

# Chapter Outline: Phase Transformations

Heat Treatment (**time** and temperature)  $\Rightarrow$  Microstructure

- Kinetics of phase transformations
- Homogeneous and heterogeneous nucleation
- Growth, rate of the phase transformation
- Metastable and equilibrium states
- Phase transformations in Fe-C alloys
- Isothermal Transformation Diagrams

*Not tested:*

*in 10.5 Bainite, Spheroidite, Martensite... (from p. 360)*

*10.6 Continuous Cooling Transformation Diagrams*

*10.7-10.9 Mechanical behavior of Fe-C alloys,  
Tempered Martensite*

## Phase transformations. Kinetics.

**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 (discussed in this chapter but not tested)

Phase transformations do not occur instantaneously. Diffusion-dependent phase transformations can be rather slow and the final structure often depend on the rate of cooling/heating.

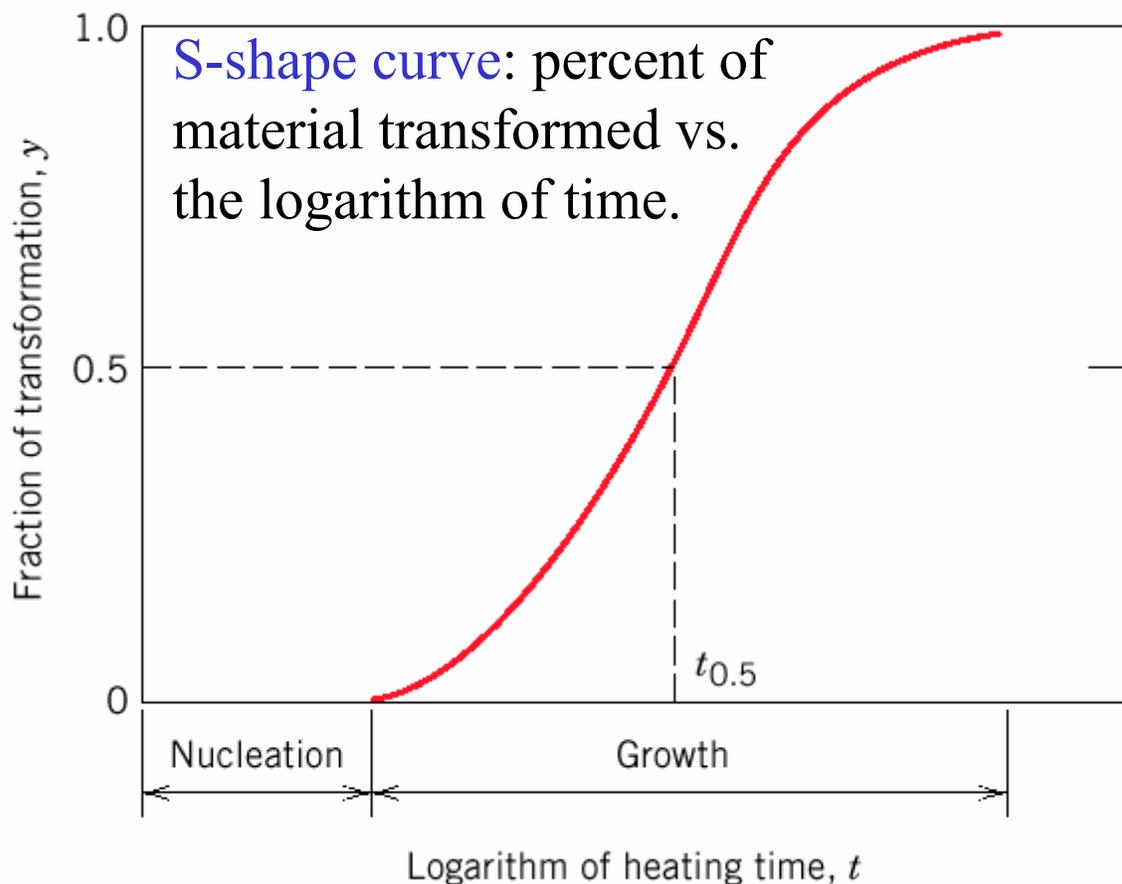
**We need to consider the time dependence or kinetics of the phase transformations.**

# Kinetics of phase transformations

Phase transformations involve change in structure and (for multi-phase systems) composition  $\Rightarrow$  rearrangement and redistribution of atoms via diffusion is required.

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).



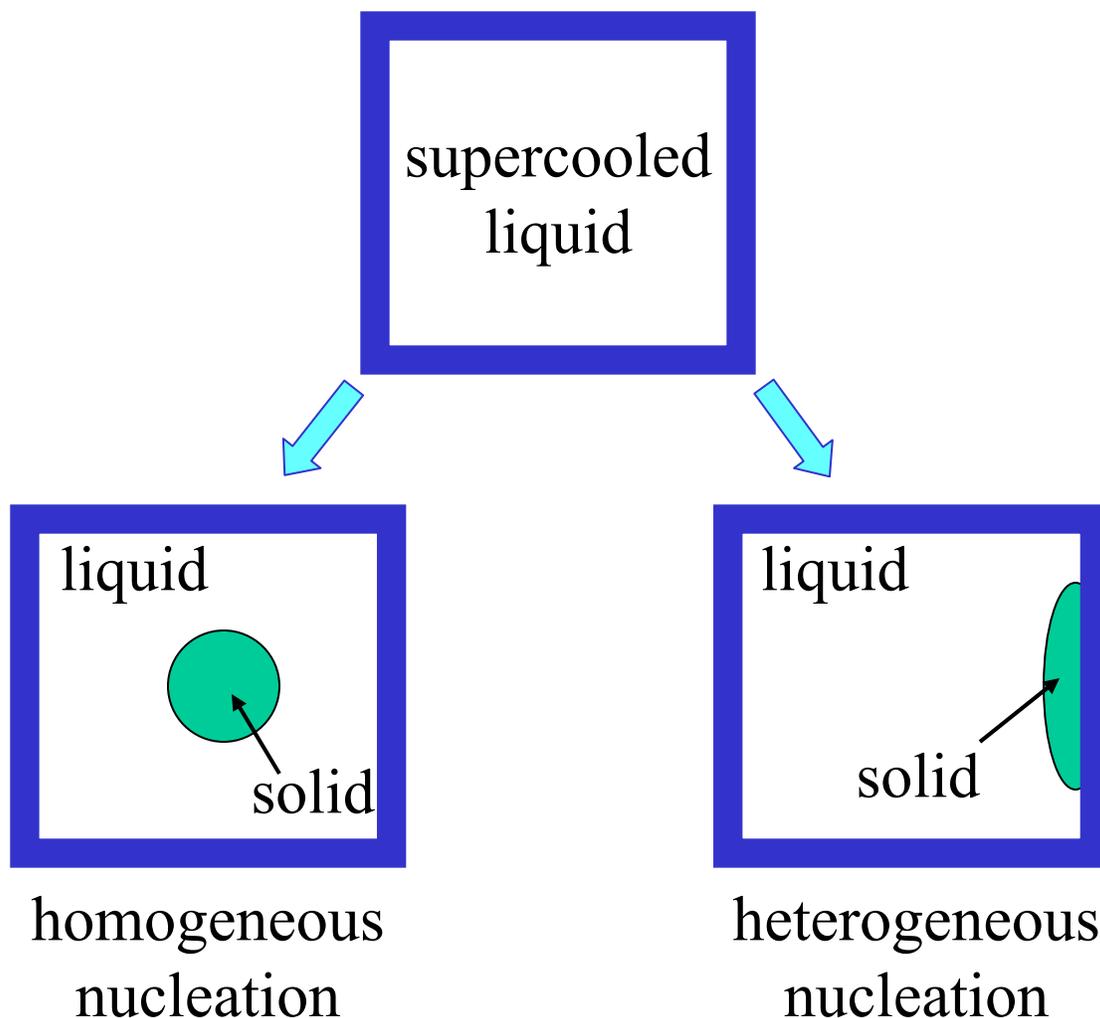
# Nucleation

Nucleation can be

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

**Homogeneous** – solid nuclei spontaneously appear within the undercooled phase.

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



## Gibbs free energy in analysis of phase transitions

It is convenient to analyze phase transformations occurring under conditions of constant temperature (T) and pressure (P) by using **Gibbs free energy (G)**.

**$G = H - TS$** , where H is the **enthalpy** and S is the **entropy**

**$H = U + PV$** , where U is the **internal energy**

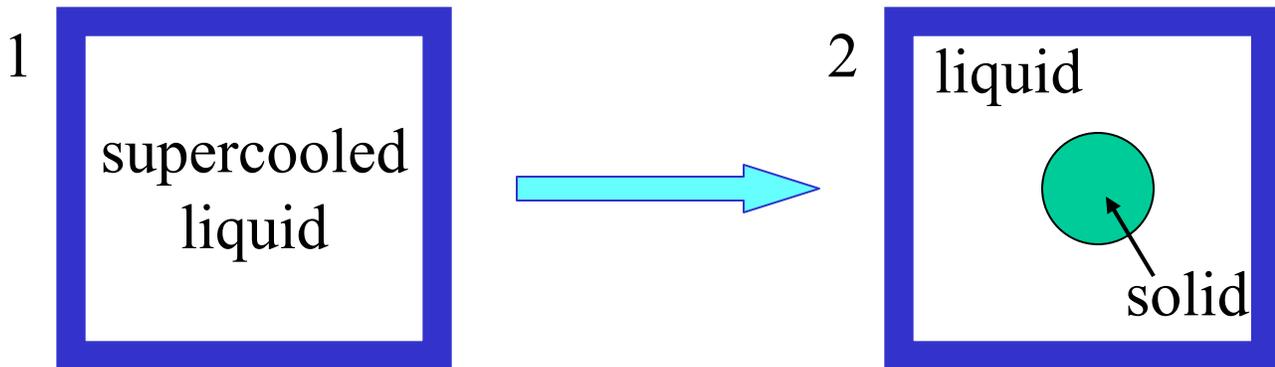
The conclusion of the thermodynamic analysis (take MSE 3050 to learn about the details) is that the equilibrium under conditions of  $T = \text{const}$ , and  $P = \text{const}$  corresponds to **the minimum of G** and a phase transformation occurs spontaneously only when **G decreases** in the course of the transformation

**Gibbs free energy ( $G = H - TS$ ):**

**Equilibrium is trade-off between minimization of enthalpy and maximization of entropy**

A change to a lower enthalpy state ( $\Delta H < 0$ ) usually decreases the randomness ( $\Delta S < 0$ ):

## Homogeneous nucleation



Is the transition from undercooled liquid to a solid spherical particle in the liquid a spontaneous one?

That is, is the Gibbs free energy decreases?

The formation of a solid nucleus leads to a Gibbs free energy change of  $\Delta G = G_2 - G_1 = \underbrace{-V_S (G_v^L - G_v^S)}_{\text{negative below } T_m} + \underbrace{A^{SL}\gamma^{SL}}_{\text{always positive}}$

negative below  $T_m$

$V_S$  is the volume of the solid sphere

$A^{SL}$  is the solid/liquid interfacial area

$\gamma^{SL}$  is the solid/liquid interfacial energy

$\Delta G_v = G_v^L - G_v^S$  is the volume free energy difference

at  $T < T_m$ ,  $G_v^S < G_v^L$  – solid is the equilibrium phase

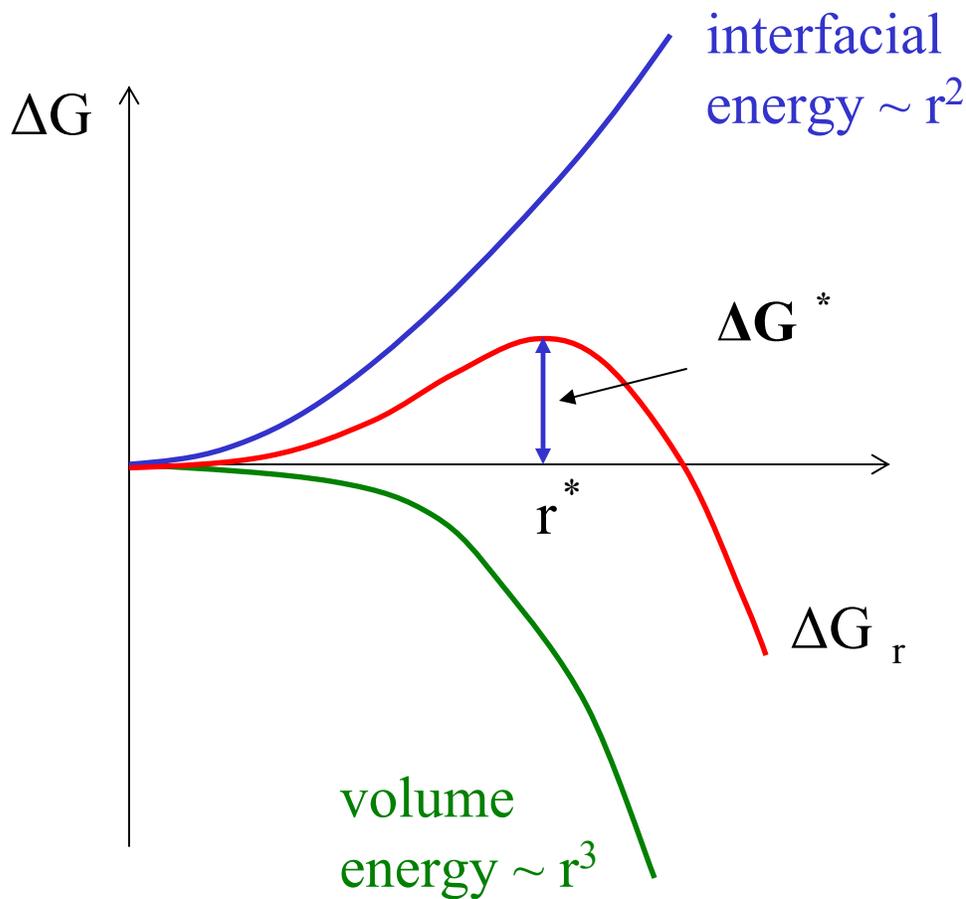
always  
positive

## Homogeneous nucleation

$$\Delta G = G_2 - G_1 = -V_S \Delta G_v + A^{SL} \gamma^{SL}$$

For a spherical nucleus with radius  $r$ :  $V_S = \frac{4}{3} \pi r^3$

$$\Delta G = -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma^{SL} \quad A^{SL} = 4\pi r^2$$



For nucleus with a radius  $r > r^*$ , the Gibbs free energy will decrease if the nucleus grows.  $r^*$  is the **critical nucleus size**.

## Homogeneous nucleation

$$\text{At } r = r^* \quad \frac{d\Delta G}{dr} = -4\pi r^2 \Delta G_v + 8\pi r \gamma^{SL} = 0$$

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

The difference between the Gibbs free energy of liquid and solid (also called “driving force” for the phase transformation) is proportional to the undercooling below the melting temperature,  $\Delta T = T_m - T$ :

$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

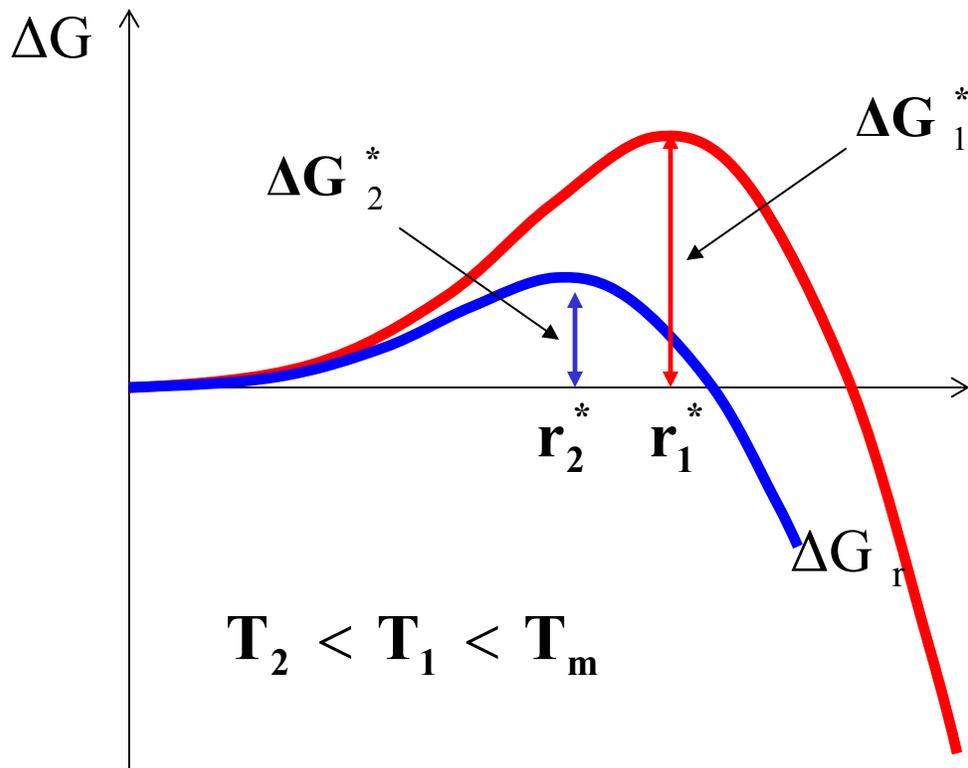
where  $H_m$  is the latent heat of melting (or fusion)

$$\text{Therefore: } r^* = \left( \frac{2 \gamma^{SL} T_m}{\Delta H_m} \right) \frac{1}{\Delta T}$$

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

Both  $r^*$  and  $G^*$  decrease with increasing undercooling

## Homogeneous nucleation



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

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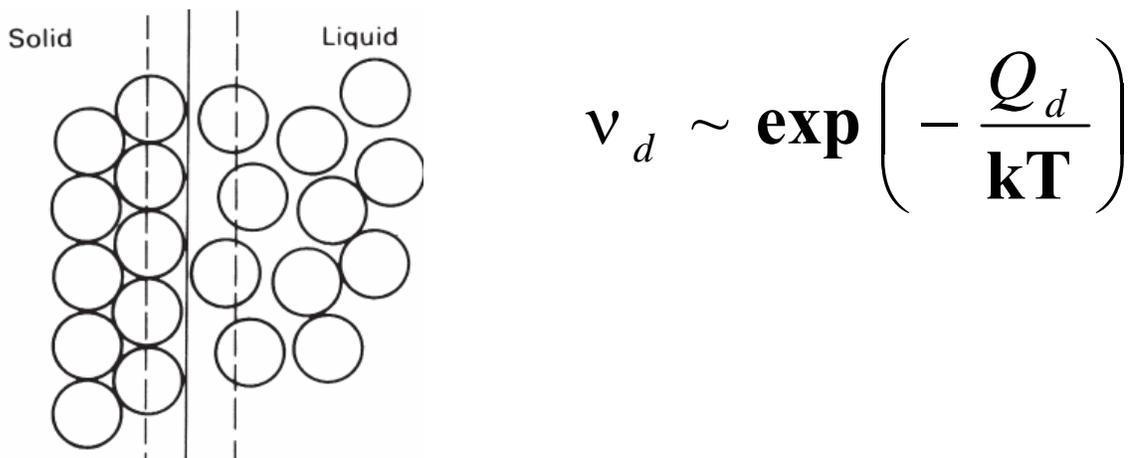
Both  $r^*$  and  $G^*$  decrease with increasing undercooling

## Homogeneous nucleation

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

$$\dot{N} \sim v_d \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{nuclei per m}^3 \text{ per s}$$

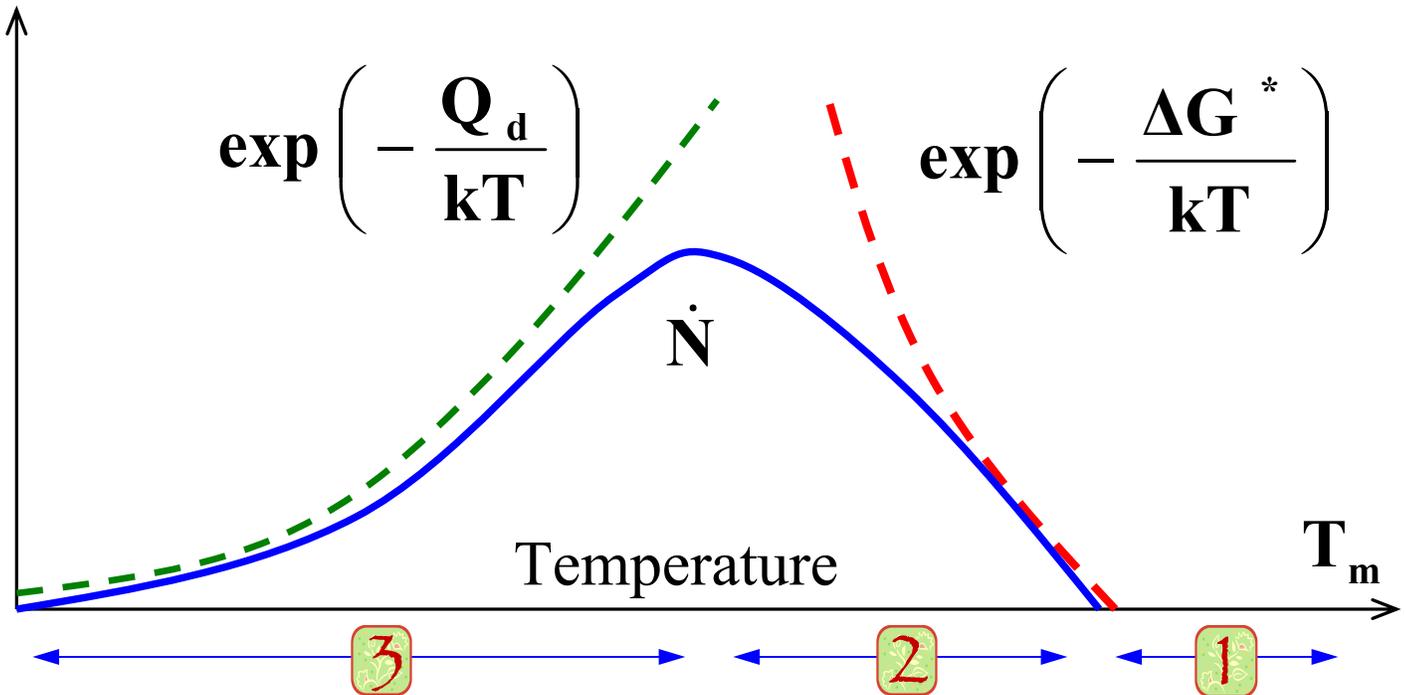
where  $v_d$  is the frequency with which atoms from liquid attach to the solid nucleus. The rearrangement of atoms needed for joining the solid nucleus follow the same temperature dependence as the diffusion coefficient:



Therefore: 
$$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$

## Rate of homogeneous nucleation

$$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right)$$



**1**  $\Delta G^* > Q_d \Rightarrow \exp(-\Delta G^*/kT) \ll \exp(-Q_d/kT)$

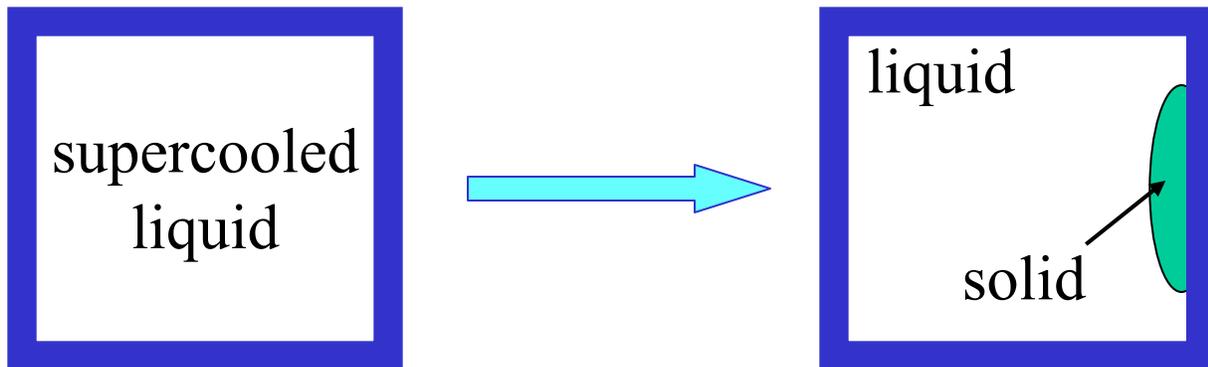
$\Delta G^*$  is too high - nucleation is suppressed

**2**  $\Delta G^* \leq Q_d \Rightarrow \exp(-\Delta G^*/kT) > \exp(-Q_d/kT)$

$\Delta G^* \sim 1/\Delta T^2$  - decreases with  $T$  - sharp rise of homogeneous nucleation (diffusion is still active)

**3**  $\exp(-Q_d/kT)$  - too small - low atomic mobility suppresses the nucleation rate

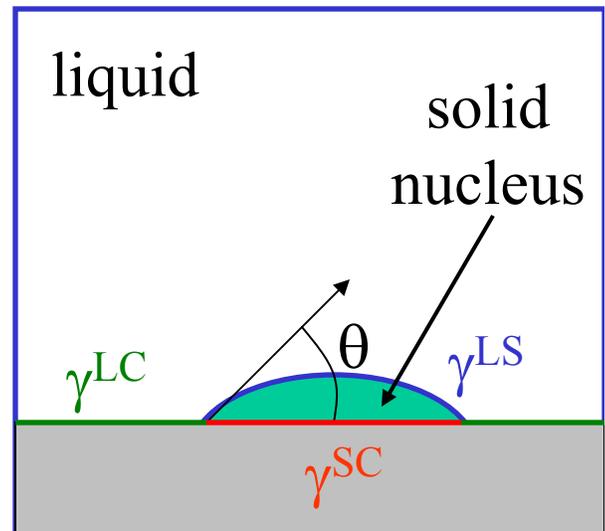
## Heterogeneous nucleation



the new phase appears on the walls of the container, at impurity particles, grain boundaries, etc.

Let's consider a simple example of heterogeneous nucleation of a nucleus of the shape of a spherical cap on a wall of a container. Three surface energies:

$\gamma^{LC}$  – liquid container interface,  
 $\gamma^{LS}$  – liquid-solid interface,  
 $\gamma^{SC}$  – solid-container interface.



Balancing the interfacial tensions in the plane of the container wall gives  $\gamma^{LC} = \gamma^{SC} + \gamma^{LS} \cos(\theta)$  and the **wetting angle**  $\theta$  is defined by  $\cos(\theta) = (\gamma^{LC} - \gamma^{SC}) / \gamma^{LS}$

## Heterogeneous nucleation

The formation of the nucleus leads to a Gibbs free energy change of  $\Delta G = -V_S \Delta G_v + A^{SL} \gamma^{SL} + A^{SC} \gamma^{SC} - A^{SC} \gamma^{LC}$

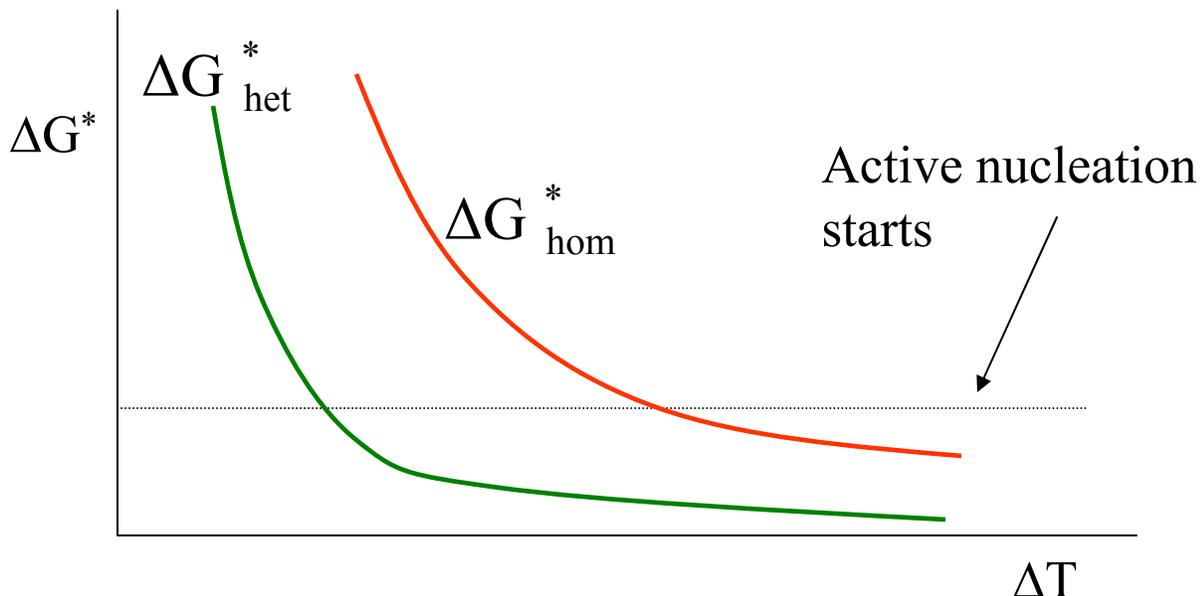
One can show that

$$\Delta G_r^{\text{het}} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma^{SL} \right\} S(\theta) = \Delta G_r^{\text{hom}} S(\theta)$$

where  $S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4 \leq 1$

$$\text{At } r = r^* \quad \frac{d\Delta G_r}{dr} = (-4\pi r^2 \Delta G_v + 8\pi r \gamma^{SL}) S(\theta) = 0$$

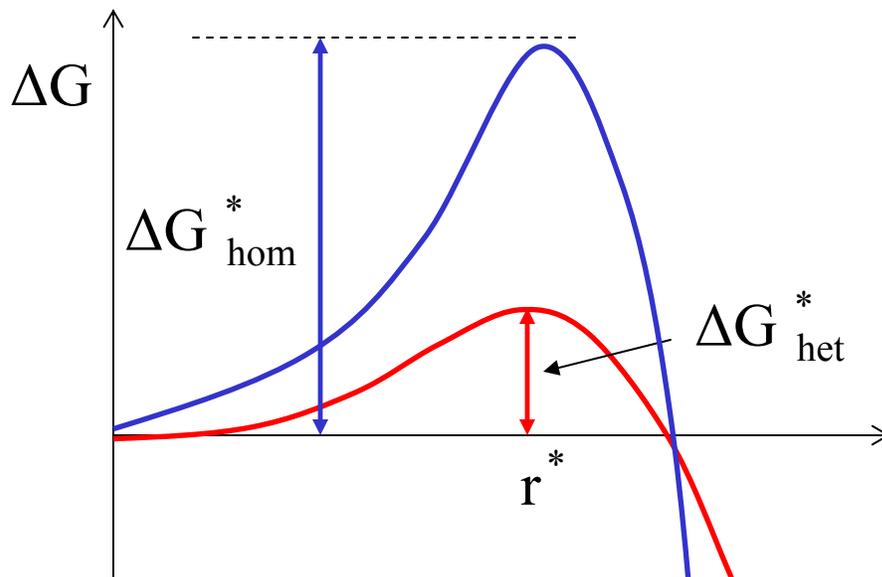
$$r^* = \frac{2 \gamma^{SL}}{\Delta G_v} \quad \Delta G_{\text{het}}^* = S(\theta) \frac{16 \pi (\gamma^{SL})^3}{3 (\Delta G_v)^2} = S(\theta) \Delta G_{\text{hom}}^*$$



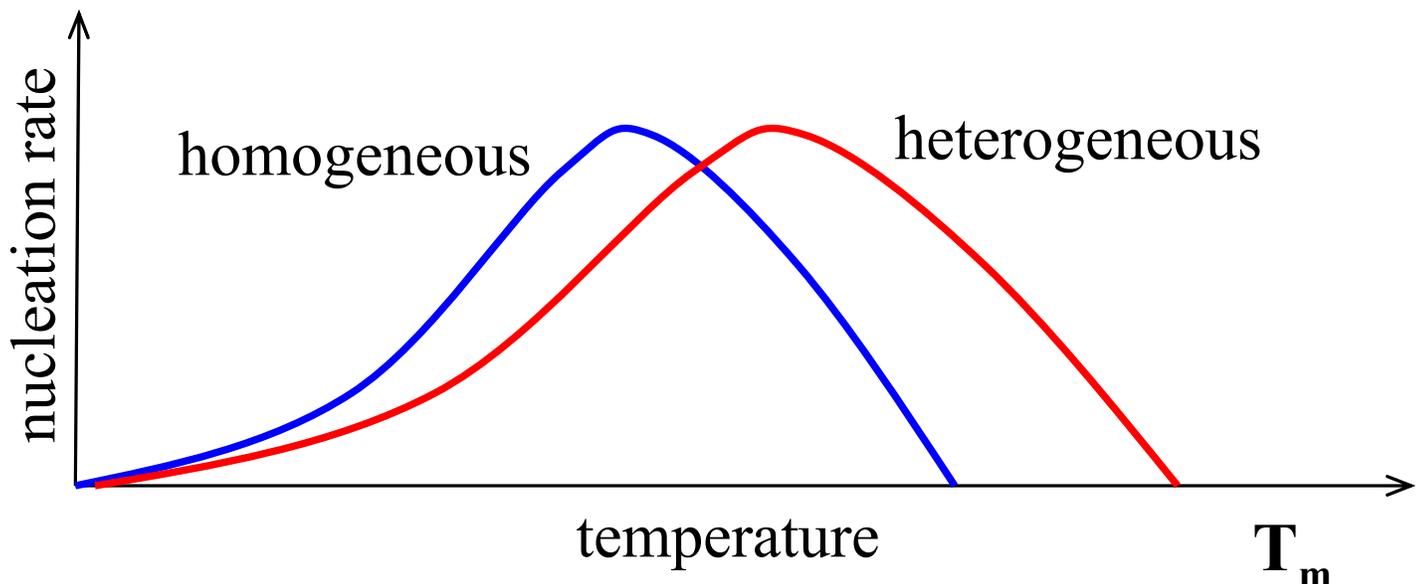
## Heterogeneous nucleation

$$r^* = \frac{2 \gamma^{SL}}{\Delta G_v} \quad \Delta G_{het}^* = S(\theta) \Delta G_{hom}^*$$

$$\text{if } \theta = 10^\circ \quad S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4 \approx 10^{-4}$$

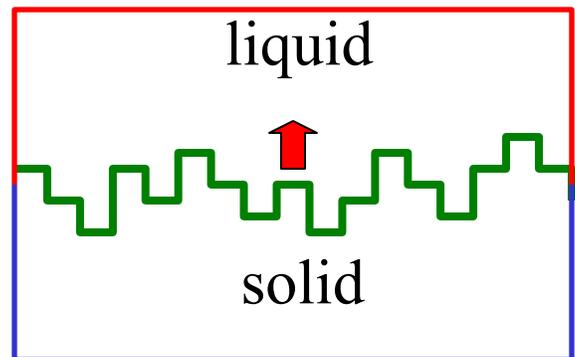
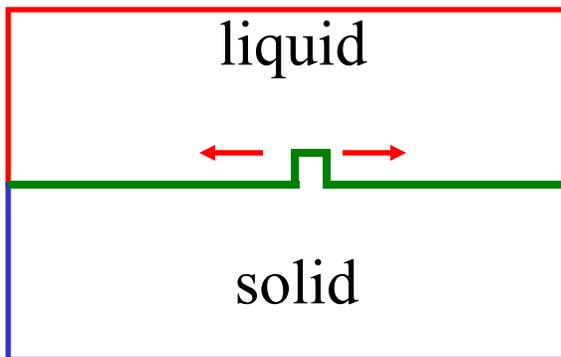


*heterogeneous nucleation starts at a lower undercooling*



## Growth

Once a stable nucleus of the new phase exceeding the critical size  $r^*$  is formed, it starts to grow. Atomically rough interfaces migrate by continuous growth, whereas atomically flat interfaces migrate by ledge formation and lateral growth.



In multi-component systems, non-congruent phase transformations can involve long-range solute diffusion necessary for achieving the equilibrium phase composition.

The atomic rearrangements necessary for growth of a one-component phase or growth in a congruent phase transformation, as well as the long-range diffusion of components in multi-component systems, involve thermally-activated elementary processes and can be described by Arrhenius equation:

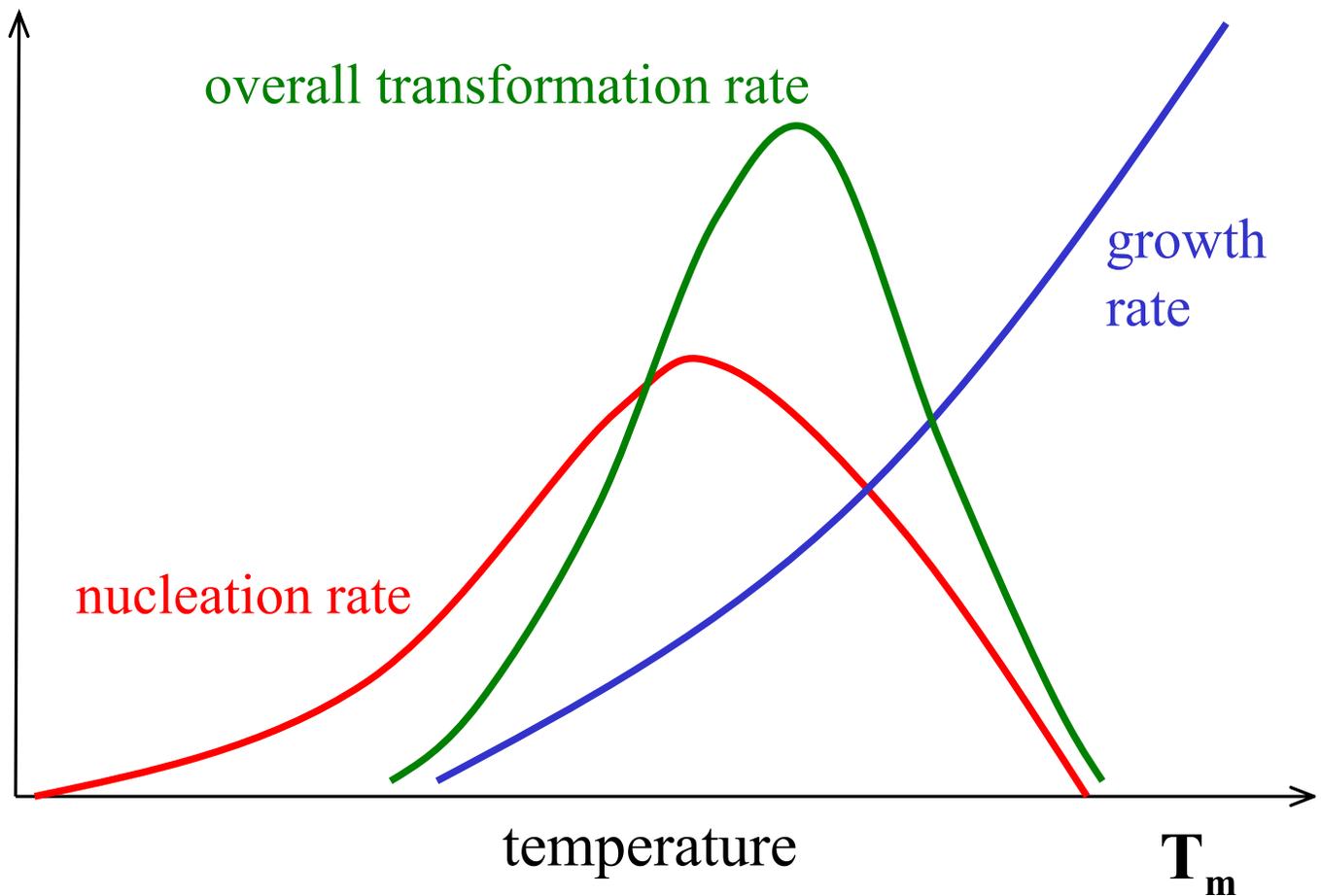
$$\text{Growth rate} = C \exp(-Q_A/kT) = C \exp(-Q_m/RT)$$

↑  
per atom

↑  
per mole

## 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).

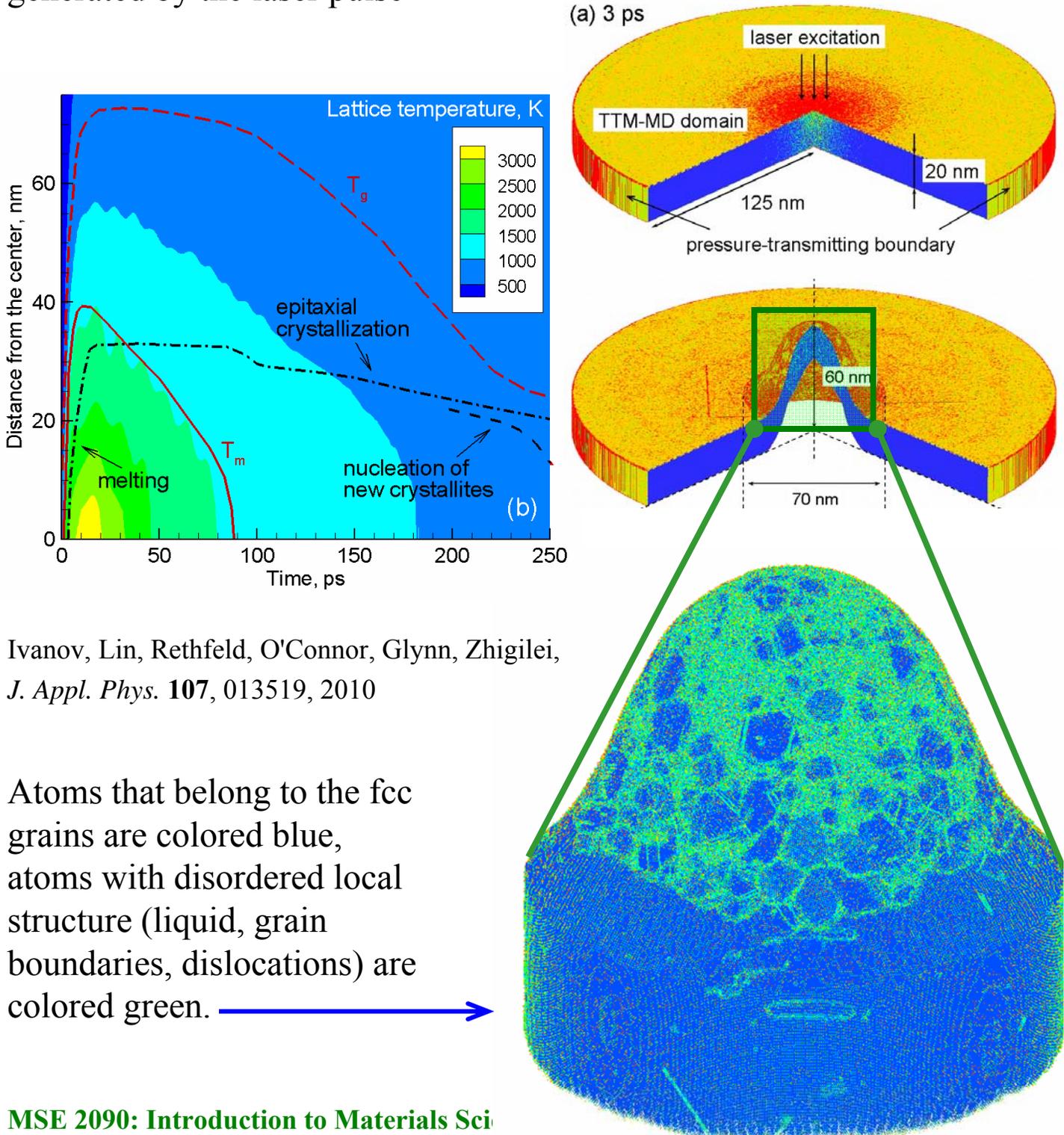


**high T (close to  $T_m$ ):** low nucleation and high growth rates  
→ coarse microstructure with large grains

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

## Example of solidification under conditions of extreme undercooling

Localized excitation of a metal film by a short laser pulse results in very steep temperature gradients, fast heat conduction and extreme cooling rates exceeding  $10^{12}$  K/s  $\rightarrow$  deep undercooling of the melt  $\rightarrow$  high nucleation rate  $\rightarrow$  nanocrystalline structure of the surface feature generated by the laser pulse



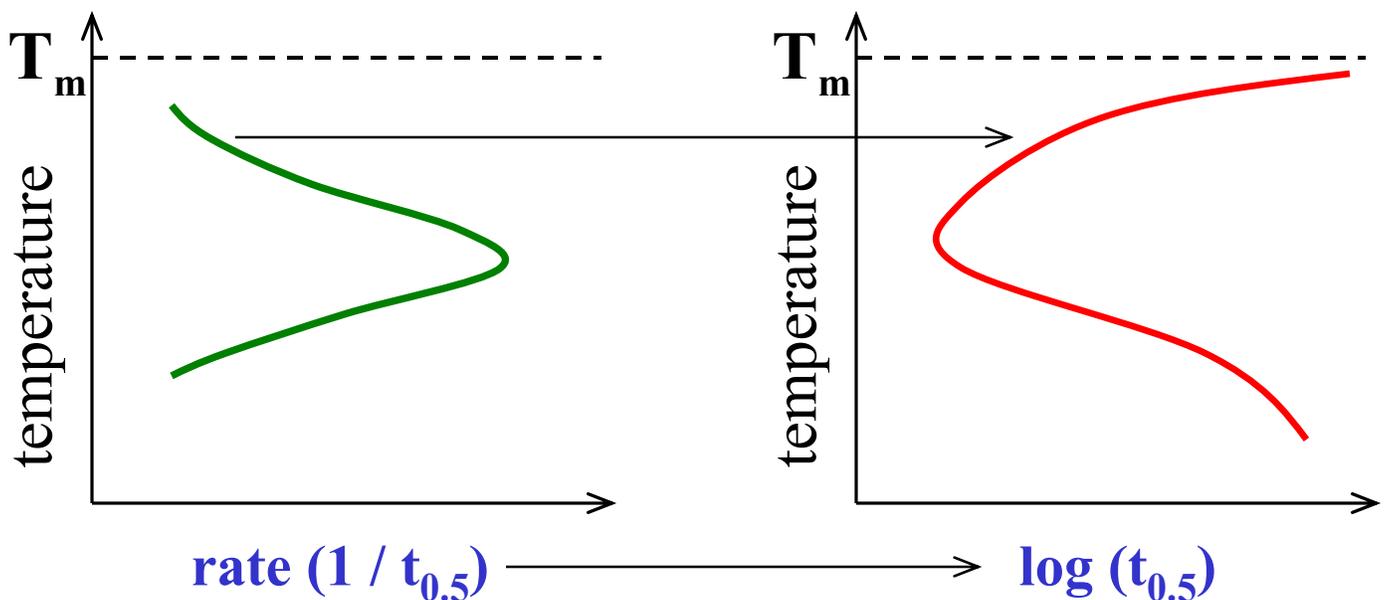
Ivanov, Lin, Rethfeld, O'Connor, Glynn, Zhigilei, *J. Appl. Phys.* **107**, 013519, 2010

## Rate of phase transformations

To quantitatively describe the rate of a phase transformation, it can be defined as reciprocal of time for transformation to proceed halfway to completion:

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

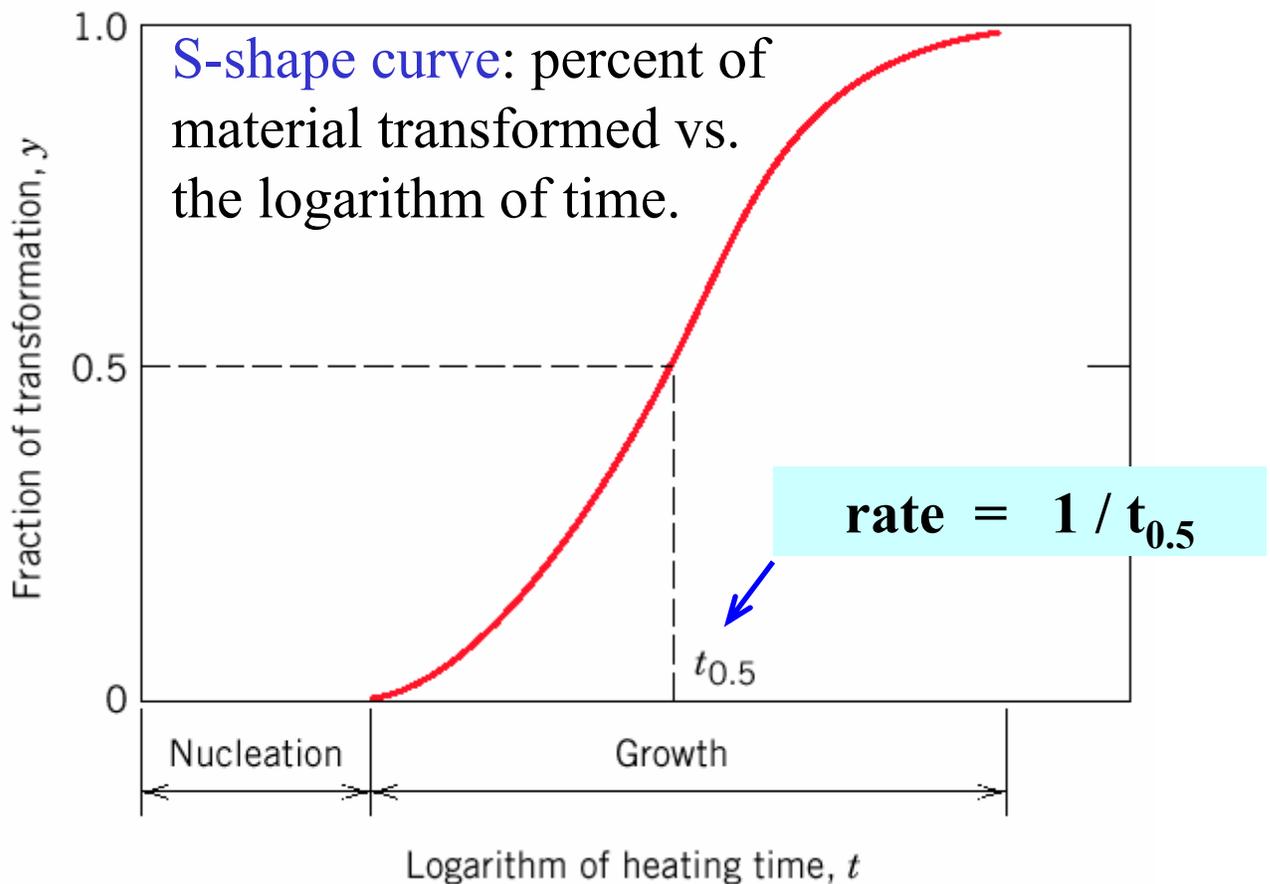
Plotting the transformation time vs temperature results in a characteristic C-shaped curves:



The analysis performed above for solidification can also be extended to other phase transformations, e.g. solid-state phase transformations.

## Kinetics of phase transformations

The time dependence of solid-state phase transformations at a fixed temperature is often described in terms of the time dependence of the fraction of transformation ( $y$ ):



This time dependence of the fraction of transformation follows the Avrami equation:

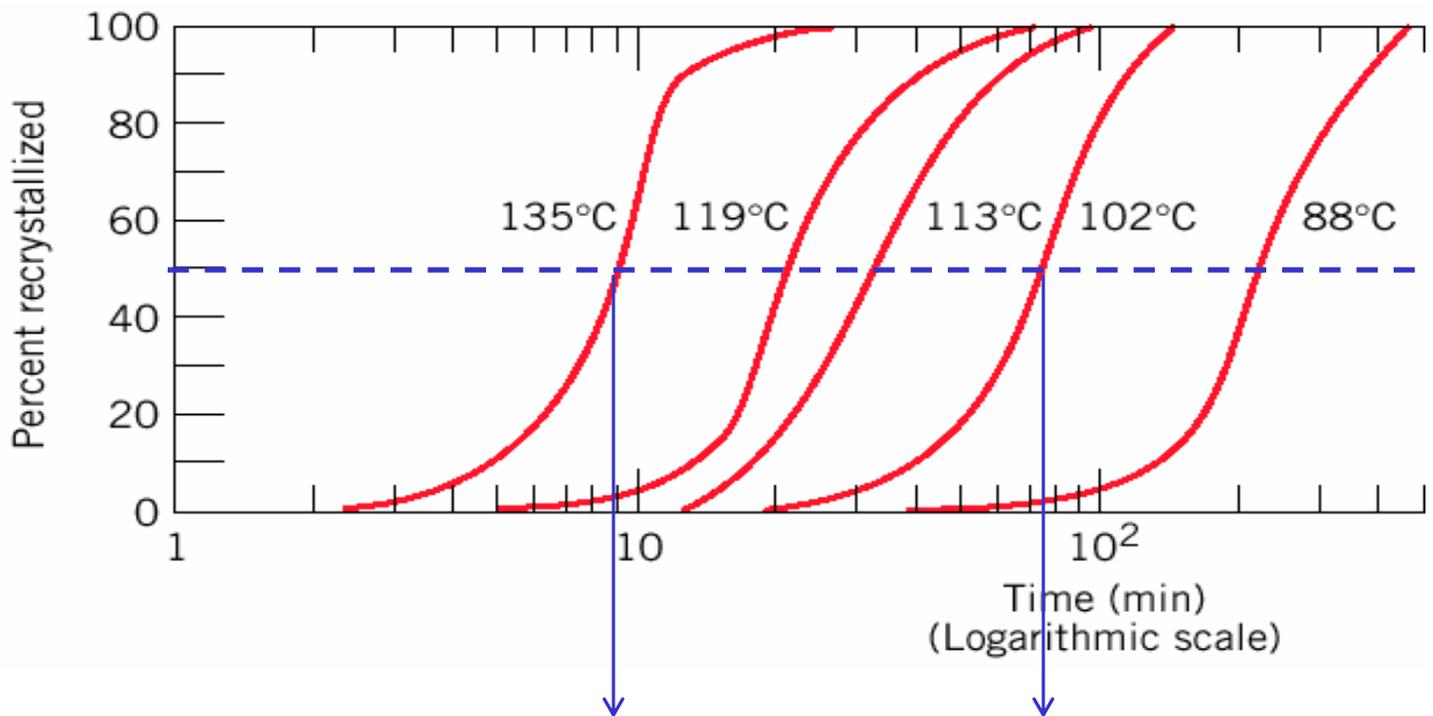
$$y = 1 - \exp(-k t^n)$$

where  $k$  and  $n$  are time-independent constants for the particular transformation

## Kinetics of phase transformations

Temperature has a strong effect on the kinetics of the phase transformation and, therefore, on the rate of the phase transformation.

Percent recrystallization of pure copper at different T:



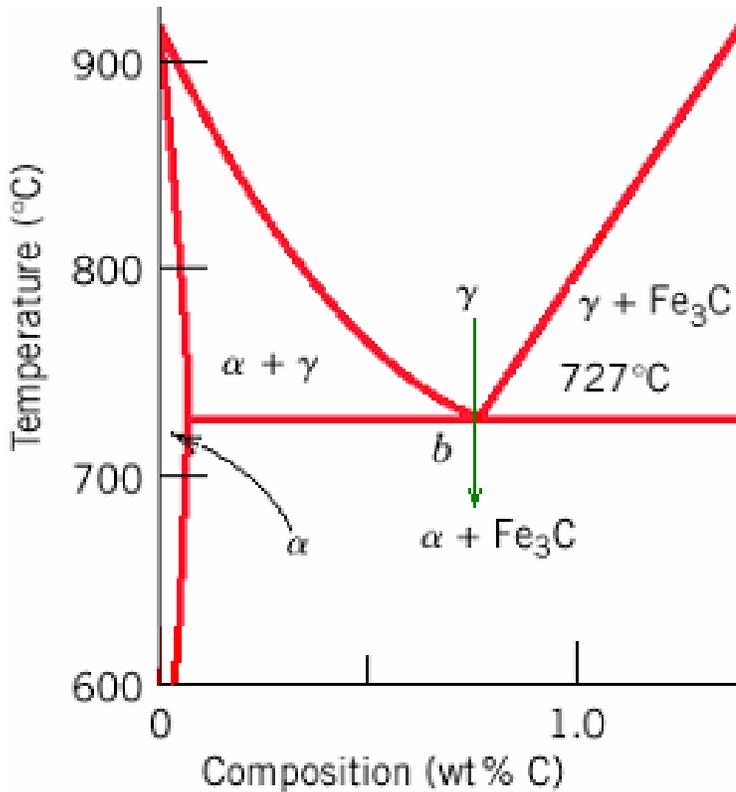
$$\text{rate} = 1 / t_{0.5}$$

$$\text{rate (135}^\circ\text{C)} \gg \text{rate (113}^\circ\text{C)}$$

## Superheating / supercooling

- Upon crossing a phase boundary on the composition-temperature phase diagram, phase transformation towards equilibrium state is induced.
- But the nucleation and growth of the equilibrium structure takes time and the transformation is delayed.
- During cooling, transformations occur at temperatures less than predicted by phase diagram: **supercooling**.
- During heating, transformations occur at temperatures greater than predicted by phase diagram: **superheating**.
- Degree of supercooling/superheating increases with rate of cooling/heating.
- **Metastable states** can be formed as a result of fast temperature change. **Microstructure is strongly affected by the rate of cooling.**
- Below we will consider the effect of time on phase transformations using iron-carbon alloy as an example.

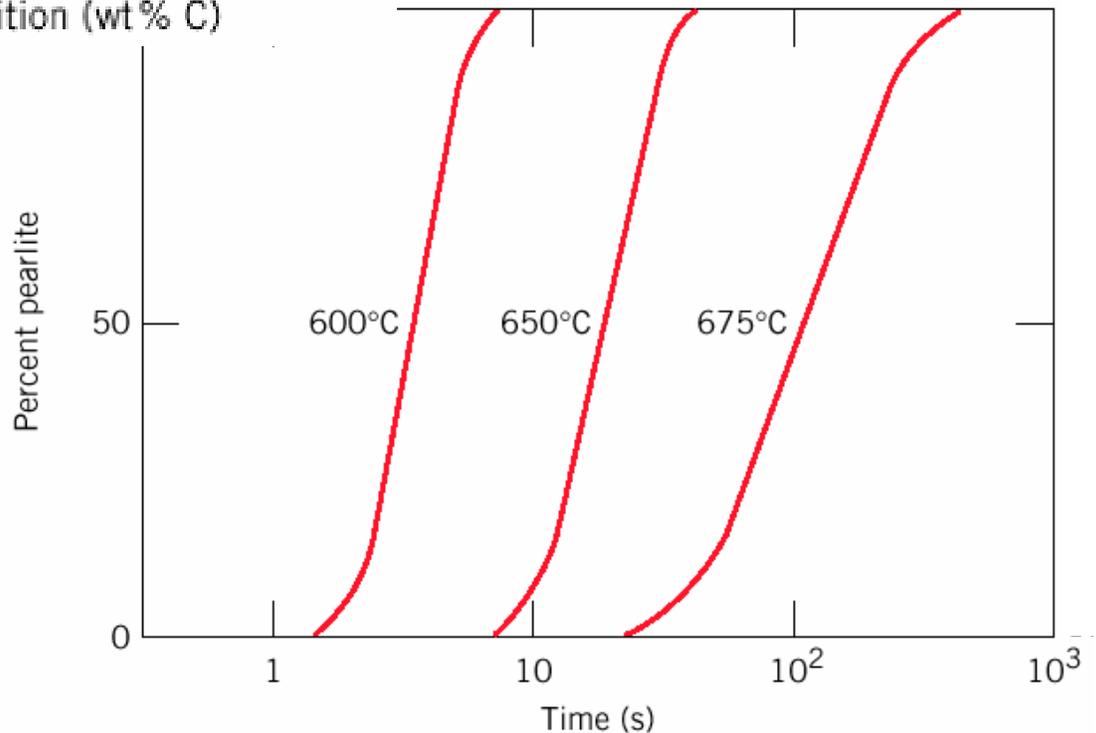
## Let us consider eutectoid reaction as an example



eutectoid reaction:

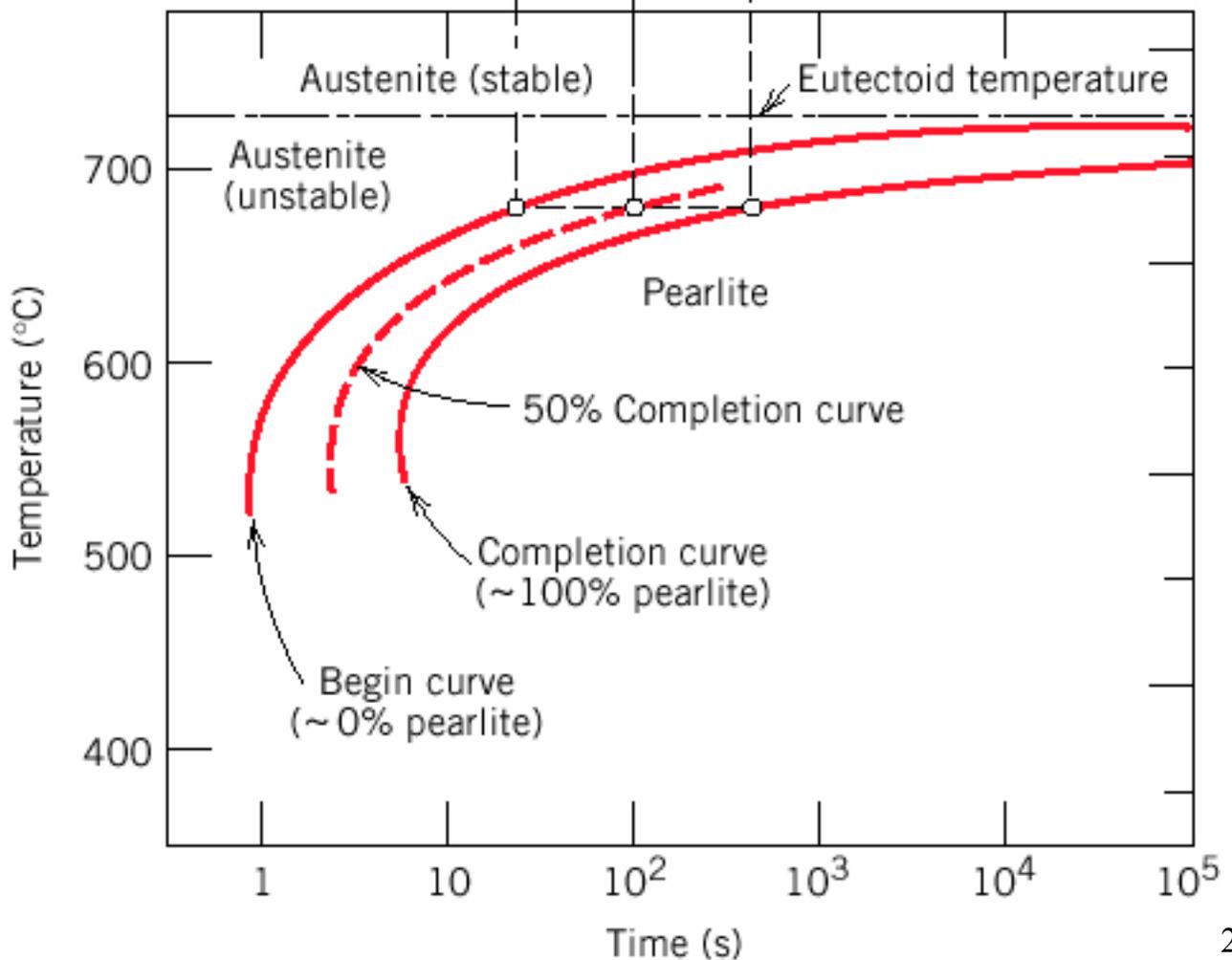
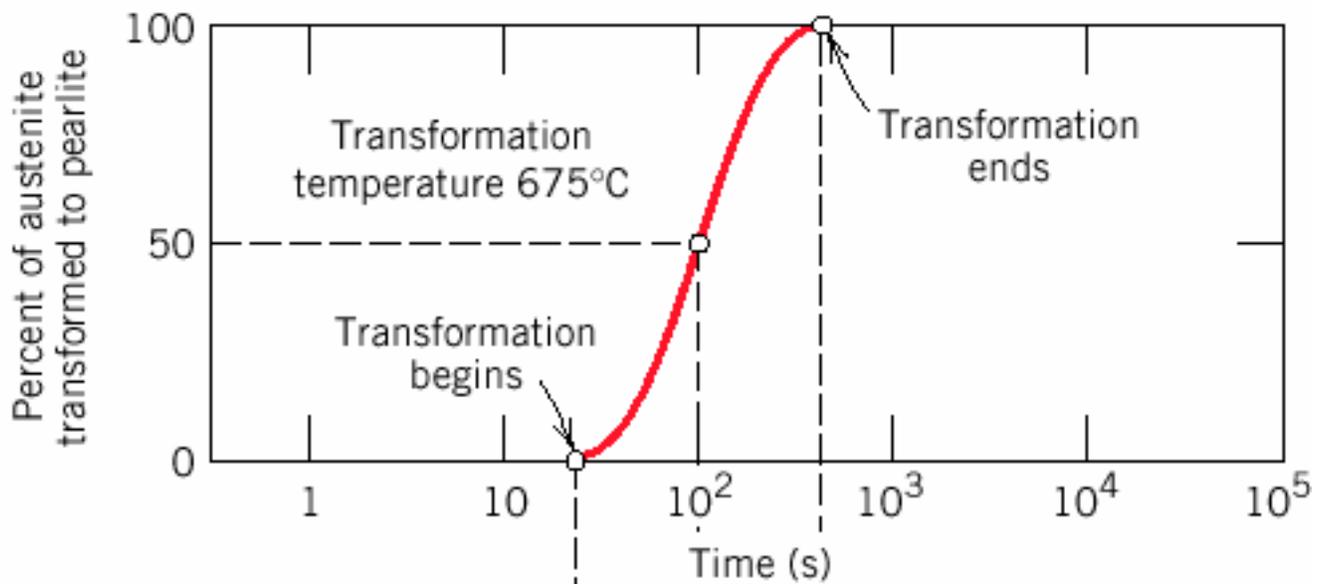


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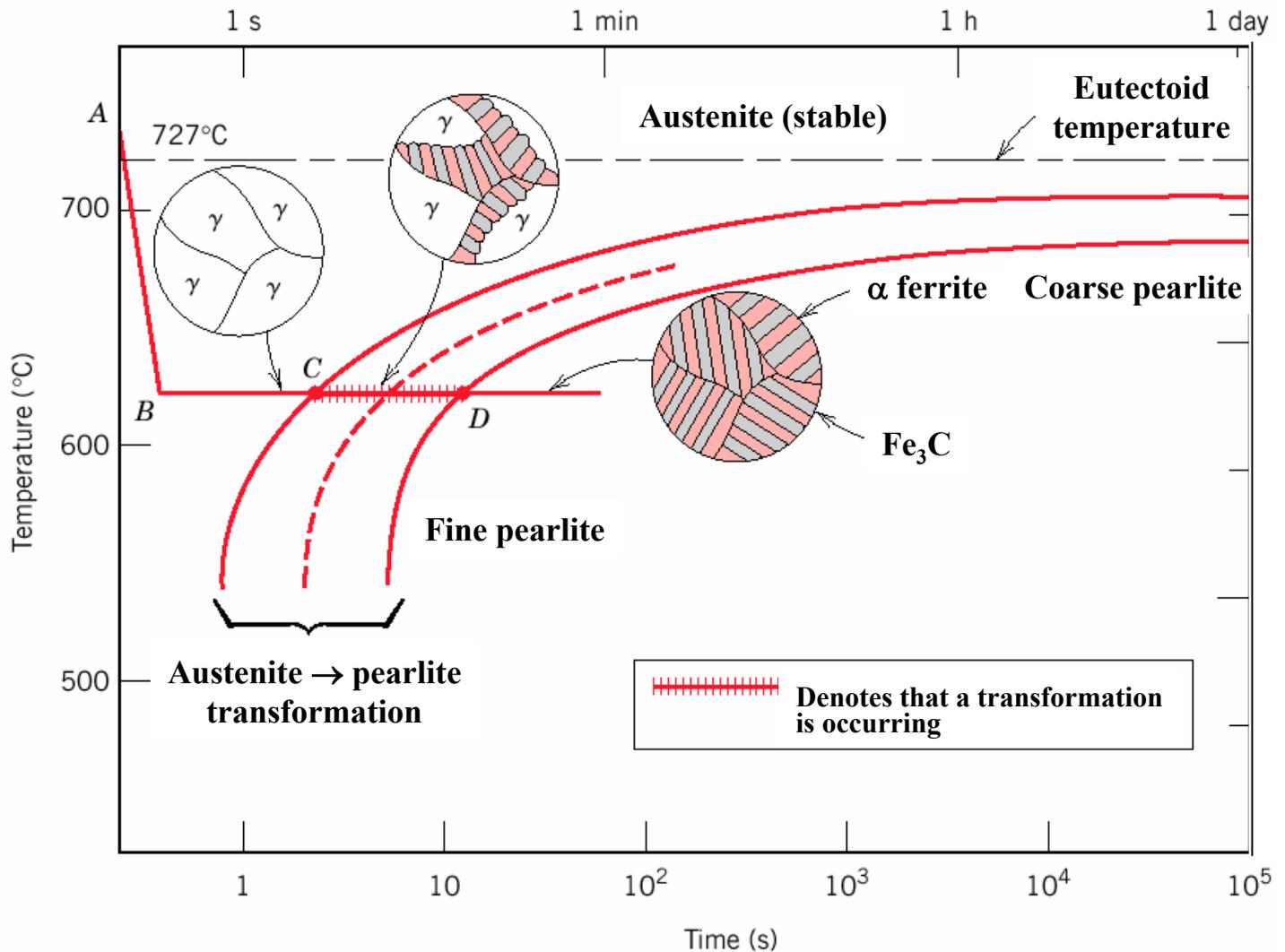


The S-shaped curves are shifted to longer times at higher T showing that the transformation is dominated by nucleation (nucleation rate increases with supercooling) and not by diffusion (which occurs faster at higher T).

# Isothermal Transformation (or TTT) Diagrams (Temperature, Time, and % Transformation)



# TTT Diagrams



The thickness of the ferrite and cementite layers in pearlite is  $\sim 8:1$ . The absolute layer thickness depends on the temperature of the transformation. The higher the temperature, the thicker the layers.

## TTT Diagrams

- A family of S-shaped curves at different T are used to construct the TTT diagrams.
- The TTT diagrams are for the **isothermal** (constant T) transformations (material is cooled quickly to a given temperature before the transformation occurs, and then keep it at that temperature).
- At low temperatures, the transformation occurs sooner (it is controlled by the rate of nucleation) and grain growth (that is controlled by diffusion) is reduced.
- Slow diffusion at low temperatures leads to fine-grained microstructure with thin-layered structure of pearlite (**fine pearlite**).
- At higher temperatures, high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (**coarse pearlite**).
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexist with pearlite. Additional curves for proeutectoid transformation must be included on TTT diagrams.

# Summary

Make sure you understand language and concepts:

- Avrami equation (for fraction of transformation)
- Coarse pearlite
- “Driving force” for phase transformation
- Fine pearlite
- Growth of a new phase
- Heterogeneous nucleation
- Homogeneous nucleation
- Isothermal transformation diagram
- Kinetics of phase transformations
- Nucleation barrier
- Phase transformation
- Rate of the phase transformation
- Size of the critical nucleus
- Supercooling
- Superheating
- Transformation rate