University of Babylon/ College of Materials Engineering
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Phase Transformations in Ceramic Materials

1. Interfaces in Solids and Their Migration.
2. Solidification.

Phase Transformation Involving Interfaces

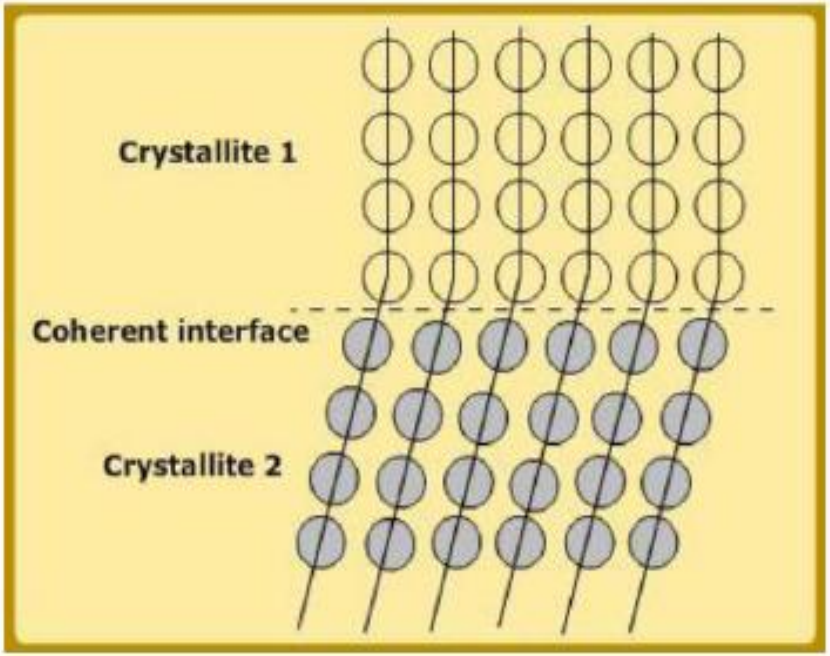
There are three types of interfaces that they form, namely, solid-solid, solid-liquid and solid-vapour interfaces. The surface of a single crystal (of a pure element) is an example of a solid-vapour interface. The solidification front is an example of a solid- liquid interface. Any engineering material, 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 called homophase inter-faces. 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 classed into three broad categories. They are as follows:

1- Coherent interfaces

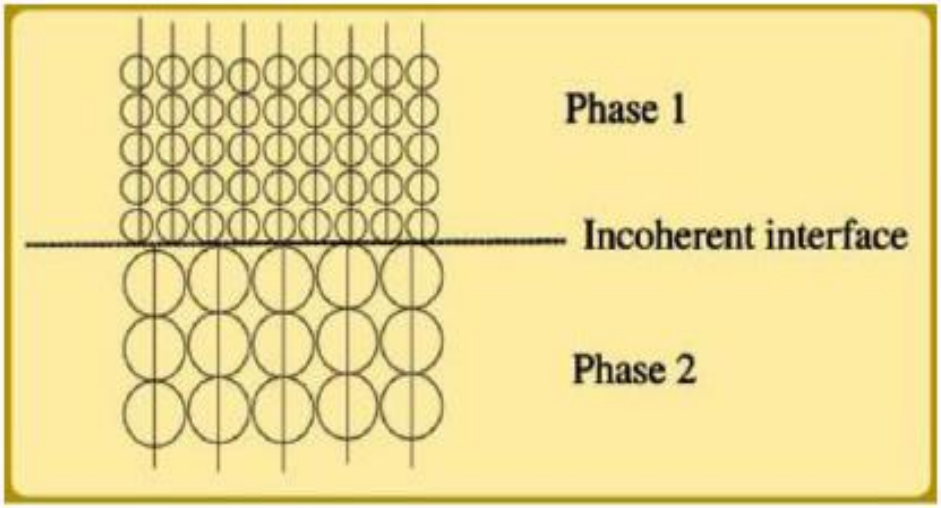
Coherent interfaces, as defined earlier, are interfaces across which the lattice planes are continuous. In some cases, the continuity can be maintained without any distortion of lattice planes; see Figure. 1 for a schematic. However, in most of the coherent interfaces, the lattice planes are elastically strained to maintain continuity; see Figure. 2 for a schematic. 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.

2- Incoherent interfaces

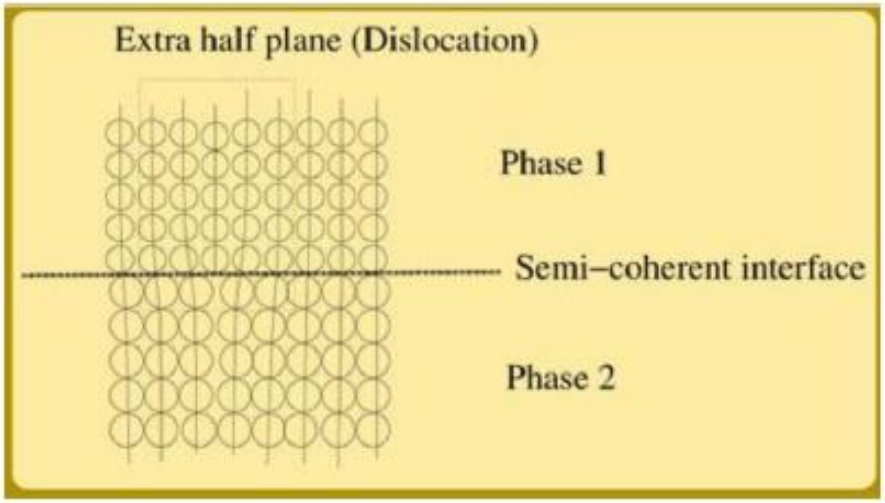
Incoherent interfaces, as defined earlier, are interfaces across which there is no continuity of lattice planes. In Figure we show, schematically, an in-coherent boundary. There is an elastic energy associated with incoherent boundaries, which is due to the difference in the volume of the particle with-out any constraints and the volume of the matrix available for the particle.



inclusions in alloys (for example, MnS in steel) have incoherent interfaces.

3- Semi-coherent interfaces

Interfaces across which some planes are continuous and some are not are knwon as semi-coherent interfaces.



Interface Migration :

Most phase transformations in metal systems are conducted by means of nucleation and growth processes. An interface is created at the nucleation stage and it subsequently migrates into a metastable matrix during the growth stage. Growth brings relocation of atoms via the moving interface. This is the heterogeneous type of transformation: the system can be split into the master and resultant phases at any moment during the transformation process.

There are two types of interfaces: glissile and non-glissile.

A glissile interface migrates in terms of a coordinated sliding movement of dislocations, which induces shear transformation (deformation) of the source phase into a new phase. The movement of a glissile interface is relatively independent from temperature; it is therefore called an athermal growth

However, most of the interfaces are of non-glissile type and these migrate with more or less random atom jumps across interfaces. The additional energy required by atoms to execute a free jump from an old phase and join a new phase is supplied by means of thermal activation. That makes migration of any ***non-glissile interface*** strongly dependent on temperature.

Summary

Interphase interface: an interface separating two phases.

Coherent interface: an interface with perfect atomic coherence within the interfacial plane. If there are two adjacent phases with identical crystal structure but their lattice parameters are slightly different, the misfit of lattice planes can be accommodated by coherent elastic deformations.

Semicoherent interface: misfit within the coherent interface reaches such an extent that it must be accommodated by the formation of dislocations.

Incoherent interface: the interfacial plane of adjacent crystals features very different atomic configurations; there is no possibility of good coherence within atomic configuration across the interface plane. An incoherent interface is characteristic for the high value of interfacial surface energy, whereas the contribution of coherent deformation energy is equal to zero.

Glissile interface: this interface contains dislocations with the Burgers vector which lies in the slip planes of both old and new phases. Coordinated movement of these dislocations results in phase transformation, which may be accompanied by shape deformation.

Non-glissile interface: the movement of this interface is driven by random jumps of atoms across the interface. The movement of this interface can be controlled by volume diffusion or by the interface control.

Questions :

1. What types of interface in solids do you know?

2. How do coherence strains develop?

3. What is the difference between interphase surface energy of coherent and semicoherent interfaces?

4. What is the difference between a glissile and non-glissile interfaces?

Solidification

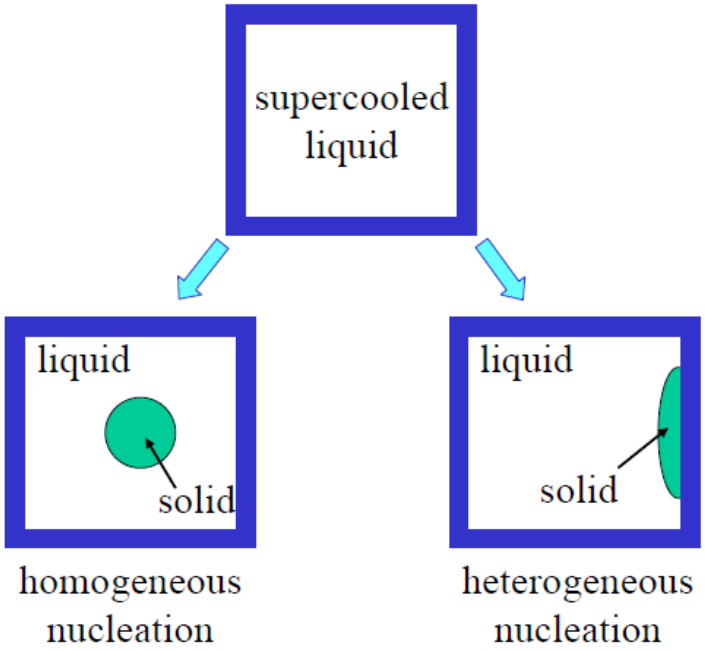
Solidification and melting represent transitions between the solid and liquid states. These phase transformations are essential for such technological applications as production of castings and ingots, continuous casting, growth of monocrystals for semiconductors, fusion welding and recently also metallic glasses. Understanding of the solidification mechanism and the impact of parameters such as the temperature gradient, rate of cooling and doping of alloys, is important for inspection of mechanical characteristics and structure of cast materials and welded joints.

Nucleation can be:

Homogeneous – solid nuclei spontaneously appear within the undercooled phase.

Heterogeneous – the new phase appears on the walls of the container, at impurity particles, etc.

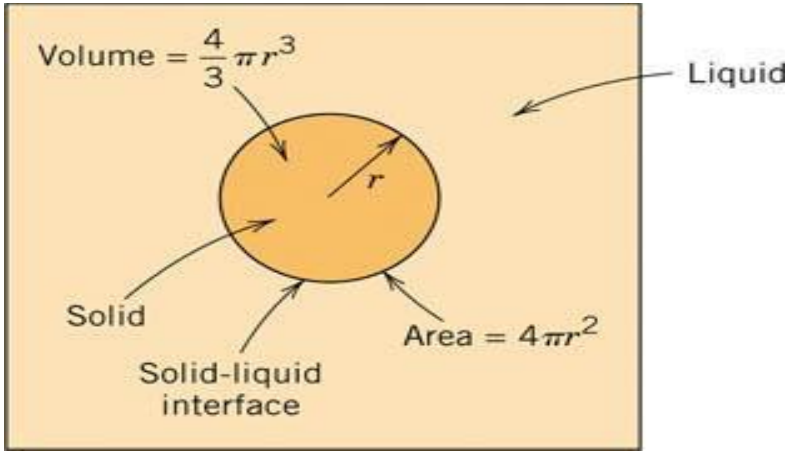
Let's consider solidification of a liquid phase undercooled below the melting temperature as a simple example of a phase transformation.



Homogeneous nucleation

homogeneous nucleation the probability of nucleation is same throughout the volume of the parent phase. The simplest example of nucleation is solidification of a metal, Above melting point Tm, liquid free energy, Gl < Gs (Solid free energy) and free energy change for solidification G > 0.Below Tm, G < 0 and nuclei of the solid phase form.

Nuclei of the new phase form uniformly throughout the parent phase. Will occur spontaneously only when free energy change ΔG is negative. Figure below solidification of a pure material from liquid phase.



** There are two contributions to the total free energy change that accompany a solidification transformation:

- Free energy difference between the solid and liquid phase :Volume free energy: $\Delta G_v < 0$.
- Formation of the solid-liquid phase boundary: surface free energy: $\gamma > 0$

$$\Delta G = \frac{4}{3}\pi r^3 \times \Delta G + 4\pi r^2 \times \gamma$$

Surface tension in phase transformation

is the energy per unit area (or force per unit length) required to create an interface between two phases—such as solid-liquid, liquid-gas, or solid-gas—acting as an elastic, contracting skin. It originates from unbalanced molecular cohesive forces at the boundary, determining the nucleation, stability, and shape of the new phase (e.g., spherical drops)

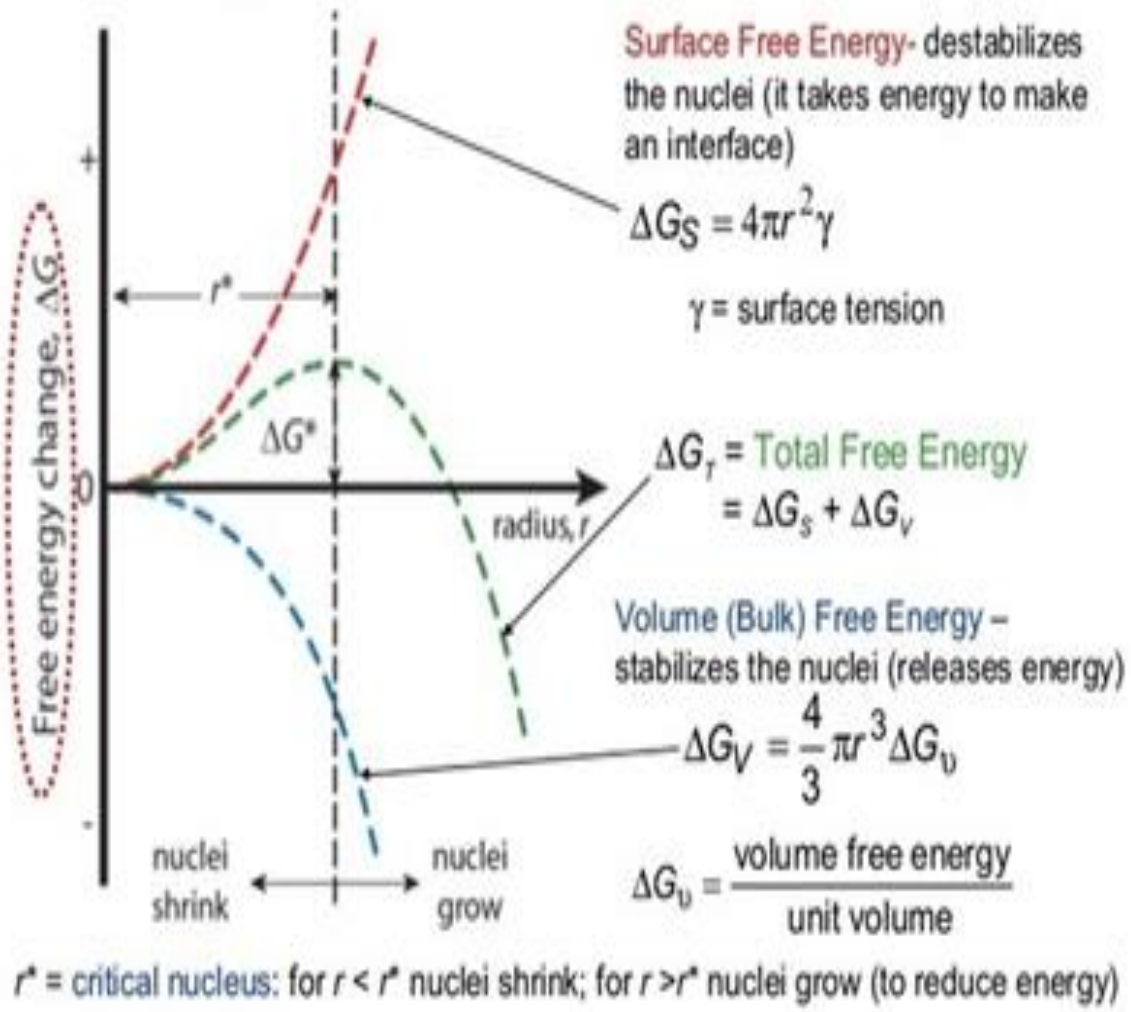
In other words, when a new phase forms (like solid nuclei inside a liquid), an **interface** appears between the parent phase and the new phase. Atoms at this interface are **less stable** (higher energy) than atoms inside the bulk.

So, creating this interface **costs energy**, and this energy per unit area is called **surface tension**.

The tiny particle of the solid that forms first will be stable only when it achieves a critical radius (r*).

Below the critical radius it is unstable and is called **embryo**.

Since r* and G* appear at the maximum on the free energy-versus-radius curve of figure derivation of expressions for these two parameters is a simple matter.



- **1. Free Energy Change (ΔG) during Nucleation**

When a tiny spherical nucleus forms, the total Gibbs free energy change (ΔG) has **two competing terms**:

(1) Volume Free Energy (ΔG_v)

- Energy change due to formation of a *more stable phase*
- **Negative** (favorable)

(2) Surface Free Energy (ΔG_s)

- Energy needed to create a new interface between phases
- **Positive** (unfavorable)

Total Free Energy:

$\Delta G = 4/3\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

Where:

r = radius of nucleus

ΔG_v = free energy change per unit volume (negative)

γ = surface energy

- At **small radius** → surface term dominates → $\Delta G > 0$ → unstable
- At **large radius** → volume term dominates → $\Delta G < 0$ → stable

So there is a **maximum point** in ΔG curve.

2. Critical Radius (r*)

The **critical radius (r*)** is the size of the nucleus at which:

-- ΔG is **maximum**

-- Nucleus is in **unstable equilibrium**

Formula for Critical Radius:

$r^* = -2\gamma/\Delta G_v$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$

If **r < r*** → nucleus shrinks (dissolves)

If **r > r*** → nucleus grows spontaneously

3. Critical Free Energy Barrier (ΔG*)

This is the **energy barrier** that must be overcome for nucleation to occur.

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2}$$

Represents the activation energy for nucleation

-- Higher ΔG* → harder nucleation

-- Lower ΔG* → easier nucleation

4. Physical Picture (Very Important)Imagine:
Small clusters form randomly
Most disappear (too small → unstable)
Only clusters larger than r* survive and grow

5. Effect of Undercooling (ΔT)
Increasing undercooling → makes ΔG_v more negative
This leads to:
Smaller r*
Smaller ΔG*
Result: nucleation becomes easier

6. Summary
Total ΔG = surface (positive) + volume (negative)
Critical radius $r*$r*: boundary between growth and shrinkage
Critical energy $\Delta G*$ΔG*: nucleation barrier
Undercooling reduces both → promotes nucleation

Substitution of ΔG_V in the equation (5.4) produces:

$$r^* = \left(\frac{2\gamma_{SL}T_M}{L_V}\right) \cdot \frac{1}{\Delta T} \tag{5.8}$$

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_M^2}{3L_V^2}\right) \cdot \frac{1}{(\Delta T)^2} \tag{5.9}$$

Note how values of r* and ΔG* decrease proportionally with undercooling ΔT, Fig. 5.3.

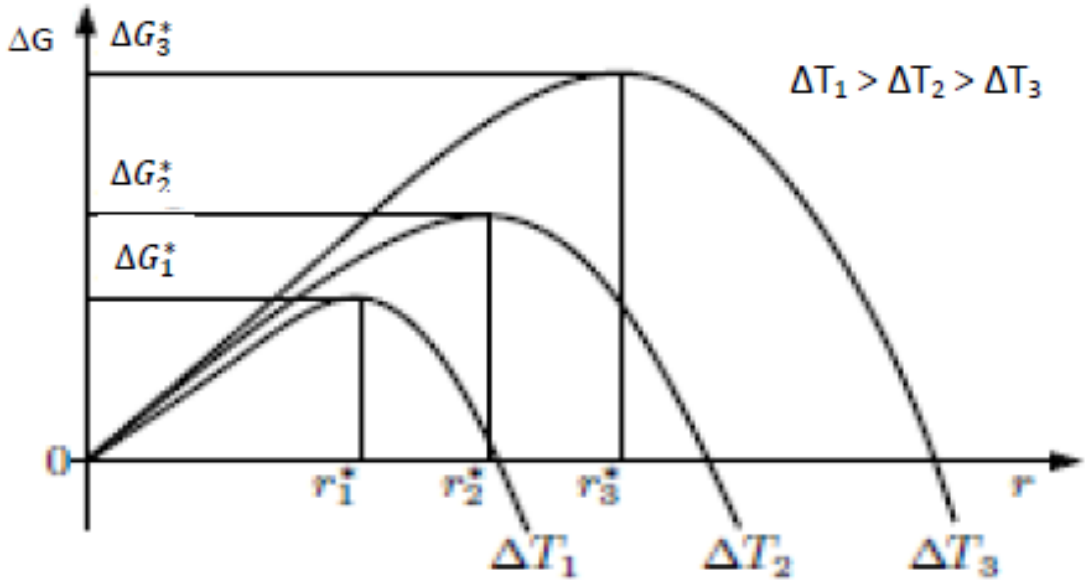
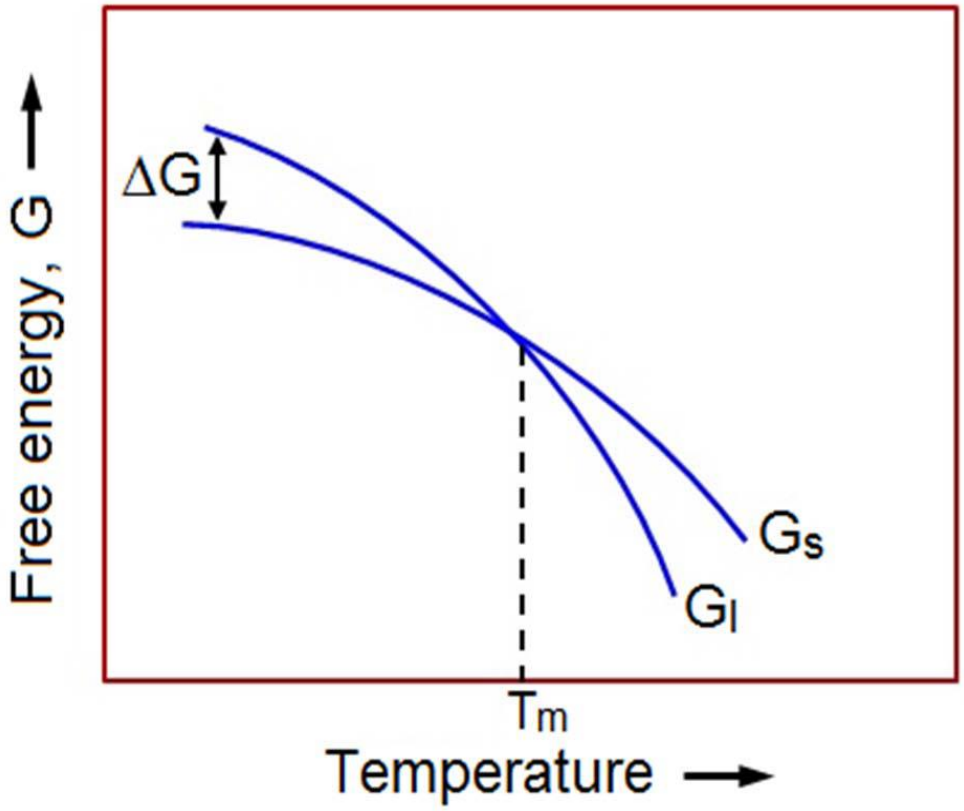


Fig. 5.3 Change of shape and position of the curve ΔG depending on the magnitude of

Nucleation

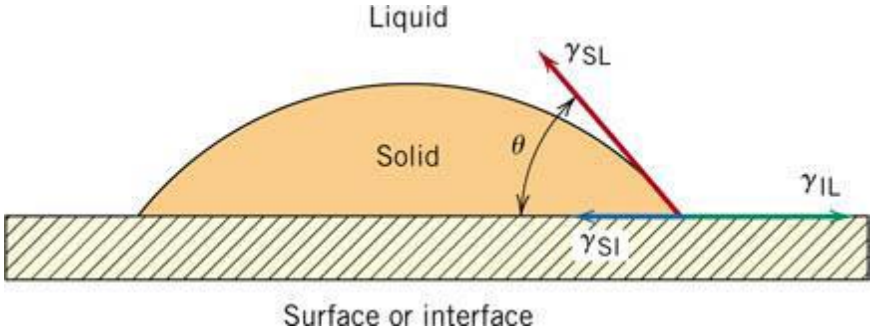
During solidification the atomic arrangement changes from a random or short-range order to a long range order or crystal structure. Nucleation occurs when a small nucleus begins to form in the liquid, the nuclei then grows as atoms from the liquid are attached to it.

Nucleation formation of a nucleus or tiny particles of the new phase. A nucleus is formed when the Gibbs free energy, *G*, of the system decreases i.e. ΔG becomes negative.



Heterogeneous nucleation

Here, the probability of nucleation is much higher at certain preferred sites such as mold wall, inclusions, grain boundaries, compared to rest of the parent phase. Example solidification of a liquid on an inclusion surface



$$\gamma_{IL} = \gamma_{IS} + \gamma_{SL}\cos\theta$$

The small value of θ ensures that the energy barrier (Δ*G*) is effectively lowered in heterogeneous nucleation. With a similar approach it can be shown that

$$r^* = \frac{\gamma_{SL}}{\Delta G_v} \qquad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2}$$

The number of stable nuclei n* (radii greater than r*) is a function of temperature:

$$n^* = K\exp\left(-\frac{\Delta G^*}{kT}\right)$$

k the boltzmann constant $=1.380)\times10^{-23}$ J·K^{-1}

Phase transformations (change of the microstructure) can be divided into three categories:

- **Diffusion-dependent with no change in phase composition or number of phases present** (e.g. melting, solidification of pure metal, allotropic transformations, recrystallization, etc.)

- **Diffusion-dependent with changes in phase compositions and/or number of phases** (e.g. eutectic or eutectoid transformations)

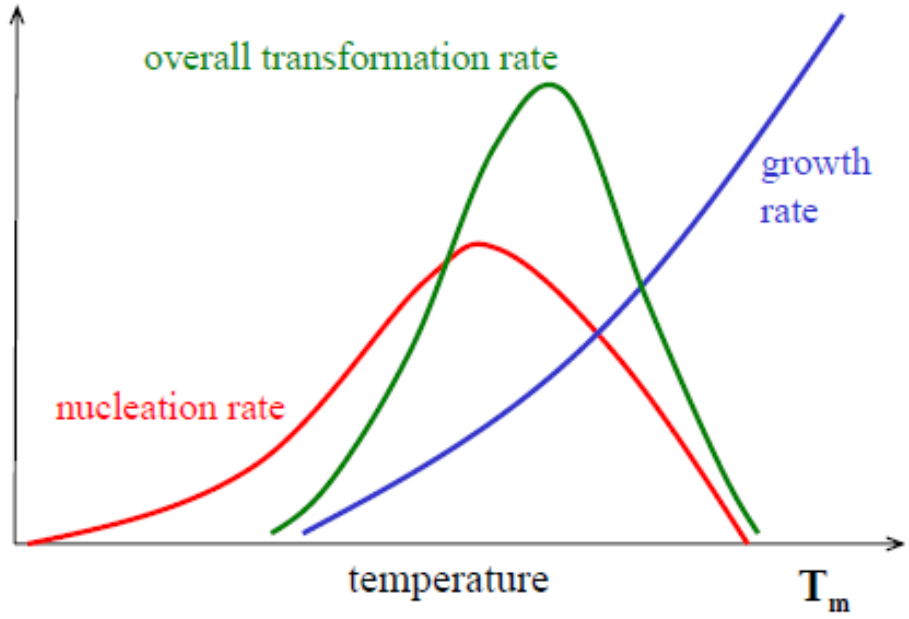
- **Diffusionless phase transformation** - by cooperative small displacements of all atoms in structure, e.g. martensitic transformation

Nucleation and Growth Kinetics

Once the embryo exceeds the critical size r*, the growth of the nucleus starts. Nucleation continues simultaneously. Nucleation and growth rates are function of temp. Nucleation rate increases with cooling rate and degree of undercooling (ΔT = Tm – T).

Rate of phase transformations

Total rate of a phase transformation induced by cooling is a product of the nucleation rate and growth rate (diffusion controlled - slows down with T decrease).



high T (close to T_m): low nucleation and high growth rates → coarse microstructure with large grains

low T (strong undercooling): high nucleation and low growth rates → fine structure with small grains

The process of phase transformation involves:

- **Nucleation** of the new phase(s) - formation of stable small particles (nuclei) of the new phase(s). Nuclei are often formed at grain boundaries and other defects.

- **Growth** of the new phase(s) at the expense of the original phase(s), in other words, involves increase in size of the nuclei at the expense of the surrounding material.