Nucleation and Growth

Course: Phase Transformations
Level: 3rd Stage | Semester: 5
Department of Materials Engineering
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Learning Objectives

By the end of this lecture, students will be able to:

- Understand the concept of undercooling and its role in phase transformations.
- Define Gibbs Free Energy and explain its significance.
- Differentiate between homogeneous and heterogeneous nucleation.
- Analyze critical radius and activation energy for nucleation.
- Understand the rate of nucleation and growth and their dependence on temperature.

How transform?

- Most phase transformations do not occur instantaneously.
- They begin by the formation of numerous small particles of the new phase(s), which increase in size until the transformation has reached completion.
- **2 stages of Phase Transformation**

1. Nucleation

Nucleation involves the appearance of very small particles, or nuclei of the new phase which are capable of growing.

2. Growth

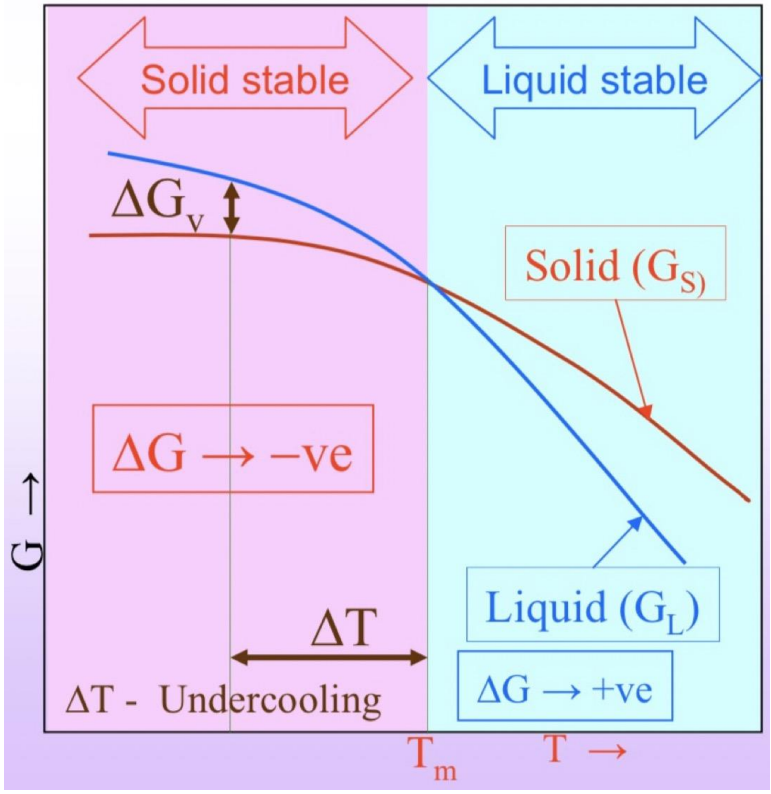
During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase.

Undercooling

- The **undercooling (ΔT)** is the difference between the equilibrium freezing temperature and the actual temperature of the liquid. As the extent of undercooling increases, the thermodynamic driving force for the formation of a solid phase from the liquid overtakes the resistance to create a solid-liquid interface.
- This phenomenon can be seen in many other phase transformations. When one solid phase (**α**) transforms into another solid phase (**β**), the system has to be cooled to a temperature that is below the thermodynamic phase transformation temperature (at which the energies of the **α** and **β** phases are equal).

When a liquid is transformed into a vapor (i.e., boiling water), a bubble of vapor is created in the liquid. In order to create the transformation though, we need to **superheat** the liquid above its boiling temperature!

Therefore, we can see that liquids do not really freeze at their freezing temperature and do not really boil at their boiling point! We need to ***undercool*** the liquid for it to solidify and ***superheat*** it for it to boil!



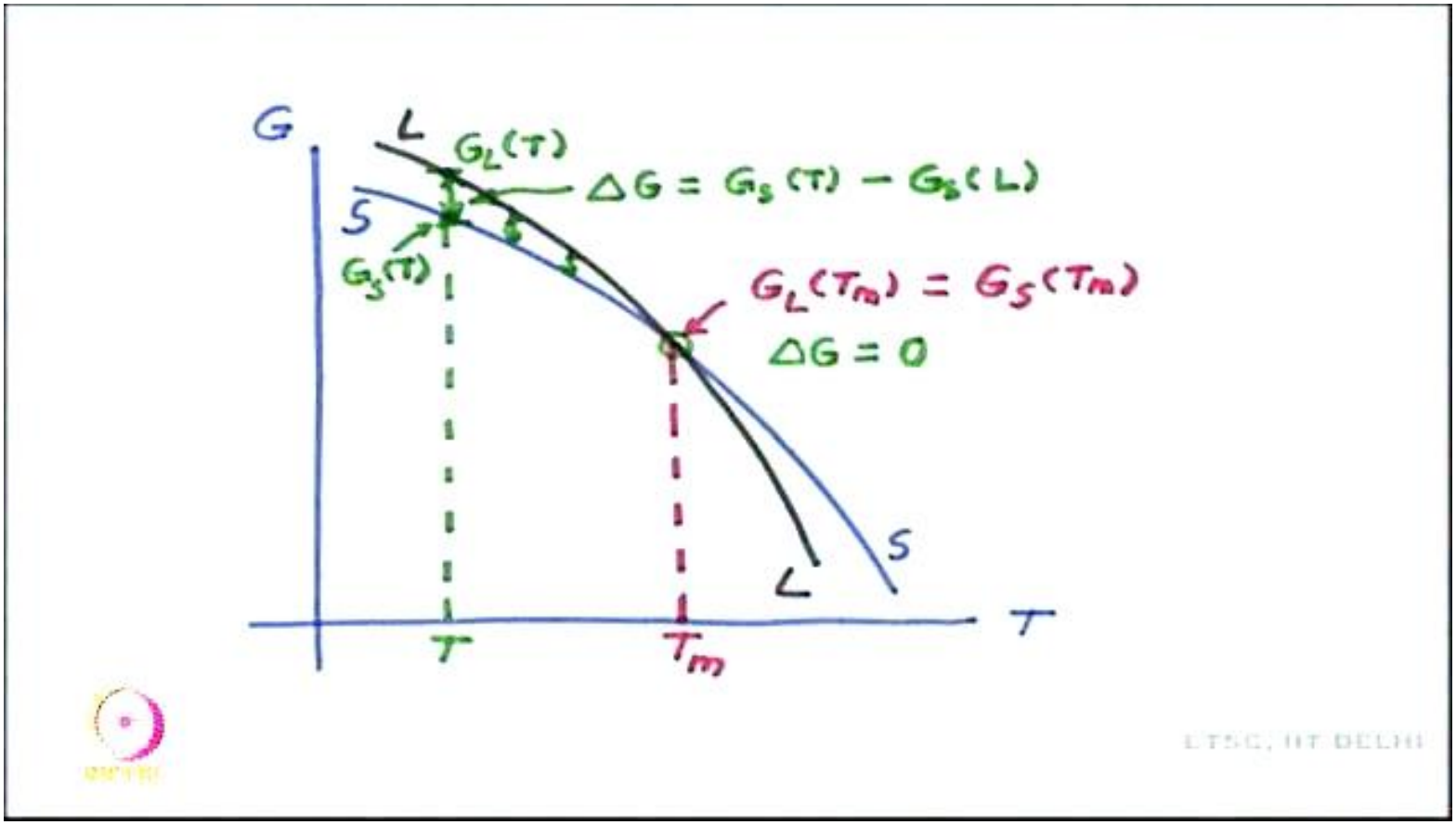
What is the thermodynamic driving force for a phase transformation?

$$\alpha \longrightarrow \beta$$

$$G_\alpha \qquad G_\beta$$

If $G_\beta < G_\alpha$ $\Rightarrow$ Transformation thermodynamically feasible

Driving force $\Delta G = G_\beta - G_\alpha$


G
L
$G_L(T)$
$\Delta G = G_S(T) - G_S(L)$
S
$G_S(T)$
$G_L(T_m) = G_S(T_m)$
$\Delta G = 0$
S
L
T
T
T_m

Gibbs Free Energy

G = H - TS

where H is the enthalpy, T the absolute temperature, and S the entropy of the system.

Enthalpy is a measure of the heat content of the system and is given by

H = E + PV

where E is the internal energy of the system, P the pressure, and V the volume.

The internal energy arises from the total kinetic and potential energies of the atoms within the system. Kinetic energy can arise from atomic vibration in solids or liquids and from translational and rotational energies for the atoms and molecules within a liquid or gas; whereas potential energy arises from the interactions, or bonds, between the atoms within the system. If a transformation or reaction occurs the heat that is absorbed or evolved will depend on the change in the internal energy of the system.

Gibbs Free Energy

Relative to phase transformations, an important thermodynamic parameter is the change in free energy ΔG; a transformation occurs spontaneously only when ΔG has a negative value (-ve).

A system is said to be in equilibrium when it is in the most stable state, i.e. shows no desire to change to infinity. An important consequence of the laws of classical thermodynamics is that at constant temperature and pressure a closed system (i.e. one of fixed mass and composition) will be in stable equilibrium if it has the lowest possible value of the Gibbs free energy, or in mathematical terms.

$$dG = 0$$

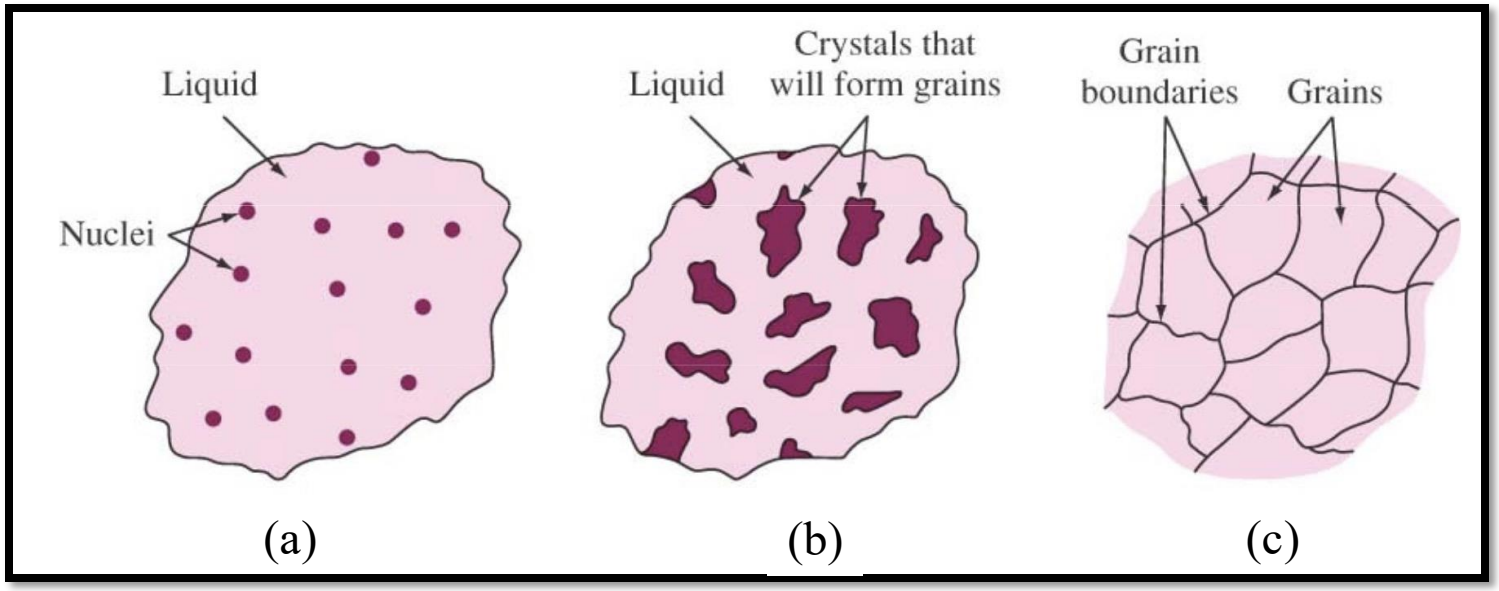
Gibbs Free Energy

It can be seen from the definition of G **(G = H – TS)**, that the state with the highest stability will be that with the best compromise between low enthalpy and high entropy. Thus at low temperatures solid phases are most stable since they have the strongest atomic binding and therefore the lowest internal energy (enthalpy).

At high temperatures however the 2TS term dominates and phases with more freedom of atom movement, liquids and gases, become most stable.

Solidification

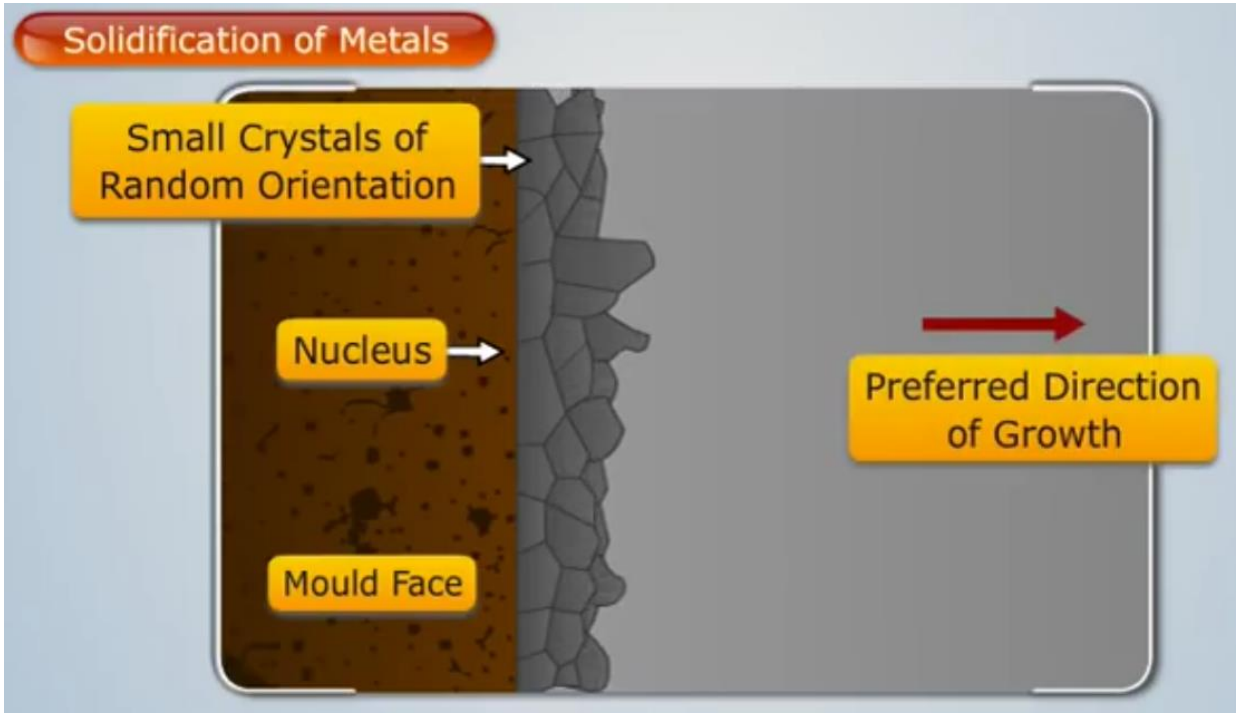
Solidification stages:

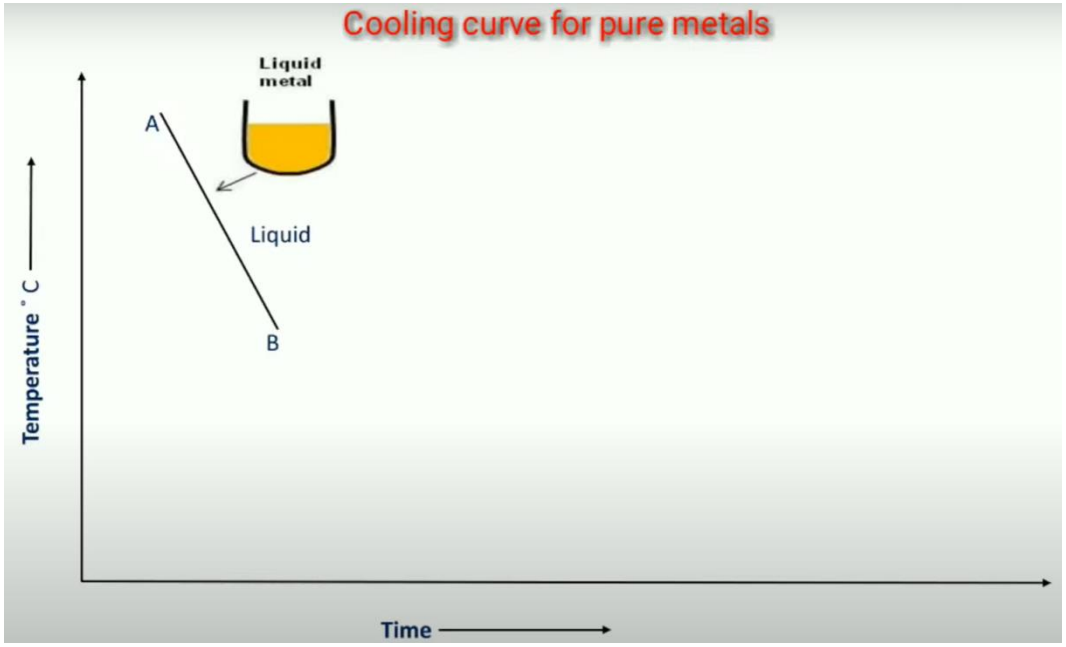


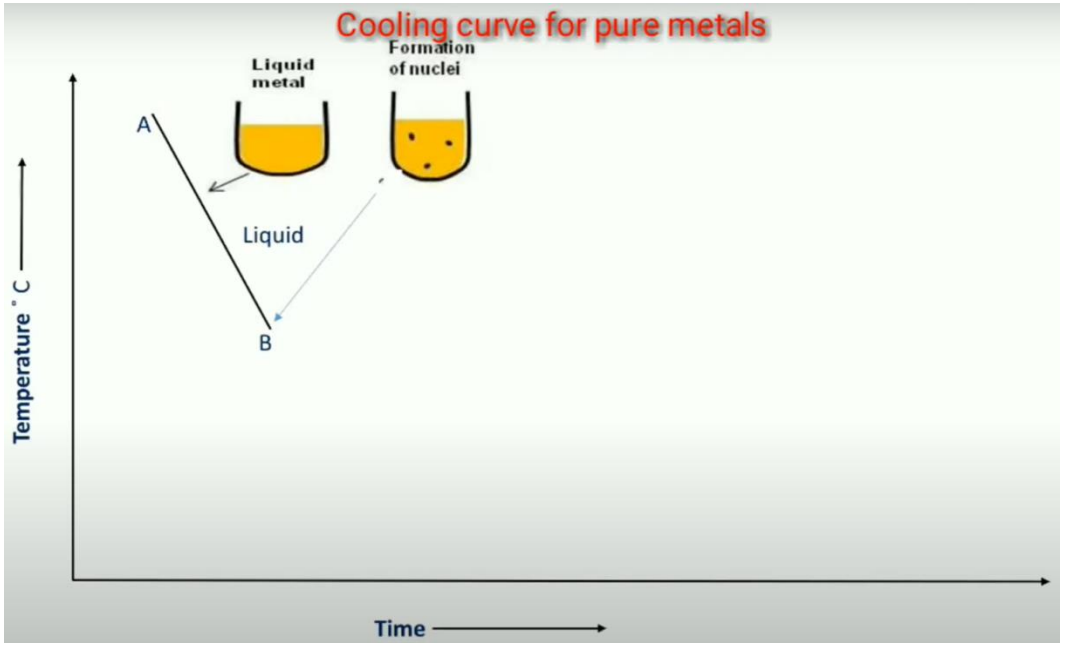
Schematic representation of solidification (a) Formation of stable nuclei (b) Growth of crystals (c) Grain structure

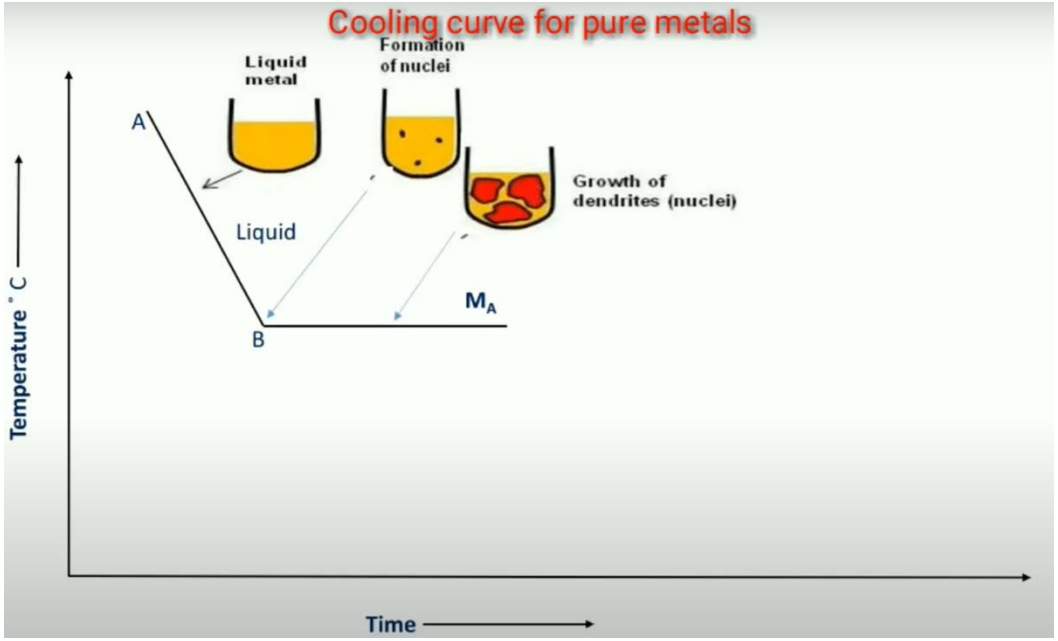
Nucleation

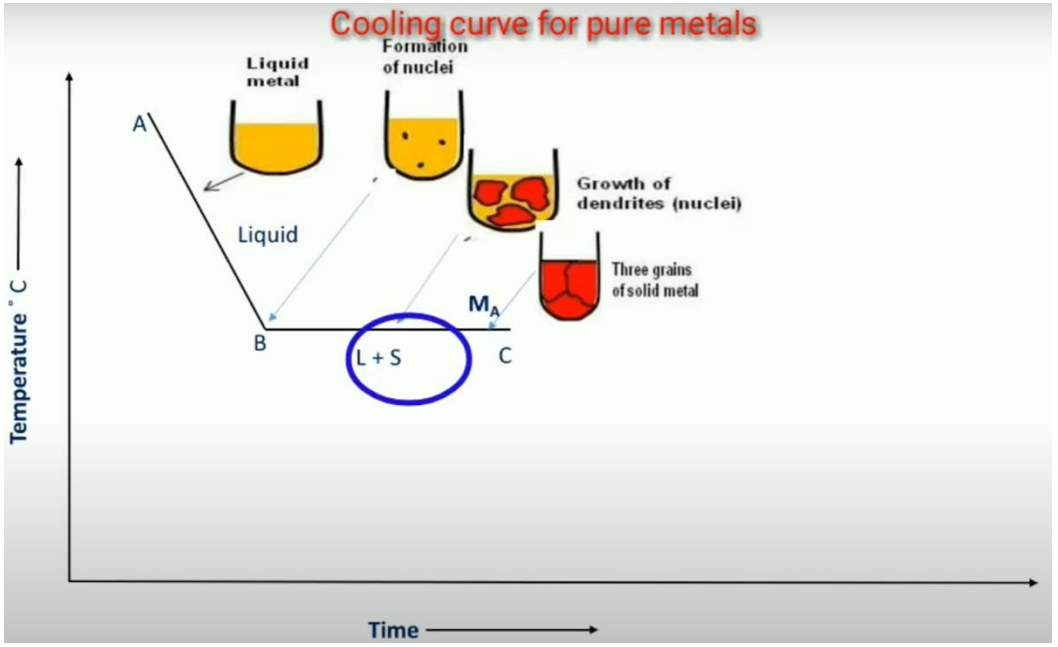
- Nuclei (seeds) act as templates on which crystals grow.
- For a nucleus to form, the rate of addition of atoms to the nucleus must be faster than the rate of loss.
- Once nucleated, growth proceeds until equilibrium is attained

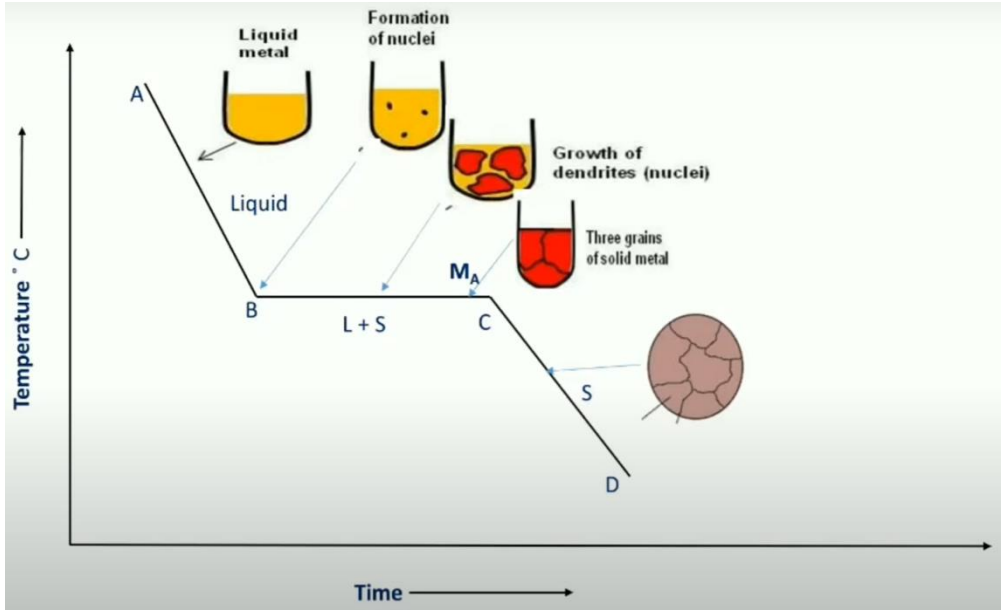



Cooling curve for pure metals
Liquid metal
A
Liquid
B
Temperature ˚C
Time

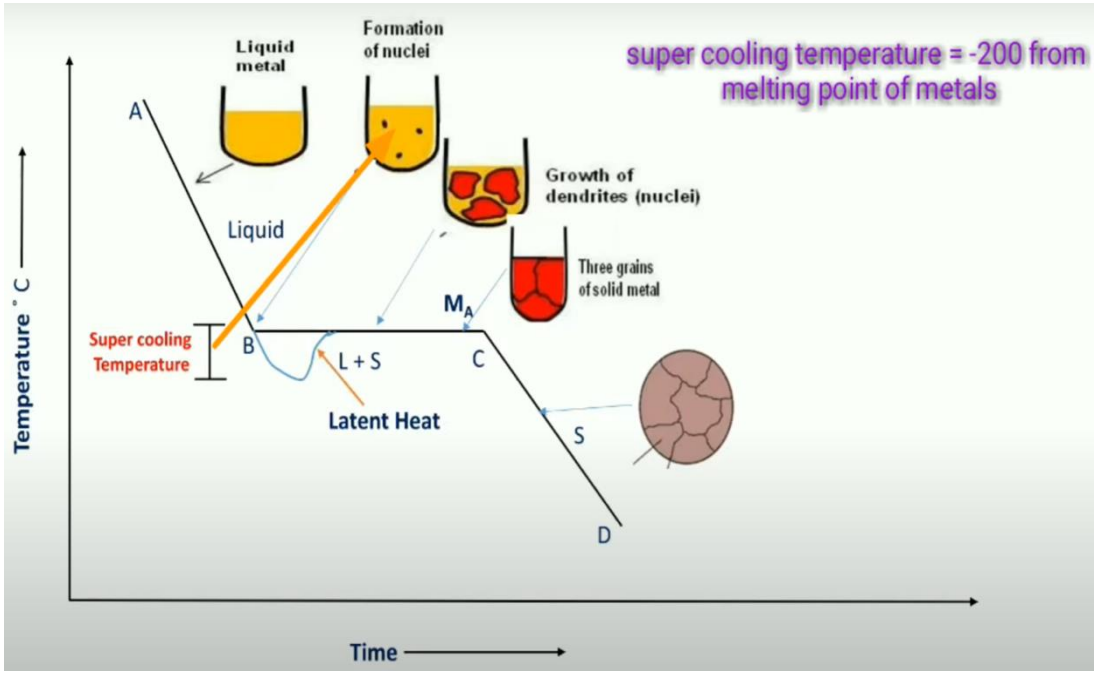

Cooling curve for pure metals
Liquid metal
Formation of nuclei
A
Liquid
B
Temperature ˚C
Time


Cooling curve for pure metals
Liquid metal
Formation of nuclei
A
Growth of dendrites (nuclei)
Liquid
M_A
B
Temperature ° C
Time


Cooling curve for pure metals
Liquid metal
Formation of nuclei
A
Growth of dendrites (nuclei)
Liquid
Three grains of solid metal
M_A
B
L + S
C
Temperature ° C
Time



The driving force to nucleate increases as we increase ΔT



Solidification: Nucleation Types

- Homogeneous nucleation
  - nuclei form in the bulk of liquid metal.
  - requires considerable supercooling (typically 80-300°C).

- Heterogeneous nucleation
  - much easier since stable "nucleating surface" is already present, e.g., mold wall, impurities in liquid phase
  - only very slight supercooling (0.1-10°C).

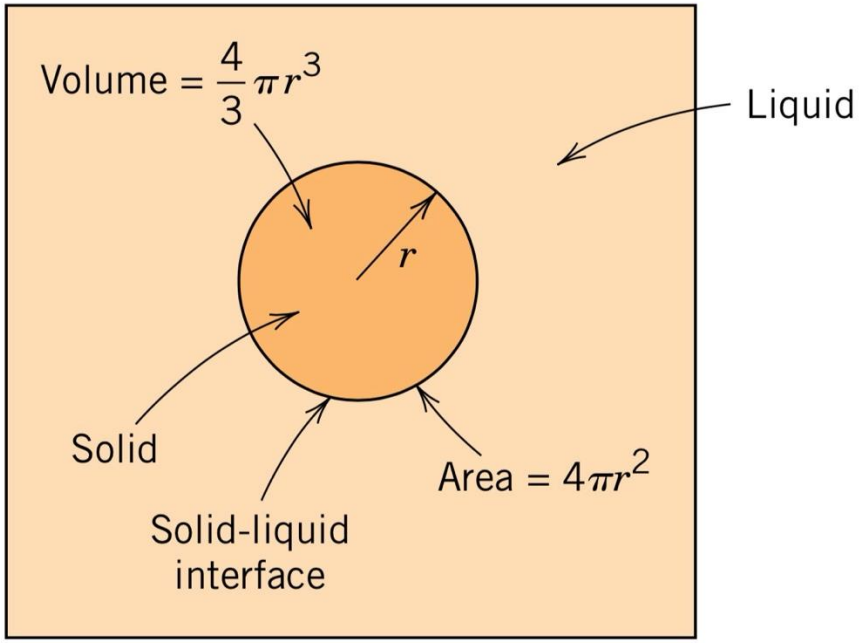
Homogeneous Nucleation

Theory of nucleation involves a thermodynamic parameter called **free energy** (or *Gibbs free energy*), *G*.

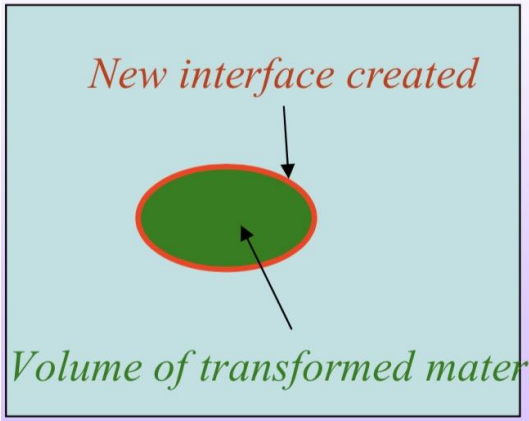
In brief, free energy is a function of other thermodynamic parameters, of which one is the internal energy of the system (i.e., the *enthalpy, H*) and another is a measurement of the randomness or disorder of the atoms or molecules (i.e., the *entropy, S*). a

Solidification of a pure material (Homogeneous nucleation)

Assuming that nuclei of the solid phase form in the interior of the liquid as atoms cluster together so as to form a packing arrangement similar to that found in the solid phase. Also each nucleus is spherical and has a radius r.



- When a volume of material (V) transforms three energies have to be considered :
  (i) reduction in G (assume we are working at constant T & P),
  (ii) increase in γ (interface free-energy),
  (iii) increase in strain energy.
- In a liquid to solid phase transformation the strain energy term can be neglected *(as the liquid can flow and accommodate the volume/shape change involved in the transformation-* assume we are working at constant T & P).

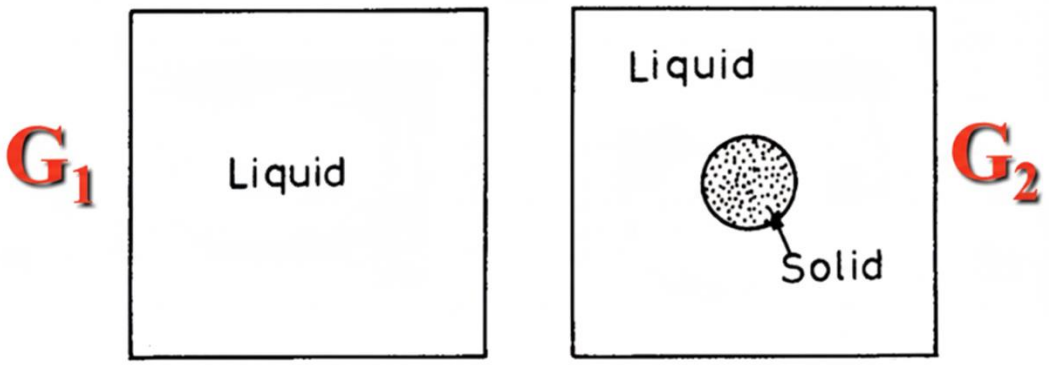


Energies involved
- Bulk Gibbs free energy ↓
- Interfacial energy ↑
- Strain energy ↑

Important in solid to solid transformations

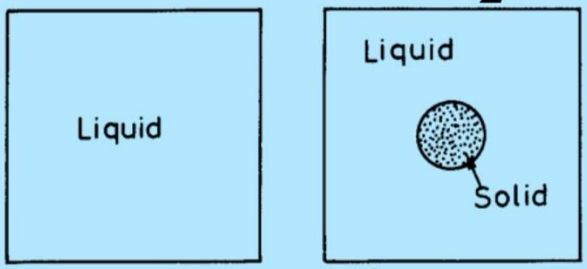
Total free energy change for a solidification transformation

Consider a volume of liquid at some ΔT below T_m with a free energy G_1.
If some atoms in the liquid cluster together to form a small sphere of solid, the free energy of the system will change to G_2.



When a liquid is cooled below its melting point (ΔT), it becomes thermodynamically unstable. At this point, atoms may start to group together to form a small solid particle (nucleus). This changes the free energy of the system from G_1 (pure liquid) to G_2 (liquid with a solid nucleus). Whether this nucleus grows or disappears depends on the total energy change, which includes the energy gained from forming solid and the energy cost of creating a surface.

$$G_2 = V_s G_v^s + V_l G_v^l + A_{sl}\gamma_{sl}$$



$$G_1 = G_v^l (V_s + V_l)$$

V_s, V_l ≡ volume of solid and liquid

G_v^s, G_v^l ≡ bulk free energy of solid and liquid

A_{sl} ≡ interfacial area between solid and liquid phases

γ_{sl} ≡ interfacial free energy

❖ When a **solid particle starts to form** inside a liquid (during cooling), the total energy of the system **changes**.

•**Before:** The system has **only liquid**, with energy = $\mathbf{G_1}$

•**After:** A small **solid sphere forms** inside the liquid, changing the energy to $\mathbf{G_2}$

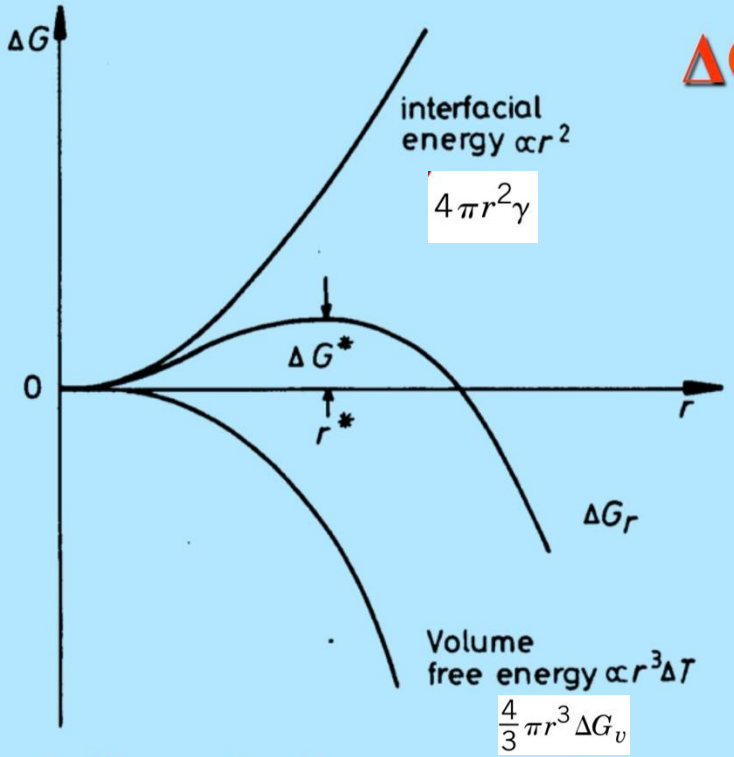
❖ This new energy $\mathbf{G_2}$ includes:

1.Energy from the **solid part**

2.Energy from the **remaining liquid**

3.Extra energy from the **surface** between solid and liquid (like a boundary)

For a solid phase to form $\rightarrow \Delta G_T = G_2 - G_1$



$$\Delta G_T = -V_s \Delta G_v + A_{sl}\gamma_{sl}$$

where $\Delta G_v = G_v^l - G_v^s$

- ΔG_T = Total free energy

ΔG_T = (volume term) + (surface area term)

When a tiny solid particle starts to form inside a liquid, the **total energy change (ΔG_t)** depends on two parts:

1.Volume energy:

2.This is **negative** and **favors solid formation** — the system becomes more stable as the solid grows.

3.Surface energy:

4.This is **positive** and **resists solid formation** — it costs energy to create a surface between solid and liquid.a

These two energies compete with each other.

📌 **Key Point (from the graph):**

•At first, forming a tiny solid increases the total energy (due to surface cost).

•If the solid gets **big enough** (past **r***), the total energy starts to decrease, and the solid keeps growing.

•**ΔG*** is the maximum energy barrier that must be overcome for solid formation to proceed.

🧠 **Final Message**

Solidification doesn't just happen — it must **overcome an energy barrier** first. After that, growth becomes favorable.

Calculation of the **free energy change per unit volume (ΔG_v)** during solidification when a liquid is **undercooling** (i.e., cooled below its melting point, T_m).

For an undercooling ΔT, ΔG_v is given by: $\mathbf{\Delta G_v = \Delta H_v - T\Delta S_v}$

...$T = T_m$ and $\Delta S_v = \Delta H_v / T_m$

but $\Delta G = 0$ at $T_m \rightarrow \Delta H_v = T_m \Delta S_v$

$$\Delta G_v = \Delta H_v - T\left(\frac{\Delta H_v}{T_m}\right) = \Delta H_v\left(1 - \frac{T}{T_m}\right)$$

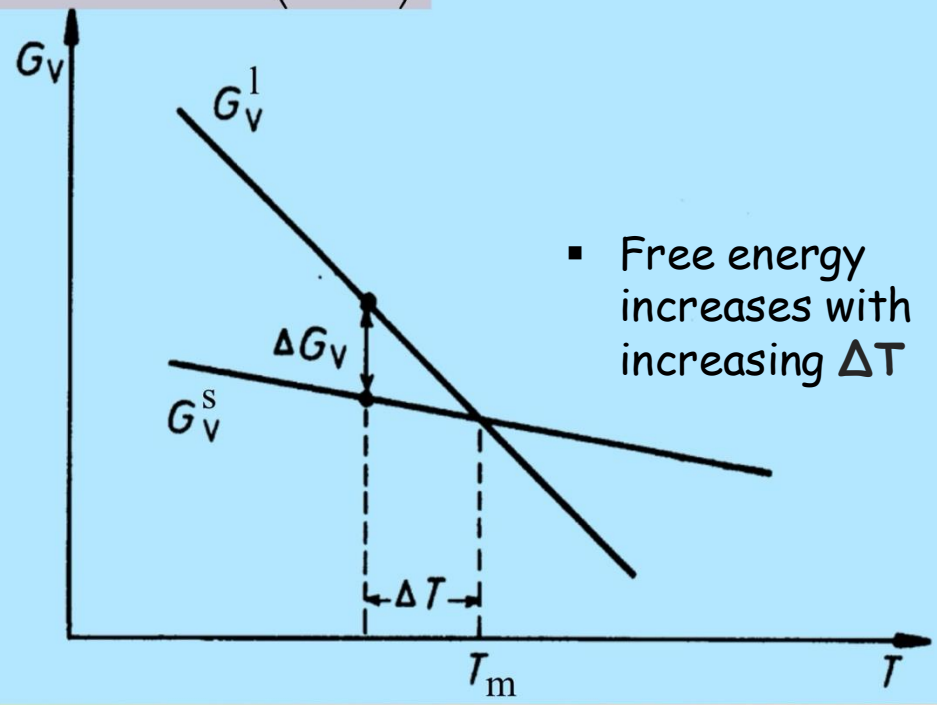
$$\Delta G_v = \Delta H_v\left(\frac{T_m}{T_m} - \frac{T}{T_m}\right)$$

$$\Delta G_v = \Delta H_v\left(\frac{\Delta T}{T_m}\right)$$

where $\Delta T = T_m - T$

$$\Delta G_v = \Delta H_v \left(\frac{\Delta T}{T_m} \right)$$

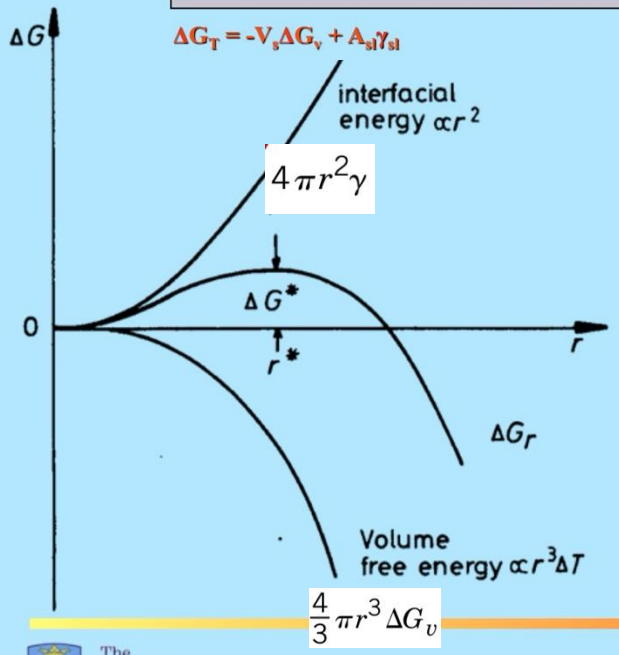
where $\Delta T = T_m - T$



- Free energy increases with increasing **ΔT**

For spherical nuclei:

$$\Delta G_T = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{sl} \qquad (1)$$



ΔG_T varies with r

For a given ΔT, there will be a certain critical radius (**r***) which is associated with a maximum excess free energy

🔷 What the Equation Tells Us:

The formula shows the total free energy change (ΔG_t) when a **spherical nucleus** of solid forms in a liquid.

- The **first term** (volume term) is **negative** → it **favors** solid formation.
- The **second term** (surface area term) is **positive** → it **opposes** formation (due to interfacial energy cost).

📌 Key Idea:

- As the nucleus radius **r** changes, the total energy ΔG_t changes.
- There's a specific **critical radius (r*)** where ΔG_t is at a **maximum**.
- If the nucleus grows past r*, energy decreases and solidification continues.
- If it's smaller than r*, it likely disappears.

🧠 Final Message:

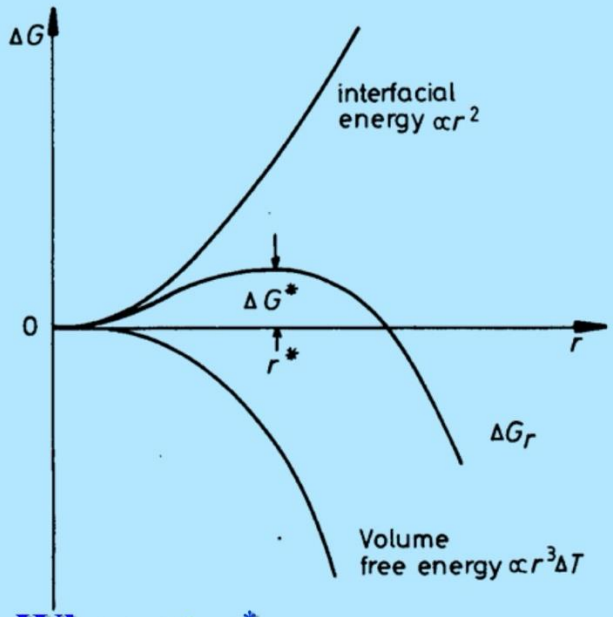
For a new solid phase to form and grow, the cluster of atoms must reach a **critical size**, this overcomes the energy barrier and allows stable transformation.

What Happens at Critical Radius (r*)?

In a physical sense, this means that as a solid particle begins to form as atoms in the liquid cluster together, its free energy first increases.

If this cluster reaches a size corresponding to the critical radius r*, then growth will continue with the accompaniment of a decrease in free energy.

However, a cluster of radius less than the critical value will shrink and redissolve. This subcritical particle is an embryo, and the particle of radius greater than r* is termed a nucleus.



When r < r*

- System can lower ΔG_T by the dissolution of solid phase
- Unstable solid particles (clusters/embryos)

When r > r*

- System can lower ΔG_T as the nucleus grows
- Since $d\Delta G_T/dr = 0$ when $r = r^*$, the critical nucleus is in unstable equilibrium with the surrounding liquid

Embryo vs. Nucleus
Critical Radius Concept

As a solid particle begins to form, its free energy first increases. If the particle reaches the critical radius r*, it becomes a stable nucleus and continues to grow, lowering the system's energy.

Particles smaller than r* (called embryos) are unstable and dissolve. Particles larger than r* are called nuclei and grow spontaneously.

Differentiation of Equation (1) with respect to r yields:

$$\frac{d\Delta G_T}{dr} = 0 = -4\pi r^2 \Delta G_v + 8\pi r \gamma_{sl}$$

Letting r = r*, and solving for r* gives:

$$r^* = \frac{2\gamma_{sl}}{\Delta G_v} \quad \textbf{(2)}$$

For homogeneous nucleation, critical radius of a stable solid particle nucleus

$r^*\uparrow$ as $\Delta G_v\downarrow$ ($\Delta T\downarrow$)

Substituting Equation (2) into Equation (1) yields:

$$\Delta G^* = \frac{16\pi\gamma_{sl}^3}{3\Delta G_v^2} \quad (3)$$

For homogeneous nucleation, activation free energy required for the formation of a stable nucleus

$\Delta G^* \uparrow$ as $\Delta G_v \downarrow$ ($\Delta T \downarrow$)

- Nucleation results from the growth of clusters
- Whenever a cluster happens to reach r^*, it becomes the nucleus of the new phase
- Activation free energy may be considered an energy barrier to the nucleation process.

The volume free energy change ΔG_v is the driving force for the solidification transformation, and its magnitude is a function of temperature. At the equilibrium solidification temperature T_m, the value of ΔG_v is zero, and with decreasing temperature its value becomes increasingly more negative.

ΔG_v is a function of temperature, where:

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

ΔH_f is the latent heat of fusion (i.e., the heat given up during solidification), and T_m and the temperature T are in Kelvin.

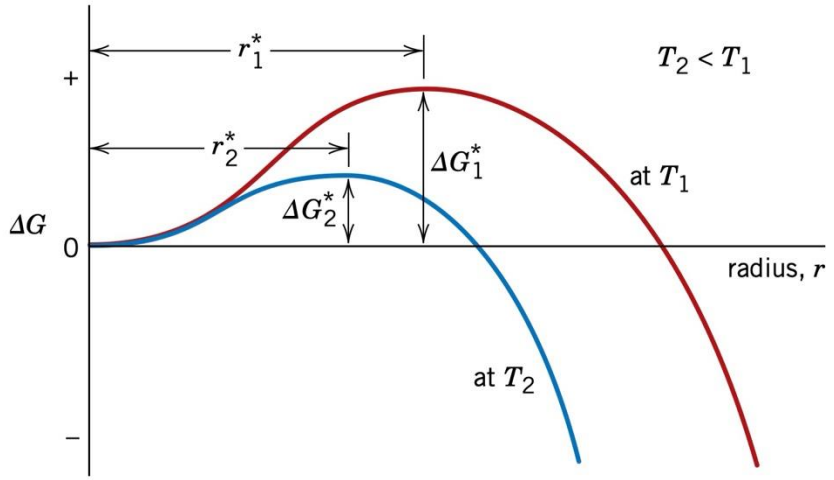
Substitution of this expression for ΔG_v into the following equations:

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

- Therefore, from these two equations, both the critical radius r* and the activation free energy ΔG^* decrease as temperature T decreases. (The $\boldsymbol{\gamma}$ and ΔH_f parameters in these expressions are relatively insensitive to temperature changes.)

Schematic free energy-versus-embryo/nucleus radius curves for two different temperatures. The critical free energy change (ΔG^*) and critical nucleus radius (r*) are indicated for each temperature.



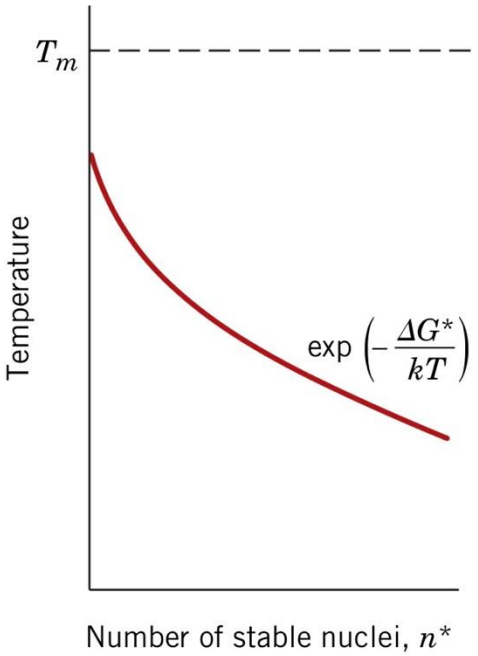
- Physically, this means that with a lowering of temperature at temperatures below the equilibrium solidification temperature (T_m), nucleation occurs more readily.

Calculation of nucleation rate for homogeneous nucleation

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

n^* is the number of stable nuclei (having radii greater than r^*). K_1 is constant related to the total number of nuclei of the solid phase. T is Absolute temperature (K). k is Boltzmann's constant, A thermal energy constant having the value of 1.38 x 10^{-23} J/atom.K (8.62 x 10^{-5} eV/atom.K).

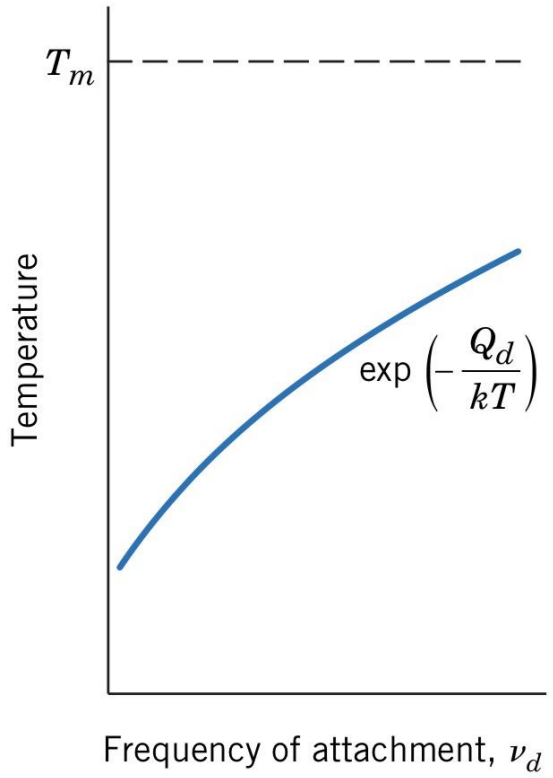
For the exponential term of this expression, changes in temperature have a greater effect on the magnitude of the ΔG^* term in the numerator than the T term in the denominator. Consequently, as the temperature is lowered below T_m, the exponential term in the Equation above also decreases, so that the magnitude of n^* increases.



Lower temperature → easier nucleation → more stable nuclei

$$v_d = K_2 \exp\left(-\frac{Q_d}{kT}\right)$$

v_d *is* the frequency at which atoms from the liquid attach themselves to the solid nucleus.
where Q_d is a temperature-independent parameter the activation energy for diffusion and K_2 is a temperature-independent constant. Thus, from the above Equation, a decrease of temperature results in a reduction in v_d.



This equation tells us how many stable nuclei form. As the temperature drops, the number of stable nuclei increases quickly. That's because the energy barrier becomes easier to overcome at lower T.

In phase transformations like solidification:

•n* tells us how many stable nuclei form (depends on undercooling).
•v_d tells us how fast atoms attach to these nuclei (depends on temperature).

🧊 At low temperatures (high undercooling):
•ΔG* becomes small → n* *increases* → many nuclei form
•But atomic mobility is low → v_d decreases → slow growth rate

🔥 At higher temperatures:
•ΔG* is large → n* *decreases* → fewer nuclei form
•But atoms move faster → v_d increases → faster growth

✅ So, successful transformation depends on the balance between:
•Enough nuclei (n*)
•Sufficient atomic mobility (v_d)

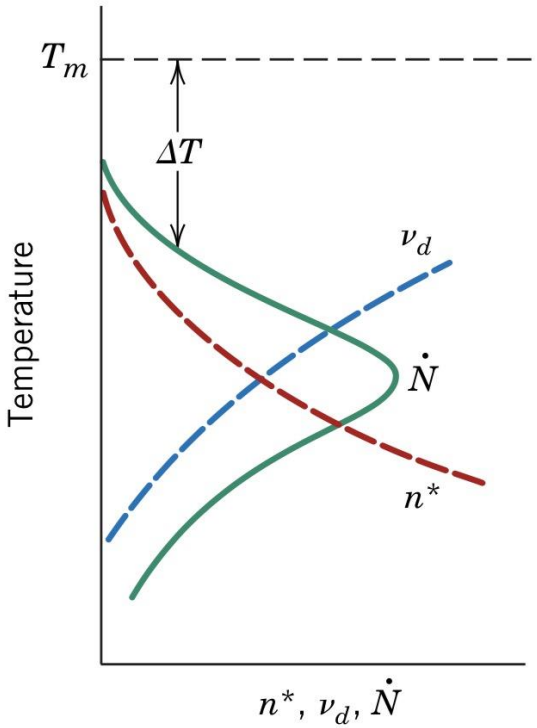
This balance controls microstructure — for example, fine grains form at moderate undercooling where both nucleation and growth are active.

Calculation of nucleation rate

$$\dot{N} = K_3 n^* \nu_d = K_1 K_2 K_3 \left[\exp\left(-\frac{\Delta G^*}{kT} \right) \exp\left(-\frac{Q_d}{kT} \right) \right]$$

$\dot{N}$ *is* the nucleation rate (which has units of nuclei per unit volume per second). K_3 is the number of atoms on a nucleus surface.

The Figure shows schematically plots nucleation rate as a function of temperature and, the Figure shows that, with a reduction of temperature from below T_m, the nucleation rate first increases, achieves a maximum, and subsequently diminishes.



➡️ *More stable nuclei (***n**) and faster attachment (**v_d**) mean **higher nucleation rate**.

🔷 **Why It Rises Then Falls with Temperature**

As temperature drops:
•n* increases — because clusters find it easier to grow into stable nuclei.
•v_d decreases — because atoms move more slowly at low temperatures.

📈 So at first, cooling **increases nucleation rate** because there are more nuclei.
📉 But too much cooling slows atom movement (low v_d), so **nucleation rate decreases again**.

👉 That's why the nucleation rate curve rises, peaks, and then falls.

EXAMPLE PROBLEM 10.1

Computation of Critical Nucleus Radius and Activation Free Energy

(a) For the solidification of pure gold, calculate the critical radius r^* and the activation free energy ΔG^* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are -1.16×10^9 J/m^3 and 0.132 J/m^2, respectively. Use the supercooling value in Table 10.1.

(b) Now, calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.413 nm for solid gold at its melting temperature.

Solution

(a) In order to compute the critical radius, we employ Equation 10.6, using the melting temperature of 1064°C for gold, assuming a supercooling value of 230°C (Table 10.1), and realizing that ΔH_f is negative. Hence

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(0.132\ \text{J/m}^2)(1064 + 273\ \text{K})}{-1.16 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{230\ \text{K}}\right)$$

$$= 1.32 \times 10^{-9}\ \text{m} = 1.32\ \text{nm}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus,

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)(0.132\ \text{J/m}^2)^3(1064 + 273\ \text{K})^2}{(3)(-1.16 \times 10^9\ \text{J/m}^3)^2}\right]\left[\frac{1}{(230\ \text{K})^2}\right]$$

$$= 9.64 \times 10^{-19}\ \text{J}$$

[Example adopted from Callister 9e, page 392]

Solution continue ..

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as gold has the FCC crystal structure (and a cubic unit cell), its unit cell volume is just a^3, where a is the lattice parameter (i.e., unit cell edge length); its value is 0.413 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\#\text{ unit cells/particle} = \frac{\text{critical nucleus volume}}{\text{unit cell volume}} = \frac{\frac{4}{3}\pi r^{*3}}{a^3} \tag{10.11}$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.32\text{ nm})^3}{(0.413\text{ nm})^3} = 137\text{ unit cells}$$

Because of the equivalence of four atoms per FCC unit cell (Section 3.4), the total number of atoms per critical nucleus is just

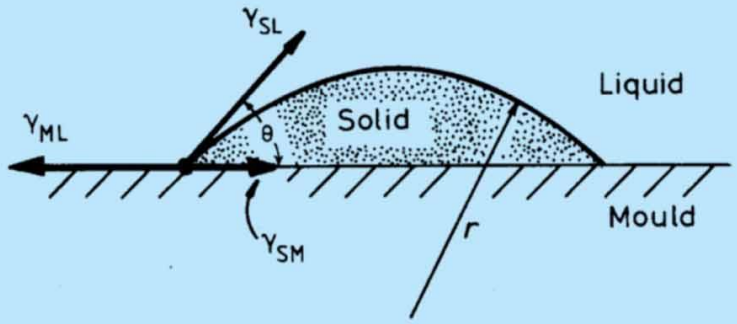
(137 unit cells/critical nucleus)(4 atoms/unit cell) = 548 atoms/critical nucleus

Heterogeneous Nucleation

From the expression for ΔG^*, for nucleation to be made easier at low ΔT, γ_{sl} must be reduced

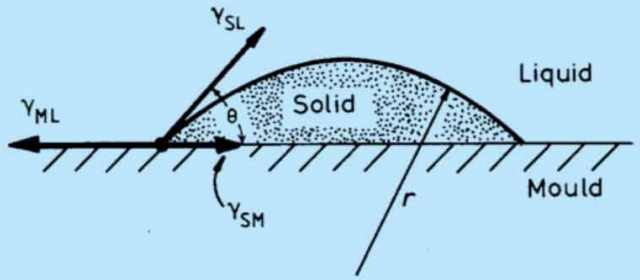
Simple way of achieving this is if the nucleus forms in contact with some heterogeneity (e.g., mould wall)

Consider the following schematic depicting a solid embryo forming in contact with a mould wall



At equilibrium:

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL}\cos\theta$$



where θ ≡ wetting angle

It is possible to derive equations for r^* and ΔG^*; these are as follows:

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

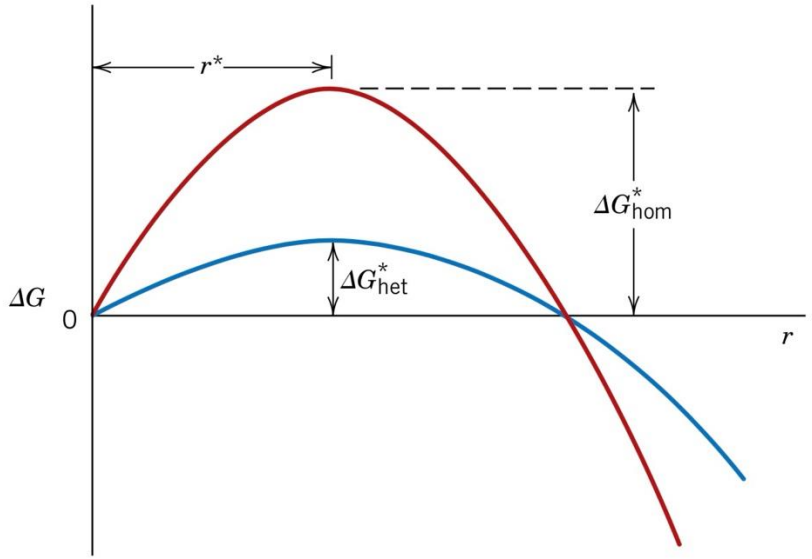
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right) S(\theta)$$

The $S(\boldsymbol{\theta})$ term of this last equation is a function only of $\boldsymbol{\theta}$ (i.e., the shape of the nucleus), which has a numerical value between zero and unity. For example, for $\boldsymbol{\theta}$ angles of 30° and 90°, values of $S(\boldsymbol{\theta})$ are approximately 0.01 and 0.5, respectively.

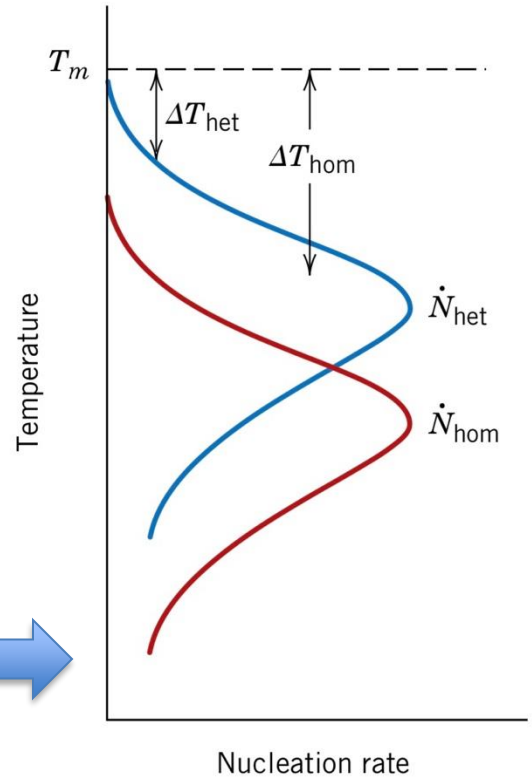
$S(\boldsymbol{\theta})$ reduces the value of ΔG^*. Thus, the activation energy barrier for heterogeneous nucleation is smaller than the homogeneous barrier by amount of $S(\boldsymbol{\theta})$.

$$\Delta G_{\text{het}}^{*} = \Delta G_{\text{hom}}^{*} S(\theta)$$

r* is unaffected and only depends on ΔT
ΔG* (het) < ΔG* (hom) by the shape factor S(θ)



A much smaller degree of supercooling (ΔT) is required for heterogeneous nucleation.



Growth

The growth step in a phase transformation begins once an embryo has exceeded the critical size, r^*, and becomes a stable nucleus. The growth rate ($\dot{G}$) can be calculated by the following formula:

$$\dot{G} = C \exp\left(-\frac{Q}{kT}\right)$$

where Q (the activation energy) and C (a preexponential) are independent of temperature.

- Once a stable nucleus is formed (i.e., it exceeds the critical radius r*), it begins to grow into a new phase.

The rate of this growth ($\dot{G}$) depends on how quickly atoms can move and attach to the growing particle — which is strongly influenced by **temperature**.

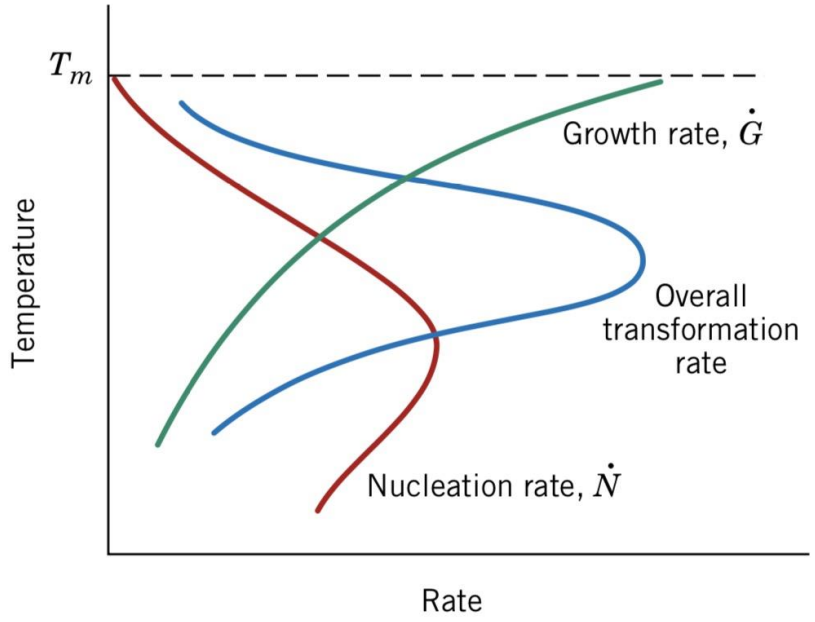
•As **temperature increases**, atoms have more energy → **faster growth**.

•The equation shows that growth rate increases **exponentially** with temperature.

Key Point:

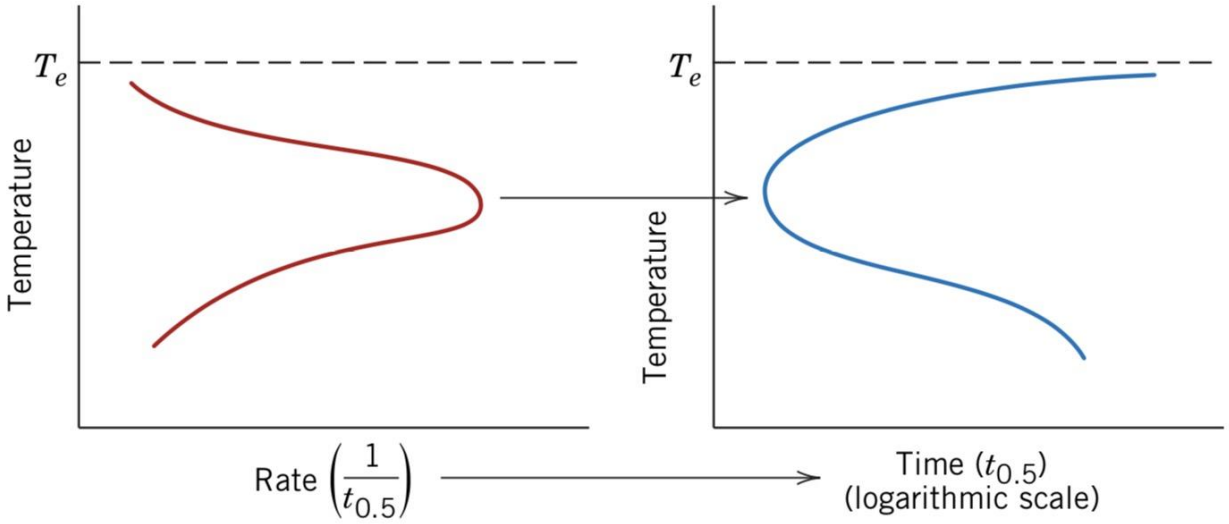
Growth starts *after* nucleation and is governed by diffusion and atomic movement — both of which require energy (activation energy Q).

At a specific temperature, the overall transformation rate is equal to some product of $\dot{N}$ and $\dot{G}$. The general shape of this curve is the same as for the nucleation rate ($\dot{N}$), in that it has a peak or maximum that has been shifted upward relative to the $\dot{N}$ curve.



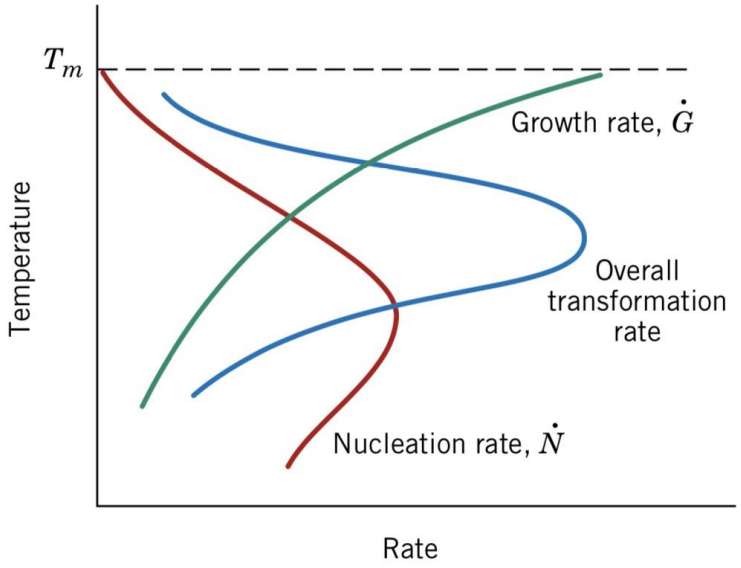
Transformation rate versus temperature and logarithm time

$$\text{rate} = \frac{1}{t_{0.5}}$$

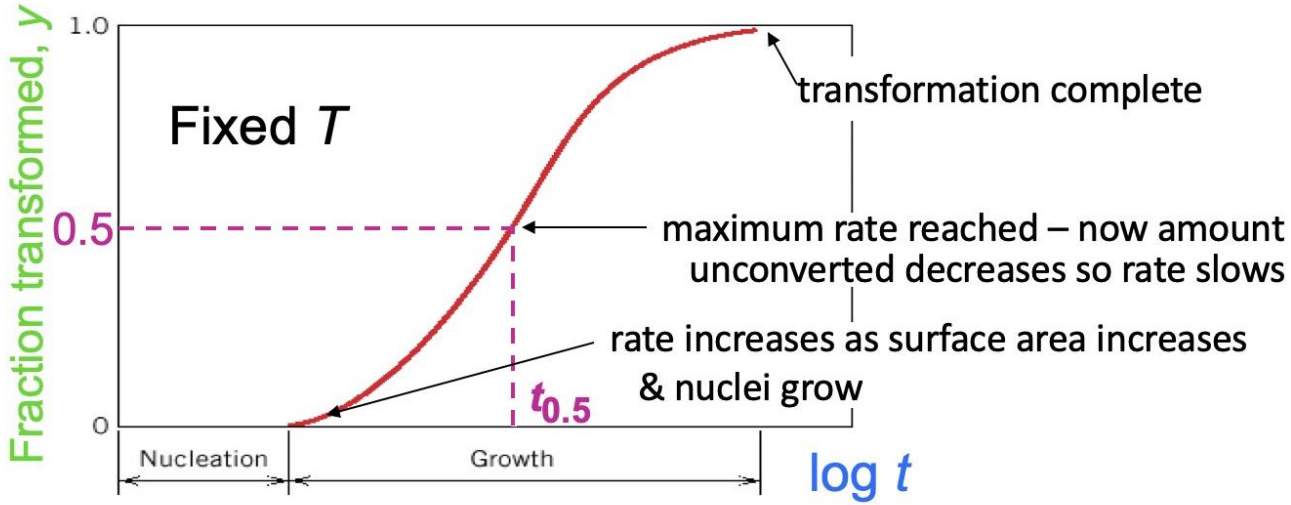


- Fastest transformation happens when **nucleation and growth are both active**.
- The **minimum transformation time** (smallest $t_{0.5}$) corresponds to the **maximum transformation rate**.
- This curve is what we build on to design **heat treatments and isothermal transformations**.

Transformations that occur at temperatures near T_m, corresponding to low nucleation and high growth rates, few nuclei form that grow rapidly. Thus, the resulting microstructure will consist of few and relatively large particles (e.g., coarse grains). Conversely, for transformations at lower temperatures, nucleation rates are high and growth rates low, which results in many small particles (e.g., fine grains).



Rate of Phase Transformation (Avrami Model)



Avrami equation => $y = 1 - \exp(-kt^n)$

fraction transformed — time

– k & n are transformation specific parameters

By convention $rate = 1 / t_{0.5}$

Rate of Phase Transformation (Avrami Model)

📈 **Graph Overview:**

• The **S-shaped curve** (sigmoid) shows how the **fraction transformed (y)** increases over time.

• At the beginning, transformation is slow — nuclei are just starting to form.

• Then it speeds up as more **nuclei grow** and more **surface area is available**.

• Eventually, it slows again — not because conditions change, but because there's **less untransformed material left**.

Rate of Phase Transformation (Avrami Model)

🧪 **Avrami Equation:**

$y = 1 - \exp(-kt^n)$

- y is the fraction transformed.
- k and n are constants that depend on the **mechanism of nucleation and growth** (i.e., how fast and in what dimension it happens).
- This equation gives the **full shape of the transformation curve**.

⏱️ **Understanding $t_{0.5}$:**

- The value $t_{0.5}$ is the time when 50% of the transformation is complete.
- It's a common way to **define and compare rates**:

  rate = $1 \backslash t_{0.5}$

Rate of Phase Transformation (Avrami Model)

🧠 **Key Message:**

• This model describes **how transformations proceed in real time**.

• The transformation rate is **not constant** — it **starts slow, peaks, and then slows down again**.

• The curve helps us **predict how long** a transformation will take, which is vital in **heat treatment and materials design**.

EXAMPLE PROBLEM 10.2

Rate of Recrystallization Computation

It is known that the kinetics of recrystallization for some alloy obeys the Avrami equation and that the value of n is 3.1. If the fraction recrystallized is 0.30 after 20 min, determine the rate of recrystallization.

Solution

The rate of a reaction is defined by Equation 10.18 as

$$\text{rate} = \frac{1}{t_{0.5}}$$

Therefore, for this problem it is necessary to compute the value of $t_{0.5}$, the time it takes for the reaction to progress to 50% completion—or for the fraction of reaction y to equal 0.50. Furthermore, we may determine $t_{0.5}$ using the Avrami equation, Equation 10.17:

$$y = 1 - \exp(-kt^n)$$

[Example adopted from Callister 9e, page 368]

Solution continue ..

The problem statement provides us with the value of y (0.30) at some time t (20 min), and also the value of n (3.1) from which data it is possible to compute the value of the constant k. In order to perform this calculation, some algebraic manipulation of Equation 10.17 is necessary. First, we rearrange this expression as follows:

$$\exp(-kt^n) = 1 - y$$

Taking natural logarithms of both sides leads to

$$-kt^n = \ln(1 - y) \tag{10.17a}$$

Now, solving for k,

$$k = -\frac{\ln(1 - y)}{t^n}$$

Incorporating values cited above for y, n, and t yields the following value for k:

$$k = -\frac{\ln(1 - 0.30)}{(20\ \text{min})^{3.1}} = 3.30 \times 10^{-5}$$

Solution continue ..

At this point, we want to compute $t_{0.5}$—the value of t for $y = 0.5$—which means that it is necessary to establish a form of Equation 10.17 in which t is the dependent variable. This is accomplished using a rearranged form of Equation 10.17a as

$$t^n = -\frac{\ln(1 - y)}{k}$$

From which we solve for t

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

And for $t = t_{0.5}$, this equation becomes

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{k}\right]^{1/n}$$

Now, substituting into this expression the value of k determined above, as well as the value of n cited in the problem statement (viz., 3.1), we calculate $t_{0.5}$ as follows:

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{3.30 \times 10^{-5}}\right]^{1/3.1} = 24.8 \text{ min}$$

And, finally, from Equation 10.18, the rate is equal to

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{24.8 \text{ min}} = 4.0 \times 10^{-2} (\text{min})^{-1}$$

Quiz Questions

1. Define undercooling and explain its role in nucleation.

2. What is the difference between homogeneous and heterogeneous nucleation?

3. Why is Gibbs Free Energy important in phase transformations?

4. What factors influence critical radius and activation energy?

5. Describe the relationship between transformation rate and temperature.