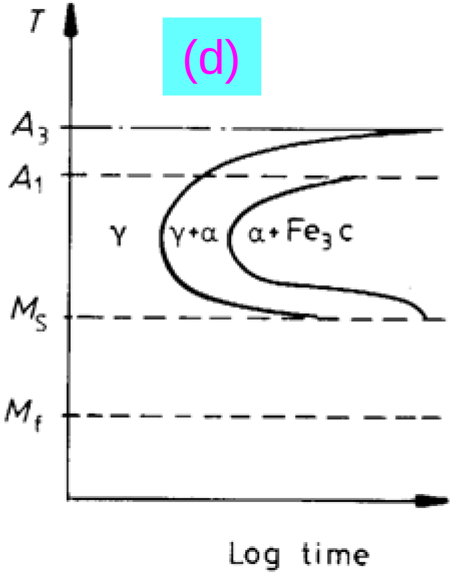
“T_0” is defined by no difference in free energy between the phases, $\Delta G=0$.

Various ways of showing Martensitic Transformations









(a) Free energy – temperature diagram for Austenite and martensite of fixed carbon concentration

(b) Free energy – composition diagram for the austenite and martensite phases at the M_s temperature.

(c) Iron-carbon phase diagram with T_0 as defined in (a), M_s and M_f superimposed.

(d) M_s and M_f in relation to the TTT diagram for alloy C_0 in C

Why tetragonal Fe-C martensite?

- At this point, it is worth stopping to ask why a tetragonal martensite forms in iron. The answer has to do with the preferred site for carbon as an interstitial impurity in bcc Fe.
- Remember: Fe-C martensites are unusual for being so strong (& brittle). Most martensites are not significantly stronger than their parent phases.
- Interstitial sites:
  FCC: octahedral sites radius= 0.052 nm
  tetrahedral sites radius= 0.028 nm
  BCC: octahedral sites radius= 0.019 nm
  tetrahedral sites radius= 0.036 nm

Carbon atom radius = 0.08 nm.

- Surprisingly, it occupies the octahedral site in the bcc Fe structure, despite the smaller size of this site (compared to the tetrahedral sites) presumably because of the low modulus in the <100> directions.
- One consequence of the occupation of the octahedral site in ferrite is that the carbon atom has only two nearest neighbors. Each carbon atom therefore distorts the iron lattice in its vicinity. The distortion is a *tetragonal distortion*.
- If all the carbon atoms occupy the *same type of site* then the entire lattice becomes tetragonal, as in the martensitic structure.
- Switching of the carbon atom between adjacent sites leads to strong internal friction peaks at characteristic temperatures and frequencies.

Massive vs. Martensitic Transformations

- There are two basic types of *diffusionless* transformations.
- One is the *massive transformation*. In this type, a diffusionless transformation takes place without a definite orientation relationship. The interphase boundary (between parent and product phases) migrates so as to allow the new phase to grow. It is, however, a civilian transformation because the atoms move individually.
- The other is the *martensitic transformation*. In this type, the change in phase involves a definite orientation relationship because the atoms have to move in a coordinated manner. There is always a change in shape which means that there is a strain associated with the transformation. The strain is a general one, meaning that all six (independent) coefficients can be different.

	CIVILIAN	MILITARY
Diffusion Required	Precipitation, Spinodal Decomposition	-
Diffusionless	Massive Transformations	Martensitic Transformations

Recovery, Recrystallization & Grain Growth

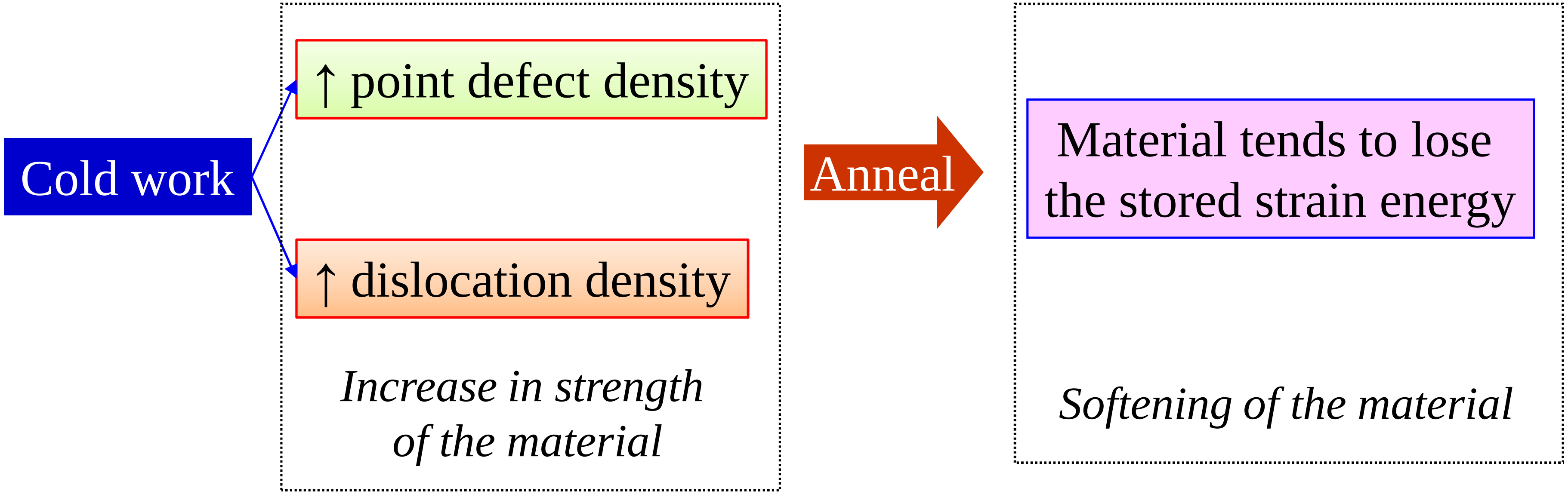
Introduction

Plastic deformation in the temperature range (0.3 – 0.5) T_m → COLD WORK

- Point defects and dislocations have strain energy associated with them
- (1 -10) % of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) → *The material becomes battery of energy..!*
- The cold worked material is in a micro structurally metastable state.
- Depending on the severity of the cold work the dislocation density can increase 4-6 orders of magnitude more. The material becomes stronger, but less ductile.
- The cold worked material is stronger (harder), but is brittle.
- Heating the material (typically below $0.5T_m$) is and holding for sufficient time is a heat treatment process called annealing.
- Depending on the temperature of annealing processes like Recovery at lower temperatures) or Recrystallization (at higher temperatures) may take place. During these processes the material tends to go from a micro structurally metastable state to a lower energy state (towards a stable state).
- Further ‘annealing’ of the recrystallized material can lead to grain growth.

$$\begin{array}{ccc} \textit{Annealed material} & & \textit{Stronger material} \\ \rho_{\text{dislocation}} \sim (10^{6}-10^{9}) & \xrightarrow{\textit{Cold work}} & \rho_{\text{dislocation}} \sim (10^{12}-10^{14}) \end{array}$$

Introduction



Cold work

↑ point defect density

↑ dislocation density

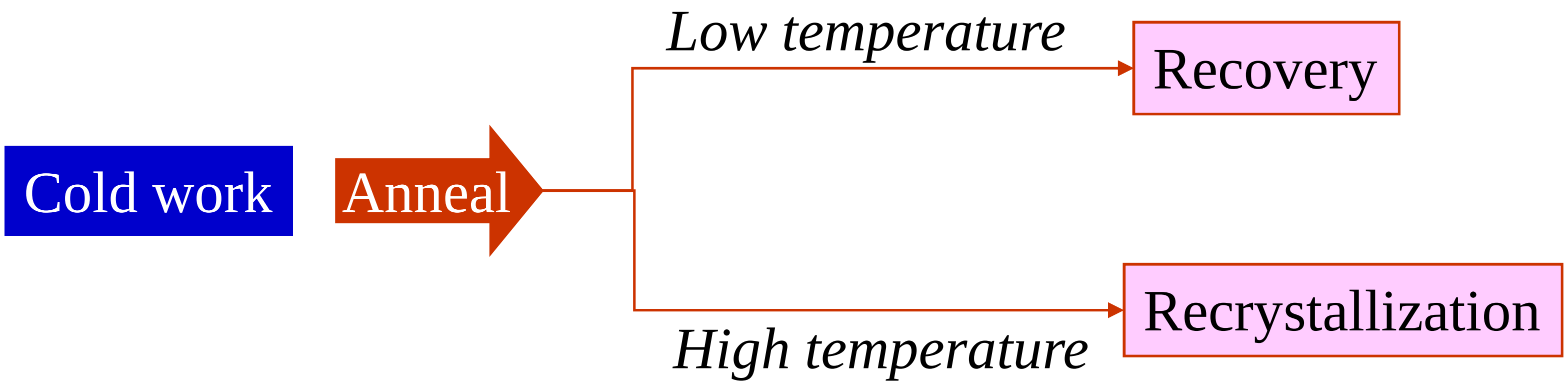
Increase in strength of the material

Anneal

Material tends to lose the stored strain energy

Softening of the material

- During cold work the point defect density (vacancies, self interstitials…) and dislocation density increase. Typical cold working techniques are rolling, forging, extrusion etc.
- Cold working is typically done on ductile metals (e.g. Al, Cu, Ni)



Cold work

Anneal

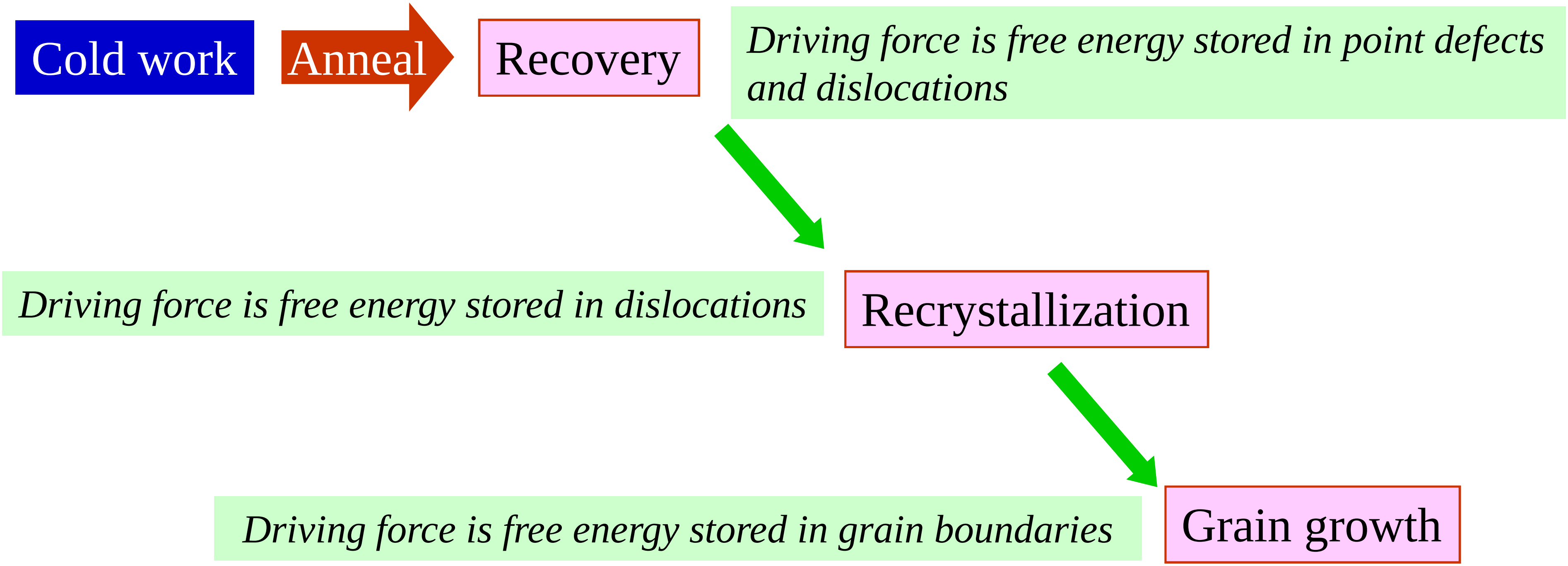
Low temperature

Recovery

High temperature

Recrystallization

Overview of processes taking place during annealing



Cold work

Anneal

Recovery

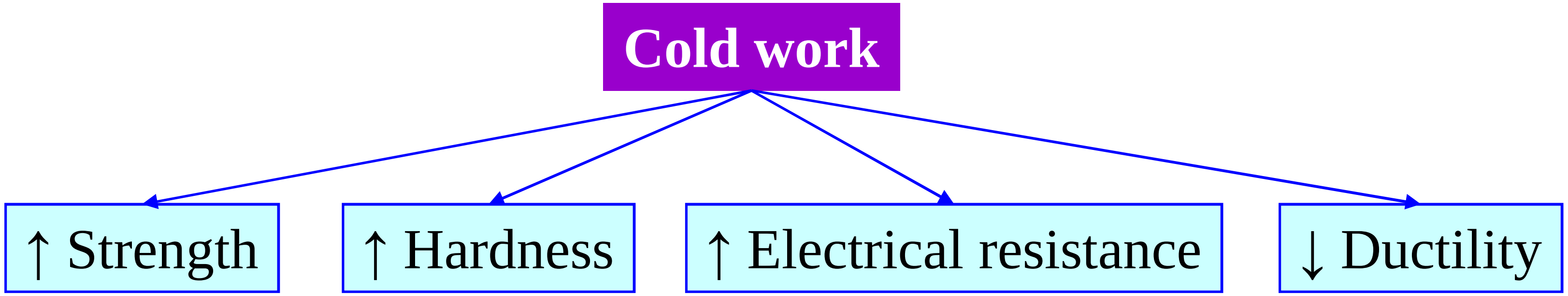
Driving force is free energy stored in point defects and dislocations

Recrystallization

Driving force is free energy stored in dislocations

Grain growth

Driving force is free energy stored in grain boundaries



Cold work

↑ Strength

↑ Hardness

↑ Electrical resistance

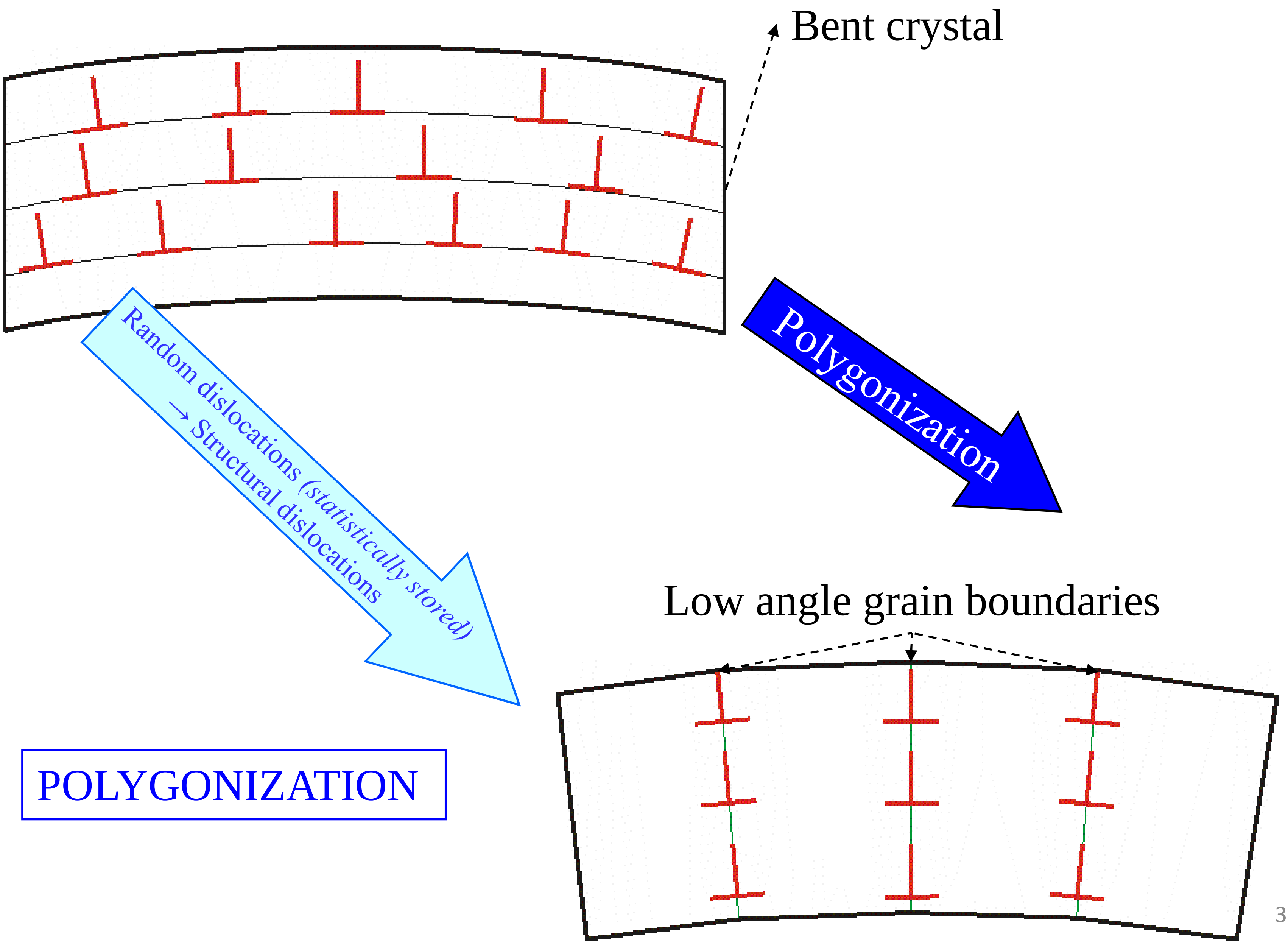
↓ Ductility

Changes occur to almost all physical and mechanical properties

Recovery

- Recovery takes place at low temperatures of annealing
- “Apparently no change in microstructure”
- Excess point defects created during Cold work are absorbed:
  - at surface or grain boundaries
  - by dislocation climb
- Random dislocations of opposite sign come together and annihilate each other
- Dislocations of same sign arrange into low energy configurations:
  - Edge → Tilt boundaries
  - Screw → Twist boundaries
    - ➔ POLYGONIZATION
- Overall reduction in dislocation density is small
- At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonized subgrain structure while the dislocation density stays almost unchanged. This process also removes the residual stresses formed due to cold working significant. The recovering of physical and mechanical properties varies with the temperature and time.

POLYGONIZATION



Bent crystal

Random dislocations (statistically stored) → Structural dislocations

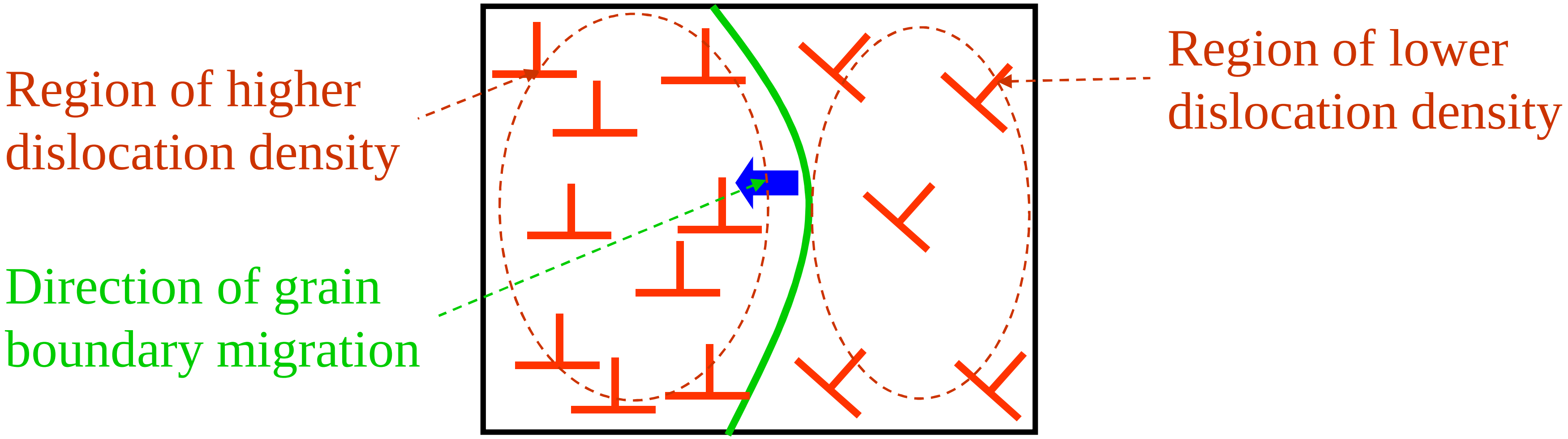
Polygonization

Low angle grain boundaries

POLYGONIZATION

Recrystallization

- ❑ $T_{recrystallization} \in (0.3 - 0.5)\, T_m$
- ❑ "Nucleation" and growth of new, strain free crystals
- ❑ Nucleation of new grains in the usual sense may not be present and grain boundary migrates into a region of higher dislocation density
- ❑ *ΔG (recrystallization) = G (deformed material) – G (undeformed material)*
- ❑ $T_{Recrystallization}$ is the temperature at which 50 % of the material recrystallizes in 1 hour



Recrystallization

- ❑ Deformation ↑ ⇒ recrystallization temperature ($T_{recrystallization}$) ↓
- ❑ Initial grain size ↓ ⇒ recrystallization temperature ↓
- ❑ High cold work + low initial grain size ⇒ finer recrystallized grains
- ❑ ↑ cold work temperature ⇒ lower strain energy stored
  ⇒ ↑ recrystallization temperature
- ❑ Rate of recrystallization = exponential function of temperature
- ❑ $T_{recrystallization}$ = strong function of the purity of the material
  $T_{recrystallization}$ (very pure materials) ~ 0.3 T_m
  $T_{recrystallization}$ (impure) ~ (0.5 – 0.6) T_m

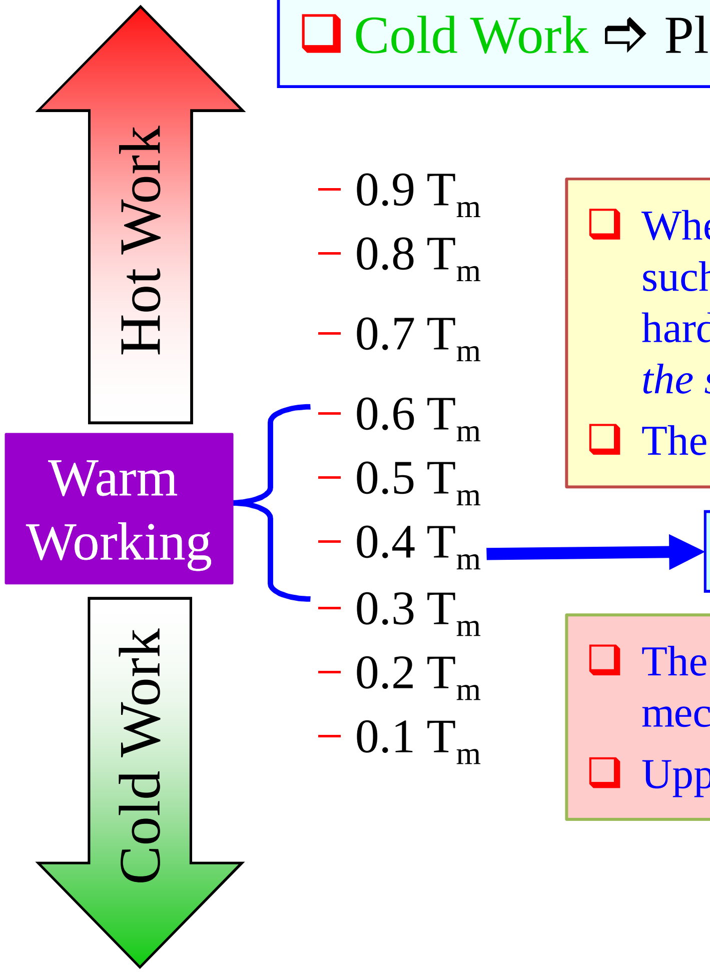
► $T_{recrystallization}$ (99.999% pure Al) ~ 75°C
$T_{recrystallization}$ (commercial purity) ~ 275°C

- ❑ The impurity atoms segregate to the grain boundary and retard their motion → *Solute drag* (can be used to retain strength of materials at high temperatures)
- ❑ Second phase particles also pin down the grain boundary during its migration

Hot Work and Cold Work

Often the range is further subdivided into Hot, Cold and Warm working as in the figure

- ❑ **Hot Work** ⇨ Plastic deformation above $T_{Recrystallization}$
- ❑ **Cold Work** ⇨ Plastic deformation below $T_{Recrystallization}$



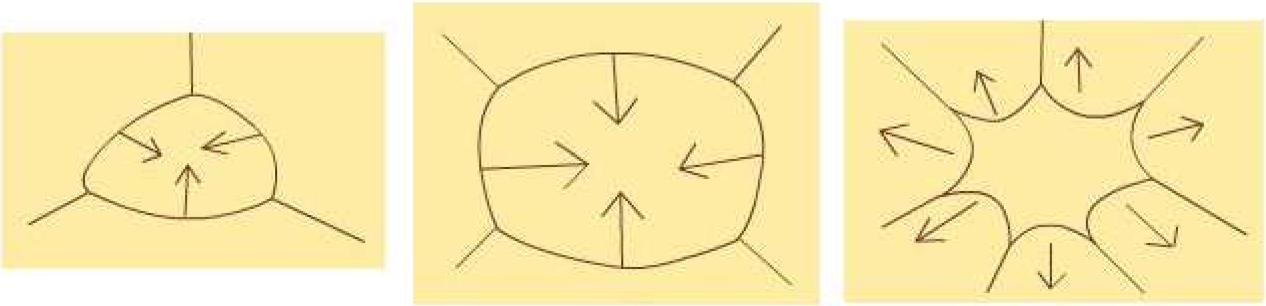
Recrystallization temperature ($\sim 0.4\ T_m$)

- ❑ When a metal is hot worked. The conditions of deformation are such that the sample is soft and ductile. The effects of strain hardening are negated by dynamic and static processes (*which keep the sample ductile)*
- ❑ The lower limit of temperature for hot working is taken as $0.6\ T_m$

- ❑ The effects of strain hardening is not negated. Recovery mechanisms involve mainly motion of point defects.
- ❑ Upper limit ►$0.3\ T_m$

Grain growth

- The interfaces in a material cost the system energy: the excess free energy associated with the interfaces is the interfacial free energy.
- Grain boundaries are the interfaces between two crystallites which are differently oriented in space; the excess free energy associated with the grain boundary is the grain boundary energy.
- The grain boundary energy acts as the driving force for the movement of grain boundaries. Hence, if a recrystallised material is further annealed, then grains growth takes place; bigger grains grow at the cost of smaller ones. This process is known as grain growth.
- Since the driving force for grain growth is the interfacial energy, and since the excess energy associated with a system due to interfaces is related to the curvature of the interface, the grain growth is curvature driven. In Figure we shown the direction of movement of grain boundaries and their relationship to curvature (in 2D systems).



Curvature driven growth of grains (in 2D)

Grain growth

- It is the velocity of the interface, then $\nu \propto \kappa$ where κ is the curvature $\left(\frac{1}{r}\right)$. More specifically

$$\nu = M\frac{2\gamma}{r}$$

- where M is the mobility, and ϒ is the grain boundary energy. In terms of the diameter (D) of the grains,

$$\frac{dD}{dt} = \frac{4M\gamma}{D}$$

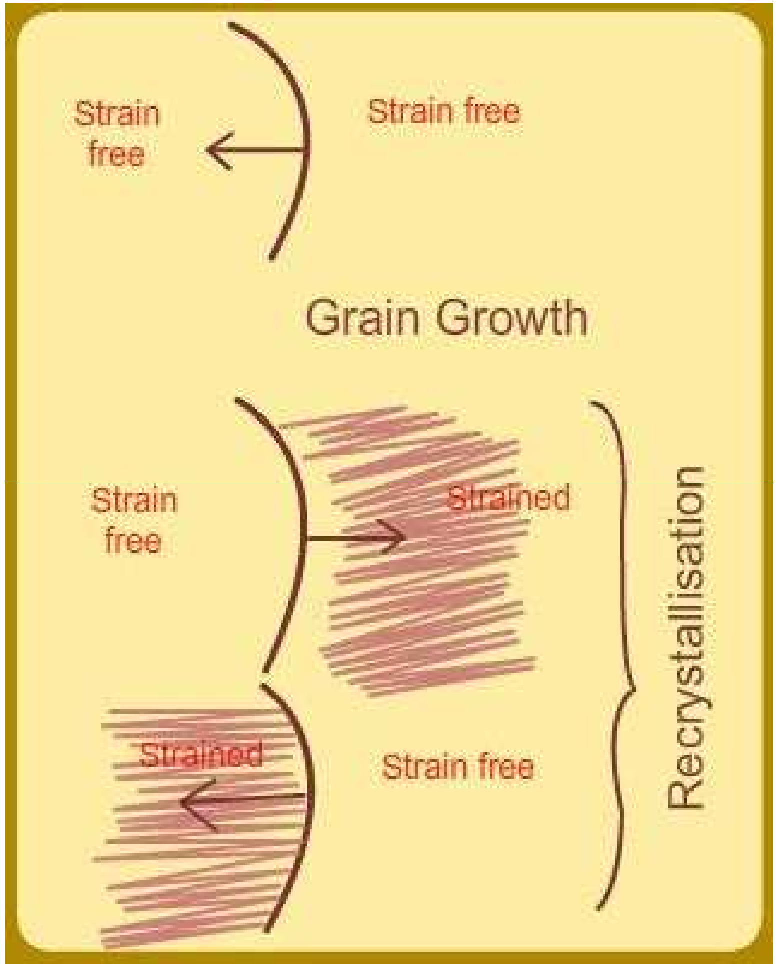
- The solution to this equation is given by

$$D^2 = D_0^2 + 4M\gamma t$$

- where D_0 is the mean size of the grain at time t = 0 and D is the mean diameter of the grains in the system.
- Experimentally, it is found that the grain size as a function of time does follow an expression of the type $D = Kt^n$,where K is a temperature dependent proportionality constant and *n is a number* much less than 0.5. The deviation of the exponent from 0.5 is not yet clearly understood.

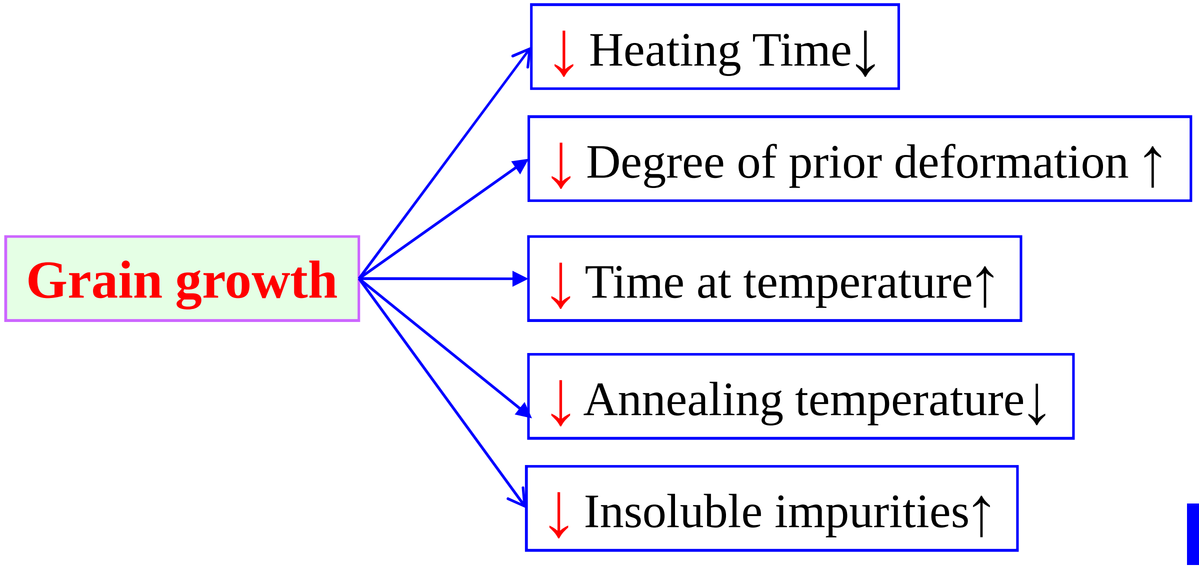
Grain growth

- ❑ Due to the differences in the driving forces for recrystallisation and grain growth, as shown in Figure the movement of the interface in these two cases are different in character; recrystallisation, as long as the growing grain is free of strain and eats into the strained grain, will proceed irrespective of the curvature of the grain; however, during grain growth, the movement of the interface is dependent on the curvature of the grain.
- ❑ During grain growth, the direction of movement of the grain boundary is completely decided by curvature. On the other hand, during recrystallisation it is decided by the strains in the grains; the strained one is eaten up by the strain free crystal; hence, the growth can sometimes be such that the boundary moves away from its centre of curvature.



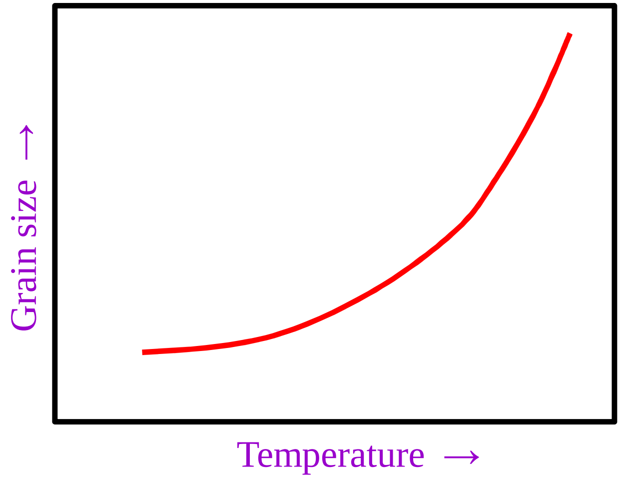
Grain growth

- Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is driving force for grain growth.
- Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid.
- At any given temperature there is a maximum grain size at which these two effects are in equilibrium



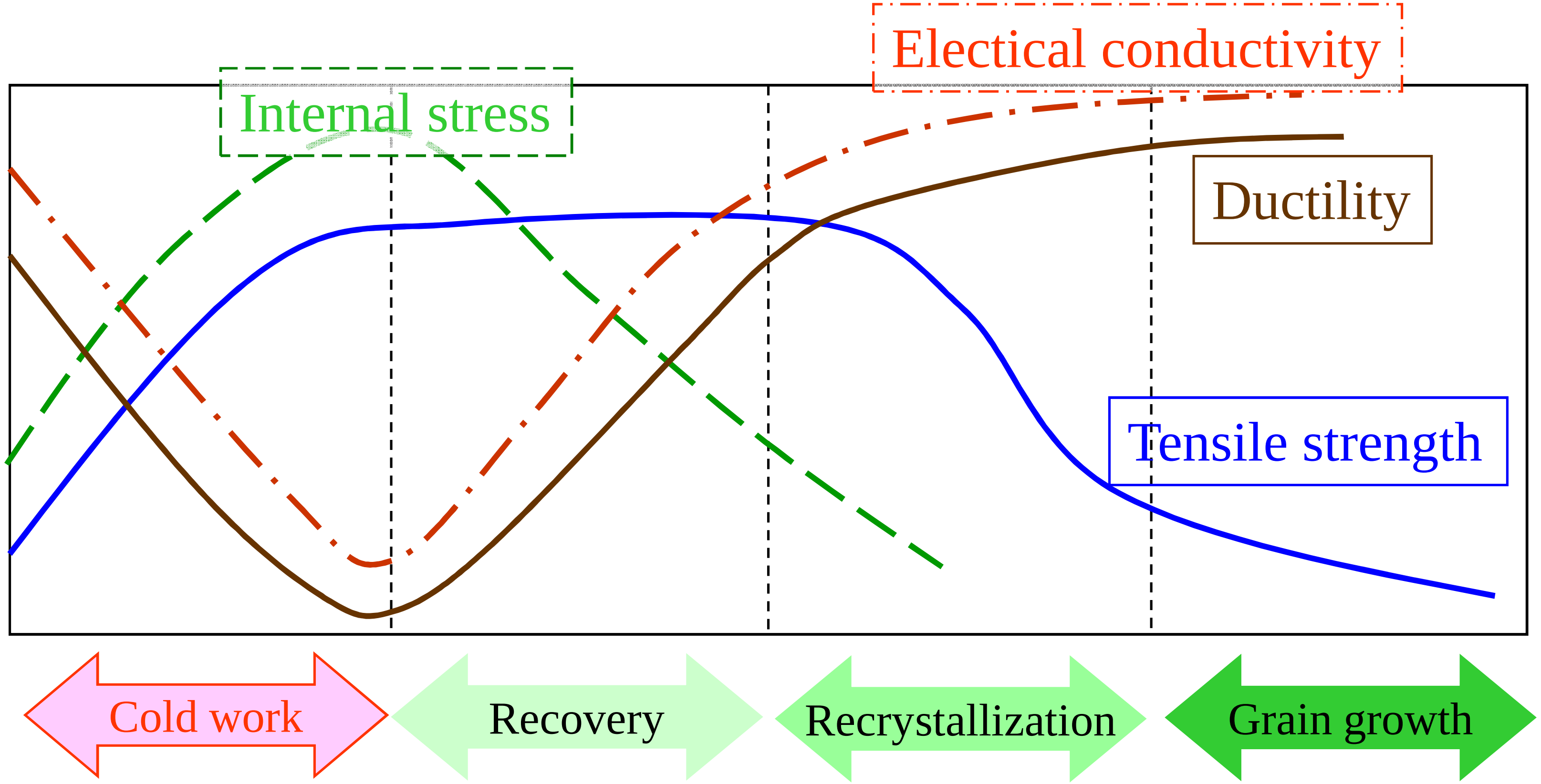
Grain growth

- ↓ Heating Time↓
- ↓ Degree of prior deformation ↑
- ↓ Time at temperature↑
- ↓ Annealing temperature↓
- ↓ Insoluble impurities↑



Effect of temperature on recrystallized grain size

Recovery Recrystallization Graingrowth



Change of properties with increased annealing temperature of a cold worked sample. Note that there are changes in properties beyond recrystallisation temperatures too due to grain growth.

THANK YOU...!